

WASTE MANAGEMENT SERIES • 4

SOLID WASTE: ASSESSMENT, MONITORING AND REMEDIATION

Irena Twardowska • Herbert E. Allen
Antonius A.F. Kettrup • William J. Lacy

SOLID WASTE: ASSESSMENT, MONITORING AND REMEDIATION

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Waste Management Series, Volume 4

SOLID WASTE: ASSESSMENT, MONITORING AND REMEDIATION

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Preface

The general idea of the book has arisen from the mutual experience of many specialists in numerous disciplines from different countries involved in the problem of environmental assessment, life cycle monitoring/pollution prevention and control approaches for chemicals generated from solid waste disposal. Solid waste worldwide issues nowadays reflect the complexity and unbalanced development of our world at the beginning of the 21st century. There remains a lack of agreement concerning the major basic definitions, e.g. which material should be considered as "waste" and which as a "beneficial raw material", which wastes are "hazardous-" and which are "non-hazardous" ones. These arguments are far from being just an academic dispute, resulting finally in the way of waste management/disposal is practiced. False-positive evaluation of material causes substantial increase of disposal costs, while false-negative error may pose serious damage to the environment from inadequately used or disposed wastes. It is remarkable, that quite often a failure in proper evaluation of environmental impact originates from an improper testing procedure or generalization of the results of a limited number of basic tests with respect to the heterogeneous high-volume wastes.

There are still a great variety of procedures for the assessment of environmental risks, not only in national regulations of different countries, but also used by different groups of analysts within the same country. The need for waste- and site-specific approaches on one hand, and harmonization of procedures for the assessment of environmental risks from solid wastes on the other hand, is therefore obvious.

In the field of solid waste management, treatment and disposal one faces the enormous (but still not sufficient) amount of information concerning specific problems of different hazardous wastes, and surprisingly limited data on the seemingly harmless great portions of the waste stream entering the environment.

Rapid progress in industry and other branches of the economy in the developing industrialized nations, not accompanied by adequate, environmentally safe waste management strategies, creates new vast "hot spots" in the formerly pristine areas.

Development of new technologies, materials and chemicals poses quite often a hazard from new waste materials of unpredictable environmental behavior and impact.

All this ballast of the old unsolved problems, lack of basic information, knowledge and recognition concerning environmental behavior of waste, the proliferation of new hazardous waste materials and chemicals, new severe damage and new risks to the environment resulted from the discordant development of the world we have taken to the 21st Century.

At the same time, the end of the 20th Century provided us with wonderful opportunities arising from the transformation of the political system of the former communist countries, the end of a cold war and the beginning of a new era of unlimited cooperation and unification in the field of optimization of relevant laws, regulations and environmental impact assessment methods in a large regional and global scale. Now, the most advanced

technologies that formerly served for military purposes have become efficient, reliable, exact and worldwide commonly available tools for monitoring and remediation of waste sites. Some of these technologies and techniques are applicable specifically to waste treatment and disposal, some are integral to the waste management problem, but have a wider scope of use. The doors to better, safer, efficient waste management strategies, and therefore to a better, safer, cleaner environment are open wide. There should be knowledge and awareness of the administration and decision makers to accept the suggestions of experts in the field of the environmentally safe waste disposal, but there should be also a will and ability of experts to evaluate adequately, and to apply properly, the new methods, techniques and technologies for optimization of waste management strategies in a national, regional and global scale and for making national waste management practices compatible with regional and global strategies. These strategies should comprise the total waste stream management and should consider all kinds of waste origins of different volume, properties and extent of the environmental impact in compliance with the up-to-date state of knowledge.

In the last decade, there has been growing awareness and interest in the environmentally safe management of non-hazardous waste; in the European Union and Accession Countries it resulted in consolidated legislative, standardization, administrative and research activity in this arena. It is aimed to develop short- and long-term waste management strategies and their consequent implementation in compliance with the formulated priorities: (1) waste minimization; (2) recycling and reuse; (3) environmentally safe disposal.

This book covers a broad group of wastes, from biowaste to hazardous waste, but primarily the largest (by volume) group of wastes that are not hazardous, but also are not inert, and are problematic for three major reasons: (1) they are difficult to manage because of their volume: usually they are used in civil engineering as a common fill, where they are exposed to atmospheric conditions almost the same way as at disposal sites, or in agriculture as soil amendments etc.; (2) they are not geochemically stable and in the different periods of environmental exposure undergo transformations that might add hazardous properties to the material that are not displayed when it is freshly generated; (3) many designers and researchers in different countries involved in the waste management are often not aware of time-delayed adverse environmental impact of some large-volume waste, and also do not consider some positive properties that may extend the area of their environmentally beneficial application.

The aim of this book is to contribute to:

- Unification of pollution-control legislation with respect to solid waste (SW) and solid waste disposal facilities (SWDFs) through critical discussion of national regulations in different countries;
- Implementation in compliance with current state of knowledge;
- Introduction of advanced, reliable and cost-effective monitoring strategies in SWDF sites that would provide an early alert for undertaking remedial actions;
- Extending information on the most promising and efficient emerging remediation technologies.

The contributors to the book are recognized experts in the various fields associated with the issues and are from different parts of the world. They present their experience and approaches, taking into consideration also local specifics. The book is addressed to the wide range of decision-makers and professionals involved in environmental issues: administration, designers, and to researchers, as well as to academic teachers and university students and is focused on waste properties, environmental behavior and management in an environmentally safe way. It considers municipal waste, hazardous waste and waste other than hazardous, with a special regard to this last and largest group that often combines properties of either biowaste or at some stages of weathering transformations also of hazardous waste. The knowledge and awareness of these properties are still limited. It was not the intention of the editors to exhaust the subject, which is extremely broad, but to give a general idea about the up-to-date trends in the field of solid waste disposal, monitoring, assessment and remedial options, exemplified also in the case studies.

The scope of the book:

1. Critically discuss international and national legislation and regulatory frameworks concerning SW in different countries representing various levels of economy development.
2. Summarize data concerning pollution potential of major groups of bulk solid wastes (both hazardous and other than hazardous as a function of time and storage/disposal conditions, on the background of existing legislation/control strategies.
3. Provide state-of-the-art information and discussion on: (i) advanced monitoring techniques and equipment for SW pollution potential evaluation and SWDF sites screening and characterization; (ii) monitoring strategies, methods, techniques and equipment to provide early means to detect, and *in situ* intercept or remediate environmental contamination; (iii) post-closure and life cycle monitoring strategies.
4. Present and critically discuss innovative methods and technologies for environmentally safe disposal and *in situ* remediation of SW.
5. Present and critically discuss emerging strategies and technologies for solid waste management with regard to adequate adjustment of environmental legislation and monitoring.

We hope this book to some extent will contribute to the harmonization of efforts directed to the proper, environmentally safe solid waste disposal practices as well as to wider and more dynamic implementation of the advanced approach, methods and techniques for waste management, monitoring and contaminated site remediation.

The Editors

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Life is sometimes cruel. An excellent author and devoted researcher, A. S. Juwarkar, untimely departed from this world. I believe that his farewell contribution will last for a long time and will receive the appreciation of the readers. The acknowledgement is due to his colleagues and co-workers, who completed the preparation of his contribution.

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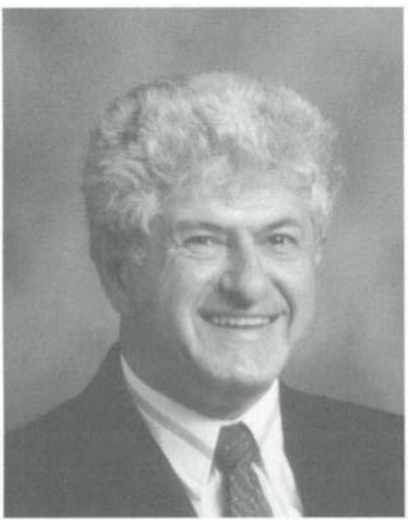
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PART I

Introduction

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Solid Waste: Assessment, Monitoring and Remediation
Twardowska, Allen, Kettrup and Lacy (Editors)
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I.1
Solid waste: what is it?

Irena Twardowska

I.1.1. Introduction

The activities of human society are always accompanied by waste generation. The fundamental environmental issue in industrial and developing countries throughout the world is how to best identify and manage waste streams. Surprisingly enough, mankind at the beginning of the 21st century still has problems with the development of a precise legal definition of a waste, as well as with international harmonization of national standards on waste terminology. This evokes serious problems with waste management and statistics at the global and even at the regional level. To start solving these problems, some apparently simple basic questions are thus to be unanimously answered:

- What is a waste?
- What is solid waste?
- What is hazardous waste?
- What is inert waste?
- What is a waste, which is not hazardous and not inert?

The legal definitions of waste exert a profound impact on the waste management system, resulting in serious consequences to environmental safety and sustainability. Despite increasing environmental awareness, the waste management practice in the world shows clearly that it generally follows the path of least cost and least regulatory control unless restrained by appropriate laws and regulations supported by adequately implemented enforcement procedures. Legal terms and definitions are an essential part of these procedures. Consequently, it is also a matter-of-course that definitions must not become a barrier to an optimum management of waste, environmental protection and economic development. At present, still many different national concepts of "waste", "solid waste", "hazardous waste" and related policies exist in the world.

The intention of this introductory chapter is to present and discuss the state of the art concerning basic terminology and legal definitions related to waste, in particular solid waste, in the USA and the European Union, with some references to national and international definitions.

I.1.2. Definitions of waste in the USA legislation

In the United States, waste identification is a generator responsibility. It is regulated within the framework of the two major federal laws: Resource Conservation and Recovery Act (RCRA) enacted in 1976 replacing the Solid Waste Act of 1965, and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980, commonly known as Superfund, with appendices and amendments. The most important latter ones include the Hazardous and Solid Waste Amendments of RCRA (HSWA, 1984) and the Superfund Amendments and Reauthorization Act (SARA, 1986). Other U.S. environmental laws related to solid waste among different sources of environmental pollution are: the Toxic Substances Control Act of 1976, Provisions of the Asbestos Hazard Emergency Response Act of 1988 and Asbestos Information Act of 1988, as well as the Pollution Prevention Act of 1990. Besides federal laws, also states may develop their own state regulations that have to comply with or exceed the stringency of the federal law.

RCRA provides several basic definitions of solid waste and hazardous waste. As used in this Act, the term solid waste means any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant, or air pollution facility and other discarded material, including solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining, and agricultural operations, and from community activities, but does not include solid or dissolved material in domestic sewage, or solid or dissolved materials in irrigation return flows or industrial discharges which are point sources subject to permits under section 402 of the Federal Water Pollution Control Act, as amended (86 Stat. 880), or source, special nuclear, or by-product material as defined by the Atomic Energy Act of 1954, as amended (68 Stat. 923).

The term *hazardous waste* means a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may

(A) cause, or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness: or
(B) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.

Regulations under RCRA designated according to the Code of Federal Regulations (CFR) in general do not refer to specific industries. The CFR, besides abridged definitions following the RCRA terms, gives detailed lists of hazardous wastes, mixture rules, and exclusions from RCRA. According to these regulations (40 CFR 261.2), *solid wastes include any liquid, solid, semisolid, or contained gas that is discarded or stored prior to discarding*. Waste classified as hazardous must meet two criteria: (i) be a solid waste; (ii) to either exhibit at least one of four hazard characteristics defined in 40 CFR 261 (ignitability, reactivity, corrosivity, extraction-procedure toxicity), or be located in the lists of hazardous wastes. The related lists and regulations are as follows:

- non-specific-source hazardous wastes (40 CFR 261.31)
- specific-source hazardous wastes (40 CFR 261.32)

- acutely hazardous wastes (40 CFR 261.33 (e)
- generally hazardous wastes (40 CFR 261.33 (f)

A number of wastes are excluded from RCRA regulations and incorporated into other environmental laws. These exclusions listed in 40 CFR 261.4 in about 18 lists comprise four major categories: (1) materials which are not solid wastes; (2) solid wastes that are not hazardous wastes; (3) hazardous wastes that are exempted from certain regulations; and (4) laboratory samples. The subcategories excluded from RCRA cover among others, the following solid wastes:

- nuclear or nuclear by-product materials as defined by Atomic Energy Act;
- mining overburden returned to the site;
- cement-kiln dust waste;
- fly ash, bottom ash, slag and flue-gas emission control waste from fossil fuel combustion;
- drilling waste in oil, gas and geothermal exploration.

Asbestos waste is regulated under separate Provisions of the Asbestos Hazard Emergency Response Act of 1986, Asbestos Information Act of 1986, Superfund Act and Toxic Substances Control Act. The Asbestos Information Act defines the term "asbestos-containing material" as "any material containing more than one percent asbestos by weight".

Also, infectious wastes and toxic chemicals such as PCBs and that originated from certain combustion processes such as dioxins are exempted from regulations under RCRA. These chemicals are regulated under the Toxic Substances Control Act. Section 222 of the 1984 RCRA Amendments, Listing and Delisting of Hazardous Waste, pertains to waste containing persistent organic pollutants (POPs) such as dioxins, dibenzofurans, chlorinated aromatics and aliphatics, and other chemicals such as dimethyl hydrazine, toluene diisocyanate (TDI), carbamates, bromacil, linuron, organobromines and waste containing hazardous chemicals such as inorganic chemical industry wastes, refining wastes, coke by-products, dyes and pigments and lithium batteries. This amendment specifically directs the EPA to list and explicitly consider for listing such wastes, and to develop additional hazardous waste characteristics, including measures of toxicity, to be added to the four basic characteristics contained in 40 CFR 261.S.

RCRA does not define "inert waste"; it also does not characterize a waste that is not hazardous and also not inert. Nevertheless, the essentially important statement given in RCRA as a Congressional finding is that "disposal of solid waste and hazardous waste in or on the land without a careful planning and management can present a danger to human health and the environment". This means that solid waste that is not hazardous is not yet safe and also may pose a serious current or future threat. The RCRA also indirectly defines all discarded recyclable materials as waste, but strongly stresses a need to separate usable materials from solid waste or to produce usable energy from solid waste. This Act in Sec. 1004 also defines the terms "disposal", "recoverable", "recovered material" and "recovered resources". The term disposal means the discharge, deposit, injection, dumping, spilling, leaking, or placing of any solid waste or hazardous waste into or on any land or water so that such solid waste or hazardous waste or any constituent thereof may enter the environment or be emitted into the air or discharged into any waters, including ground waters". The term recoverable refers to the capability and likelihood of being

recovered from solid waste for a commercial or industrial use. The term recovered material means waste material and by-products, which have been recovered or diverted from solid waste. This term "does not include those material and by-products generated from, and commonly reused within an original manufacturing process". The term recovered resources means material or energy recovered from solid waste. These definitions do not leave any spare room for misinterpretation, showing clearly that discarded waste containing usable material indisputably *remains a waste*. Recovery of solid wastes in most cases results in a separation of usable material or energy from the non-recoverable waste residue to be disposed. Recycled materials that are solid waste come under RCRA regulations.

RCRA definitions contain also the term "virgin material", which means "a raw material, including previously unused copper, aluminum, lead, zinc, iron, or other metal or metal ore, any "underdeveloped" resource that is, or with new technology will become, a source of raw material". This definition seems to be controversial, since the material has been extracted from its natural environment, processed to separate usable components and exposed to the new ambient conditions and active weathering processes. This must cause accelerated transformations of the original properties, along with potential for mobilization of metals in hazardous concentrations. The word "virgin" suggests unchanged primary character of the material. Under the circumstances, it is questionable and does not fit to the underdeveloped material.

This brief discussion shows the major terms and definitions related to solid waste and hazardous waste in the present US federal legislation and regulations, and the dynamic character of hazardous waste listing while the terms and definitions concerning waste remain unchanged.

More detailed information concerning these definitions can be found in Appendix A to Chapter I.2 that contains excerpts from Code of Federal Regulations, CITE 40CFR261.1-261.4 (CFR, Rev. 1999). The current version of CFR and any future revisions can be also downloaded from the relevant website.

I.1.3. Legal definitions of waste in the European Union: current status and trends

I.1.3.1. EU waste legislation and legal terminology

Unification of Europe has evoked a need of developing the European standards on waste, harmonization of national legislation and integration of waste management policy. Adaptation of the European Directives by the European countries and progress in the EU standardization, also in the standards on waste-related terminology, greatly contribute to achieving this goal, despite legislative discrepancies and arguments, which still exist both between the EU Directives and within the legislative bodies. To acquaint the reader with the terms and definitions given in these regulations, which stimulate the harmonization of national legislation on the European level, some major terms and lists will be discussed here in more detail.

The EU waste legislation until January 2002 was based on 3 general Directives and 2 catalogues, in particular:

- Waste Directives: Council Directive 75/442/EEC followed by the amending it Council Directive 91/156/EEC on waste.
- European Waste Catalogue 94/3/EC (*repealed*).
- Hazardous waste Directive: Council Directive 91/689/EEC on hazardous waste.
- Hazardous waste list: Council Decision 94/904/EC, establishing a list of hazardous; waste pursuant to Article 1(4) of Council Directive 91/989/EC on hazardous waste (*repealed*).

On 3 May 2000, the European Commission approved a revised version of the key official list of wastes that should be classified as hazardous in the EU. The new list with effect from January 2002 incorporates also the European Waste Catalogue (EWC, 1994) of non-hazardous wastes, creating for the first time a single EU waste list (Commission Decision 2000/532/EC amended in 2001 by Commission Decisions 2001/118/EC of 16.02.2001; 2001/119/EC of 22.01.2001, and 2001/573/EC of 23.07.2001). This one list integrates the list of wastes laid down in Decision 94/904/EC and that of hazardous wastes laid down in Decision 94/904/EC_2 and simultaneously repeals these Decisions. The single waste list markedly increases transparency of the listing system and simplifies existing provisions.

Several Council Directives enacted since 1989 and continuously updated, are related to waste incineration, mainly in conjunction with air pollution. The relevant regulations in force have been included in Council Directive 94/67/EC on the incineration of hazardous waste; in December 2000 the European Parliament and the Council approved Directive 2000/76/EC on the incineration of waste, which updates and extends a scope of the previous legislation. Waste disposal of is regulated by Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste.

A number of Council Directives are related to specific wastes, e.g. Directive 2000/53/EC on end-of-life vehicles; or Packaging Waste Directive (European Parliament and Council Directive 94/62/EC on packaging and packaging waste; amending this existing Packaging Waste Directive is in preparation—Com (2001) 0729); Animal Waste Directive (Council Directive 90/667/EEC, laying down veterinary rules for the disposal and processing of animal waste); Waste Oil Directive (Council Directive) 75/439/EEC has been continuously under revision and was amended in 1987, 1991, 1994 and 2000; Battery Waste Directive 91/157/EEC was adapted to technical progress by Council Directive 93/86/EEC and Commission Directive 98/101/EC on batteries and accumulators. Sewage Sludge Directive 86/278/EEC updated by Directive 91/692/EEC is being revised by the European Commission (EC DG ENV, 2000); also the Biowaste Directive on biological treatment of biodegradable waste is under preparation (EC DG ENV, 2001), both regulations being currently at the stage of working documents of the EC Directorate General – Environment. The Directives of the European Parliament and European Council comprise other specific waste streams, for example, Directive on Waste Electrical and Electronic Equipment (WEEE) (2003) and Directive on the restriction on use of certain hazardous substances in this waste (2003). Plastics waste (PVC and other resins) is currently being extensively studied with respect to environmental behavior; European Commission has also funded a report called "Construction and demolition waste management practices and their economic impacts" as a basis for further proposal for a Directive (EC Europa website).

Directory of Community legislation in force and in preparation on waste management and clean technology is available in the continuously updated EC EUR-Lex websites. Each of these documents provides for specific terms and definitions related to the scope of regulations.

In addition to the terms defined in the above European regulations, two European Standards prepared by the European Committee for Standardization, CEN/TC 292/WG 4: "Characterization of waste – Terminology, Part 1: Material related terms and definitions", (EN 13965-1 = WI 292025) and "Characterization of waste – Terminology, Part 2: Management related terms and definitions" (EN 13965-2 = WI 292026) underwent the formal vote (stage 49 document) in 2003. After final approval by CEN, its members are bound to comply with CEN/CENELEC Internal Regulations, which stipulate the conditions for giving it the status of a national standard of CEN member states without any alteration. The aim of these CEN standards is to develop systematic definitions of waste concepts in accordance with ISO 10241 – International terminology standards – Preparation and layout.

Waste terminology and definitions used in the EU Directives, catalogues and standards are intended to be the base of common language assuring compliance with regulatory provisions or a contractual situation between parties in waste management chain. The waste legislation in the EU, alike national waste legislation of the majority of Member States, primarily addresses environmental and public health, and to a lesser extent, resource concerns. These concerns and awareness of the consequences in the area of waste management on the recycling, treatment and disposal of wastes are reflected also in legal terms and definitions of waste. The basic prerequisite is, that these terms and definitions are to be in accordance with the Framework Directive on Waste (75/442/EEC), which constitutes the essential objective of all provisions relating to waste disposal. This objective "must be the protection of human health and the environment against harmful effects caused by the collection, transporting, treatment, storage and tipping of waste".

I.1.3.2. The EU definition of a waste

The legal definition of a waste at European level is given in the EU Council Directives 75/442/EEC and 91/156/EEC amending Directive 75/442/EEC. The latest Council Directive 91/156/EEC defines waste as *any substance or object in the categories set out in Annex I which the holder discards or intends or is required to discard* (Annex I comprises a list of 16 categories Q1 to Q16 based on the OECD Council Decision 88/90 (1988) where these categories are specified, e.g. Q1 *Production or consumption residues not otherwise specified below* or Q16 *Any materials, substances or products which are not contained in the above categories*. The list is subject to periodical review and revision – see Appendix A). This definition replaced the one given by the Council Directive 75/442/EEC on waste, which does not refer to any list, but considers differences in the national law *(waste is any substance or object which the holder disposed or is required to dispose of pursuant to the provisions of national law in force).* The revised contemporary definition of waste given in the Council Directive 91/156/EEC tends to provide a uniform European interpretation of the concept of this term. Unfortunately, the referred list of categories of the Annex 1 evokes more debates and field of misinterpretation than it has been intended, and makes this definition extremely inconvenient for use in other regulations, in particular

in those also based on lists, e.g. in the integrated waste list (Commission Decision 2000/532/EC) coded according to the generic origin or composition. This poses problems with the adopting the definition of waste of the Framework Directive 91/156/EEC for the purposes of some posterior EC Council Directives. Council Directive 94/62/EC on packaging waste, the Council Directive 1999/31/EC on the landfill of waste, the Council Regulation 259/93/EEC on the shipments of waste and Commission Decision 2000/532/EC creating for the first time a single EU waste list refer hence to waste according to non-revised Directive 75/442/EEC. The adopting the non-revised definition by these Directives, in particular, Commission Decision 2000/532/EC (amended by Commission Decision 2001/118/EC) that should comprise continuously updated coded list of waste, shows clearly that the listing in the general definition of waste is a source of confusion in many other waste-related terms and definitions. To avoid further problems, the essential Regulation (EC) No. 2150/2002 on waste statistics has stated that waste *shall mean any substance or object as defined in Article 1(a) of Council Directive 75/442/EEC of 15 July 1975 on waste.* This statement evidently gets out of the way all obstacles related to restoring the original definition of waste. Without reference to the aforementioned and exemplified list adopted from the OECD Council Decision C(88)90 Final (1988) concerning transfrontier movements of hazardous waste, the definition of waste becomes clear, simple, non-disputable and applicable to all relevant terms and definitions. At any rate, no double definition should exist in legislation for the purposes of the particular Directives.

I.1.3.3. EC list of wastes

Unlike the inclusion of waste categories into the definition of waste, the former European Waste Catalogue 94/3/EC (EWC) and also the new single EC List of wastes (Commission Decision 2000/532/EC amended by 2001/118/EC in 2001), which incorporates both the key official list of wastes that classified as hazardous in the EU, and also updated EWC of non-hazardous waste, do not intend to specify unanimously whether material is a waste. According to the introductory statement of the integrated List of wastes, "the inclusion of a material in the list does not mean that the material is a waste in all circumstances. Materials are considered to be waste only where the definition of waste in Article 1(a) of Directive 75/442/EEC is met," i.e. if this material "is disposed by the holder or is required to dispose of pursuant to the provisions of national law in force" and is outside the commercial cycle or chain of utility. For example, packaging, which is rotationally refilled or reused for the same purpose for which it was conceived will become packaging waste when no longer subject to reuse.

The main purpose of the integrated list of wastes is to increase the transparency of the listing system and to simplify existing provisions in order to establish a common terminology for the states, which adopt it, in particular for the EC Member States, to provide support to the generation of precise and reliable statistics on waste generation, which, in turn, are indispensable for improving waste management. The integrated EU List of wastes contains a register of about several hundreds items in the list divided into 20 major categories and two sub-levels of information coded principally on the basis of source or composition of waste material. The listed types of waste are defined by the six-digit code for the waste and the respective two-digit and four-digit chapter headings,

which specify 20 broad source categories of waste (two-digit) and 109 more narrow mainly product-based groups (four-digit).

I.1.3.4. The definition of hazardous waste

The definition of hazardous waste in the EU legislation is more extended and detailed than the relevant one in the US regulations. According to the Council Directive 91/689/EEC of 12 December 1991, Article 1(4), the term hazardous waste means:

- "wastes featuring on a list to be drawn up in accordance with the procedure laid down in Article 18 of Directive 75/442/EEC on the basis of Annexes I and II to this Directive.... These wastes must have one or more of the properties listed in Annex III. The list shall take into account the origin and composition of the waste and, where necessary, limit values of concentration. This list shall be periodically reviewed and if necessary by the same procedure.
- Any other waste which is considered by a Member State to display any of the properties listed in Annex III. Such cases shall be notified to the Commission and reviewed in accordance with the procedure laid down in Article 18 of Directive 75/442/EEC with a view to adaptation of the list."

In short, as it has been defined in Article 2 paragraph (c) of the Landfill Directive 1999/31/EC, the term hazardous waste means any waste, which is covered by Article 1(4) of Council Directive 91/689/EEC of 12 December 1991 on hazardous waste. The definition of hazardous waste in the Directive 91/689/EEC refers to the Directive 75/442/EEC (Article 18), and based on lists given in Annexes I, II to this Directive. This waste must have one or more properties listed in Annex III. Domestic waste has been exempted from the provisions of this Directive in order to take into consideration the particular nature of this waste. Waste classified as hazardous need not meet a criterion of being solid waste. This is a significant difference compared to the US definition under RCRA, where waste classified as hazardous must be a solid waste according to the definition.

The full quotation of Annexes I, II and III is given in the Appendix B to this Chapter (Excerpt from Council Directive 91/689/EEC on hazardous waste):

- Annex I (parts I.A. and I.B.) comprises currently 40 categories or generic types of hazardous waste listed according to their nature or the activity, which generated them (waste may be liquid, sludge or solid in form);
- Annex II contains list of constituents (C1–C51) of the wastes listed in Annex 1.B., which render them hazardous when they have the properties, described in Annex III;
- Annex III defines properties of wastes which render them hazardous (H1–H14): explosive, oxidizing, highly flammable, flammable, irritant, harmful, toxic, corrosive, infectious, toxic for reproduction, mutagenic, releasing toxic gases, yielding another harmful substance, ecotoxic. The last term, which may have different meaning elsewhere, is defined as "substances and preparations, which present or may present immediate or delayed risks for one or more sectors of the environment".

Wastes classified as hazardous are considered to display, as regards H3 to H8, H10(6) and H11 of the Annex III to Directive 91/680/EEC, one or more of the properties specified

in the Commission Decision 2001/118/EC amending Decision 2000/532/EC (see Appendix C).

The list of hazardous waste pursuant to Article 1 (4) of Council Directive 91/689/EEC on hazardous waste was established by the Council Decision 94/904/EC of 22 December 1994. Commission Decision 2000/532/EC replaced Commission Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1 (4) of Council Directive 91/689/EEC on hazardous waste. Waste marked with an asterisk (*) in the list of wastes is considered a hazardous waste pursuant to article 1(4) first indent of Directive 91/689/EEC on hazardous waste.

Besides, "without prejudice to Article I (4) second indent of Directive 91/689/EEC, Member States may decide, in exceptional cases, that a waste indicated in the list as being non-hazardous displays one or more of the properties listed in Annex III to Directive 91/689/EEC". All such cases are subject to notification to the Commission and examination with a view to amending the list. The full actual list of wastes is included into the Annex to the Commission Decision 2001/118/EC amending Decision 2000/532/EC as regards the list of wastes.

I.1.3.5. Other basic terms and definitions

The definition of solid waste is given in the European Standard prEN 13965-1 as "waste that predominantly consists of material that has the properties of a solid".

The term non-hazardous waste is defined in the Article 2 paragraph (d) of the Council Directive 1999/31/EC on the landfill of waste as "waste which is not covered by paragraph (c)", i.e. by the definition of hazardous waste.

The term inert waste appears in the consecutive paragraph (e) of the Landfill Directive. It is defined as "waste that does not undergo any significant physical, chemical or biological transformations. Inert waste will not dissolve, burn or otherwise physically or chemically react, biodegrade or adversely affect other matter with which it comes into contact in a way likely to give rise to environmental pollution or harm human health. The total leachability and pollutant content of the waste and the ecotoxicity of the leachate must be insignificant, and in particular not endanger the quality of surface water and/or groundwater".

There is, though, no term either in any Directive or the European Standard on terminology that defines *waste, which is not hazardous but also not inert*. Commonly used term non-hazardous waste defined in the Landfill Directive, Article 2 (Definitions) as "waste which is not covered by paragraph (c)" includes both not hazardous and inert waste. The experience shows that *the waste not hazardous in terms of Council Directive 91/689/EEC as defined in paragraph (c) but also not inert in terms of paragraph (e) includes major amounts of waste generated and disposed of, and thus should be termed and defined.* The antithetic term and definition non-hazardous waste suggests that these wastes are "safe", which is not true. The definition of this group should refer to *waste, which is not covered by the Council Directive 91/689/EEC on hazardous waste, but at any stage of its disposal as freshly generated material or due to physical, chemical or biological transformations, by itself or in contact with other matter at the disposal site is likely to give rise to environmental pollution, and in particular can endanger the quality of*

groundwater and/or surfacewater. The term for this group of waste should reflect their life-cycle pollution potential. The notion "environmentally harmful waste" seems to be the best matching with environmental impacts of these materials. Unfortunately, the term "harmful" is already listed in the Annex III to the Council Directive 91/687/EEC on hazardous waste among the properties of wastes, which renders them hazardous in another context. According to this list the term harmful means "substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may involve limited health risk". This definition more fits for the term "noxious", though since the notion harmful has been already used instead, this term cannot be applied to another definition. Therefore, for this group of waste the synonymous term "detrimental waste" or alternatively "environmentally damaging waste" can be used.

I.1.3.6. "Recyclable waste" or "secondary raw material"?

In conjunction with a legal terminology, another issue, which arouses emotions and disputes, is the possible changing of the definition of recyclable waste. Existing legal definitions of waste refer to substances or objects "which the holder discards or intends or is required to discard", including those technically suitable for recovery. Currently, due to continuing calls from industry to exclude recyclable materials from the category of waste and to define them secondary raw material, trends to avoid the term waste and use instead a more "neutral" notions are evolving also in legislative and standardization areas. A comprehensive report on the legal definitions of waste and their impact on waste management in Europe prepared by EC Institute for Prospective Technological Studies as a first draft for comments (Bontoux and Leone, 1997) reflect the confusion in the waste debate, in particular in the issue of definitions in waste management. The study admits that "defining a material as waste or secondary raw material bears many consequences" and articulates the principal equitable thesis that "definitions must not become a barrier to an efficient and sustainable European waste management system". The basic question, which arises in this matter is the objective evaluation of whether the classification of a discarded recyclable material as waste indeed "hampers any recovery, treatment and disposal option susceptible of providing the best possible solution on an economic and/or environmental point of view", and vice versa, whether re-defining recyclable waste as secondary raw material would provide the best such solution. After discussion of some examples of the issues and concerns related to transboundary shipment of recyclable waste or the tarnishing public image and even losing market by waste management industries because of the negative public perception of the concept of waste, the discussed study among other recommendations proposes "to expressly exclude certain categories of materials from the definition of waste". Simultaneously, it refers to Article 3 of the Directive 91/156/EEC as "opening the door to such a solution". The aforementioned Article statement is as follows: "Member States shall take appropriate measures to encourage [...] the recovery of waste by means of recycling, re-use or reclamation or any other process with a view to extracting secondary raw material". It should be though stressed that this statement does not give any consent to exclude recyclable waste from the definition of waste through a simple rename of waste into e.g. secondary raw material, as the efficiency of such way of encouragement of waste recycling is more than doubtful.

Another example of the industrial pressure on the legislative bodies of the EU is the Resolution 183 of the 10th Meeting of the European Committee for Standardization, CEN/TC 292 in Vienna, Austria, Dec. 10/11, 1997, which "asks the national committees to review a possible replacement of the term waste by *material* in its current standards and standards under development – with exception of title and scope". Fortunately, this resolution was finally rejected at the 11th Meeting of CEN/TC 292 in Oslo in 1998 and after the negative results of a national committees' enquiry. Nevertheless, the calls from the industry have not ceased, and the attempts in this direction are periodically renewed, as in this case the legal term has substantial direct economic consequences. The impact of the legal definitions on the waste strategy as an essential element of global sustainable development and the environmental protection should be thus thoroughly understood. One of the essential prerequisites is that the legal definition in no case should absolve the producer or the holder from the responsibility for the generated waste from the moment of generation until it is utilized in an environmentally safe end product or is taken for utilization by an end-user. Since assignment of waste from producer to end-user occurs, the end-user is to bear the legal responsibility for the proper management of waste if it is not converted instantly into an environmentally neutral or friendly product, unless another agreement between the generator and end-user defining the scope of responsibility of each party exists.

It is clear that waste disposal must have direct economic consequences for the waste generator or holder to make the legal definitions and regulations work properly in the implementation arena not just in the European, but also in a global scale. The best proof of the efficacy of the legislation and regulatory system is in an implementation area. The pro-environmental and pro-recovery/recycling policy must be based on the term waste and on the "polluter pays" principle. A good example is utilization of coal combustion waste (CCW) in countries where its generation is high. It is well known that this waste due to its properties can be used in a wide array of field-proven applications on par with competing virgin, processed and manufactured engineering material. It is also known that the use of this waste in high CCW producing countries is strongly affected by local and regional factors including production rates vs. market demand and saturation; processing, transportation and handling costs; availability and price of competing materials, etc. In the USA, of approximately 82 million tons of CCW produced in 1992, only 27% were utilized. The remainder went to disposal sites (Tyson, 1994). More recent data does not show any improvement in this field, reporting the amounts in 1996 to be of over 92 million tons generated with about 25% of it utilized (Butalia and Wolfe, 1999; Chugh and Sengupta, 1999; Stewart, 1999). Huge amounts of this waste are already lying in disposal sites throughout the country.

In India, at the current level of coal and power production, around 50 million tons of CCW is generated annually, and a further growth up to 90 million tons/a is anticipated. At present, the utilization rate there is negligible (2–5% in total), mainly due to the weakness of implementation and enforcement system (Kumar et al., 1996; Singh and Gambhir, 1996; Prasad et al., 2000). This reflects a global status concerning CCW utilization, despite the fact that several European countries, small CCW producers, where the demand for CCW and its generation is fortunately balanced, use almost all the CCW that they produce (Clarke, 1994).

In Poland, 18.8 million tons (Mt) of CCW was generated in 2001, out of which 13.8 Mt (73%) of the annual production was utilized (Central Statistical Office, 2002). This places Poland at the top of the countries, which are producing comparably high amounts of CCW with respect to the percentage of use of this waste. In the mining area of the Upper Silesia coal basin, 87% of CCW generated was utilized, mainly in the deep mines for backfilling, goaf filling (stowing), simplification of ventilation system and fire prevention (State Environmental Protection Inspectorate, 2001). For these purposes, CCW in this area has been used since 1989. Therefore, coal mines are indisputable beneficents of CCW utilization. Though, all expenses connected with the environmentally safe CCW hermetic transportation by specialized firms, preparation of transportable mixtures and their location in the mines, along with testing, environmental control, etc. are being covered by power producers, which are generators of CCW. The basis for this expenditure by the power producers is a cost-benefit study: the power plants benefit from the difference between the charge for disposal of CCW, regulated currently by the National Directive of the Cabinet of 2003 *on charges for the use of the environment*, which replaced earlier Directive of 1998 with amendments of 1999, Directives updated annually in 1993–1997 and Directive of 2001 *on charges for the disposal of wastes*. Thus, there are five beneficent at once: power plants, coal mines, CCW transportation companies, and last but not the least, the whole region and the country. This is the best proof of the efficiency of the system based on the financial responsibility of waste generators. Defining CCW by a neutral term, e.g. secondary raw material or "by-product" would bring about disastrous consequences. Power plants would not have any incentive for bearing the costs of CCW utilization. Mines, which benefit from use of CCW, would not be able or willing to cover additional expenses that raise the costs of coal production. Transportation companies would collapse. Environment and safety in mines would get worse. This example shows that seemingly innocent playing on words can be dangerous. Waste is waste. Economic and technical factors not associated with waste generation dictate the major production. The amounts and place of its generation only occasionally fit to the demand for waste. Calling waste material will not reduce the waste stream. Waste generators would immediately use the opportunity to shift off the responsibility as producers of a "beneficial raw material".

Waste technically suitable for recovery does not become automatically a raw material if there is no market for it, or its use is commercially not effective. A sound waste management strategy requires global thinking and regional acting. Global thinking starts from the terminology. Well thought-out regional enforcement systems including incentives, charges and penalties based on the precise terms may greatly improve utilization of waste.

Our experience shows that majority of waste is not environmentally safe. Very often its strong adverse environmental impact is time-delayed, e.g. occurs in the post-closure period of a waste site. Waste as a freshly generated anthropogenic material is not geochemically stable. There is extensive evidence of a striking discrepancy between long-term risk assessment based on accelerated simulation tests or predictive models, and real situations (Twardowska and Szczepańska, 2001). This shows the insufficient knowledge of the long-term environmental behavior of many kinds of waste. Therefore, waste should not be put into the same bag as natural raw material. To facilitate waste utilization in an environmentally safe way and to prioritize its use, special environmentally safe

reuse-oriented enforcement strategies and regulations should be developed with respect to waste and not "materials" or secondary raw materials, or "by-products". Charges for waste disposal should encourage waste producers to advance their seeking of opportunities for waste utilization, minimization of the waste stream generated during the production or rendering it harmless by means other than disposal. The charges for the disposal are ought to be the highest with respect to recoverable waste, which use is technically and technologically sound, commercially effective and environmentally safe. Systems of charges should be directed to advancing waste utilization, among others through financial support of waste recycling industries and end-users by waste generators, as well as to stimulating technologies, which assure waste minimization.

The replacement of the legally defined term waste by the broad notion that softens the definition and makes it vague and meaningless will not facilitate improving waste management.

I.1.3.7. Waste disposal, recovery and recycling

To make the questions concerning waste management clear along with the above discussion on what is waste and why, and what is not, the terms "waste disposal", "recovery" and "reuse" must be well defined. In a wider regional or global scale, these terms should not be conflicting or incompatible with other national or regional definitions. The Framework Council Directive 75/442/EEC and amending it Directive 91/156/EEC on waste, defines disposal as "any of the operations provided for in Annex II.A." This Annex which "is intended to list disposal operations such as they occur in practice", specifies 15 such operations (D1–D15). The term recovery means "any of the operations provided for in Annex II.B", which is "intended to list recovery operations as they are carried out in practice" and specifies 13 such operations (R1–R13). The specification of these operations uses as synonyms such wording as "recycling, reclamation, regeneration, recovery of components and re-use" (operations R1–R8). Storage pending any of the operations defined either as "disposal of" or recovery is also included in the list of acceptable operations. In accordance with Article 4 (of the Directive) waste must be either disposed of or recovered "without endangering human health and without the use of processes and methods likely to harm the environment" (see Appendix A).

In Council Directive 94/62/EC on packaging waste, for the purposes of this Directive, a differentiation between the terms "reuse", recovery and "recycling" has been made. While the definitions disposal and recovery mean "any applicable operations provided for Annex IIA" and "Annex II B to Directive 75/442/EEC", the term reuse means any operation by which packaging, which has been conceived and designed to accomplish within its life cycle a minimum number of trips or rotations, is refilled or used for the same purpose for which it was conceived, with or without the support of auxiliary products present on the market enabling the packaging to be refilled; such reused packaging will become packaging waste when no longer subject to reuse. In this definition, reused packaging is not a waste as long as it remains continuously in the production cycle. "Recycling means the reprocessing in a production process of the waste materials for the original purpose or for other purposes including organic recycling but excluding energy recovery". Lastly, "energy recovery shall mean the use of combustible packaging waste as a means to generate energy through direct incineration with or without other waste but

with recovery of the heat". Thus, discarded package used for recycling or energy recovery is a waste.

In general, the more extended general definitions of the terms disposal, and recovery do not conflict with the US Solid Waste Disposal Act (RCRA). Like in the definition of reused package in Council Directive on packaging waste, the definition of the recovered material in RCRA clearly indicates that "the materials and by-products generated from, and reused within an original manufacturing process" are not a waste. Any other recovered material is a waste.

I.1.4. International definitions

Besides EU definitions that are not considered here to be international in face of gradual harmonization and unification of laws and regulations within the European Union, other international regulations of a wider geographical coverage are in force in the EU area. In particular, these regulations comprise OECD Council Decisions and the Basel Convention related to transboundary movements of wastes. The 29 Member Countries of OECD, besides the EU members, include associated (Norway) or pre-accessory stage countries (Poland, Hungary and Czech Republic), as well as 8 non-European countries, including the most developed ones: Australia, Canada, Iceland, Japan, Korea, Mexico, New Zealand, and USA.

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal has been ratified as for 19 June 2002 by 151 parties all over the world and thus has the strongest impact on the waste terminology and legislative area worldwide. The Parties to the Basel Convention, besides the EU Member States, comprise most of Asia, Oceania and South America. The biggest white spot area occurs in Africa, Central and North America, due to the United States not joining the Convention (Tieman, 1998). Also several new counties – former republics of the USSR in Europe and Asia – have not yet ratified the Convention.

Adoption of the terminology used in OECD and Basel Convention legislative documents and regulations brings about the requirement of harmonization of the legal definitions to avoid all the discrepancies between the directives in force, which unavoidably leads to intended or unintended misinterpretation and legislative confusion.

I.1.4.1. Waste definitions in OECD regulations

The OECD Council Decision C(88)90 Final of 27 May 1988, which was enacted to control the transfrontier movement of hazardous wastes, defines waste as *materials other than radioactive materials intended for disposal, for reasons specified in Table 1* Table 1 is entitled "Reasons why material are intended for disposal" and contains 16 different categories of waste (Q1–Q16) (see Appendix I). These categories were introduced into the definition of waste in the Framework Directive on Waste 91/156/EEC of 1991 as "set out in Annex 1" to comply with the OECD Council Decision C(88)90 Final. The European Commission, in accordance with the procedure laid down in Article 18, was required to draw up "a list of wastes listed in Annex 1" not later than 1 April 1983. The European Waste Catalogue (EWC), which was developed as a realization of this obligation, and the

EC list of wastes that replaced EWC in 2000 (Commission Decision 2000/532/EC), consists of 20 categories (two-digit code), as well as four-digit subcategories and six-digit types of waste. In fact, it has no definite relation to the OECD list, but constitutes a well systemized and easy-to-handle inventory of waste. This has evoked a serious problem with regard to the general definitions of waste in the Framework Directive 91/156/EEC and OECD Council Decision C(88)90 with double listing, and as discussed above, resulted in simultaneous adopting the general definition of waste from the non-amended Framework Directive 75/442/EEC, Article 1(a) by the Council Directives 91/989/EEC on hazardous wastes, 94/62/EC on packaging waste, Council Directive 1999/31/EC on the landfill of waste and Council Regulation 259/93 on the shipment of waste.

On the other hand, the adoption in 1992 by OECD Member States of the Council Decision Concerning the Control of Transfrontier Movements of Wastes Destined for Recovery Operations C(92)39/Final, which uses the same definition of waste as that in the OECD Council Decision C(88)90 Final, implies the alignment of the OECD Member Countries on this definition until it is in force. For the EU countries, that means the aforementioned burden with double legal definitions of the term waste.

The OECD Council Decision C(88)90 Final also gives the definition of hazardous wastes as those belonging to the categories listed in Table 3 of its Annex entitled "Generic types of potentially hazardous wastes". Again, this list differs from the "Categories or generic types of hazardous waste..." listed in the Annex I to the Council Directive 91/689/EEC on hazardous waste, from the repealed list of hazardous waste annexed to the Council Decision of 22 December 1994 and from the list of hazardous waste incorporated into the integrated list of wastes (Commission Decision 2001/532/EC amended by 2001/118/EC).

The Council Decision Concerning the Control of Transfrontier Movements of Wastes Destined for Recovery Operations C(92)39/Final does not define the waste- and hazardous waste-related terms, but indirectly introduces the three-level gradation of waste according to the increasing potential hazard: the Green, Amber and Red Tiers. Wastes belonging to the Amber and Red Tiers are considered hazardous; these of the Red Tier display the highest level of hazard.

The Council Regulation 259/93/EC on the shipment of waste has been harmonized with the OECD Council Decision C(92)39 Final to enable its formal implementation through national legislation, and therefore refers to the same three tiers, despite the fact that some discrepancies between these listings and the European List of Hazardous Waste established by Council Decision 94/904/EC and at present incorporated into the harmonized list of wastes enacted by the Commission Decisions 2000/532/EC and 2001/118/EC also occur.

In the question of distinguishing waste from "non-waste", OECD proposed a step-by-step approach organized in a flow chart, where the destination of the material, its environmental and public health protection and economic criteria are considered (OECD ENV/EPOC/WMP (96)1, (97)2, 1996, 1997). From these criteria can be concluded, that if the material can only be used with being subjected to recovery operation, it is ultimately a waste. If the material can be used without being subjected to recovery operation, a further consecutive analysis is to be accomplished to identify clearly its nature.

I.1.4.2. The terms and definitions of the Basel Convention

The definition of waste used by the Basel Convention is convergent with that of the Framework Directive 75/442/EEC and is formulated as follows: "Wastes are substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law." The discrepancy of this basic term between two international regulations justifies parallel functioning of the two definitions of waste in the EU legislation referring to two international regulations being simultaneously in operation in its area. Other countries, which ratified both OECD Council Decisions and the Basel Convention, face the same problems. On the other hand, much wider spread of the Basel Convention, as well as a short and clear definition free of unnecessary listing, gives this definition an advantage to become a harmonized worldwide one.

The term hazardous waste like definitions in other regulations discussed above refers to the list of categories and to the properties making the waste hazardous. It is defined as: " (a) wastes that belong to any category contained in Annex I, unless they do not possess any of the characteristics contained in Annex III; and (d) wastes that are not covered under paragraph (a) but are defined as, or considered to be hazardous wastes by the domestic legislation of the Party of export, import and transit". Radioactive wastes are excluded from this definition. The list of categories to be controlled, which is contained in Annex I, has been adopted from the OECD Council Decision C(88)90/Final, which designated a "core list" of wastes unanimously considered hazardous. This way, at least two international lists in force have been harmonized. This list contains two categories of waste. Waste to be controlled covers 45 categories (Y1–Y45) having as constituents organic and inorganic hazardous substances. Waste of particular concern includes two categories Y46 and Y47 (household waste and the residues from their incineration) (see Appendix A in Chapter II.2).

A further development of international regulations on hazardous waste transboundary movement under the Basel Convention was a ban on the export of hazardous recyclable waste from OECD countries to non-OECD countries since January 1, 1998. For the purpose of this regulation, new lists were set up to specify the waste to be covered by the export ban:

- list A contains the hazardous waste covered by the ban;
- list B contains the waste not covered by the ban as non-hazardous;
- list C contains the waste to be classified in either the list A or list B.

Lists A and B were incorporated into the text of the Basel Convention as Annex VIII and IX, respectively (SBC, 1999). (For more information concerning the Basel Convention see Chapter II.2).

The efforts to harmonize the EC regulations with the Basel Convention resulted in amendment of Council Regulation 259/93/EC on the shipment of waste by the Council Regulation 120/97. It added to the Amber and Red Tiers incorporated from OECD Council Decision C(92)39 in Annexes III and IV, an Annex V referring to the Basel Convention's export ban. Council Decision 97/640/EC of 22 September 1997 updated regulations on the control of transboundary movements of hazardous wastes and their disposal in accordance with Decision III/1 of the Conferences of the Parties of Basel Convention.

I.1.5. National definitions

The national definitions related to waste differ from country to country and depend predominantly on the level of economic and cultural development, besides the specificity of the local geographical, political and historical conditions. These factors greatly influence the general status of the national environmental legislation. While some countries suffer from overgrowth of the incompatible legislative regulations, others have no national legislation on waste at all. Both cases can result in fatal errors in the waste management practice, although of different nature.

The European Framework and Council Directives on waste have contributed to harmonization of the waste-related definitions in the EU Member States to the extent that can be achieved considering the lack of harmony between the Directives itself and attachment of some EU Member countries to their national regulations. For example, Belgium, Denmark, Germany, Ireland, Italy, The Netherlands and the UK, in their national legislation, adopted the definition of a waste according to Framework Directive 91/156/EEC. Spain, Greece and Portugal use the non-amended Framework Directive 75/442/EEC. French Act 75-633 1975 revised in July 1992 defines waste as "material originating from a production or transformation process, or use, which the holder discards or intends to discard". Luxembourg defines waste as any substance or object, which the holder disposes of, or it is required to discard. Also the product and any substance for recovery operations is considered waste till it enters again in the commercial cycle (Bontoux and Leone, 1997).

All the EU Member States and candidate countries (Poland, Hungary, Czech Republic) adopted the definition of hazardous waste from Council Directive 91/689/EEC Art. 1 (4) and the continuously updated list of hazardous waste currently incorporated into the EC list of wastes (Commission Decisions 2000/532/EC and 2001/118/EC).

In most cases national regulations of the EC Member States follow the general definition of the Framework Directives on waste also in the question of recyclable discarded material, which is indirectly defined as a waste. Several EC Member countries (Belgium, Germany, France, Luxembourg, The Netherlands, the UK) have developed specific *criteria for distinguishing waste from non-waste*, which are articulated in a different way, but may be summarized on a basis of the common approach. According to this approach, the major prerequisite of not being considered waste is that the material, besides having a use value and fulfilling high environmental protection demands, should: (i) be continuously integrated into a production process, commercial cycle or chain of utility; (ii) have guaranteed immediate use (i.e. have stable users, be transported directly and have set and contractual relations between producer and user); and (iii) not be subjected to any process comparable to waste disposal or recovery. These criteria comply with the definition of waste given in Framework Council Directive 75/442/EEC and amending it Framework Council Directive 91/156/EEC. In general, they are also consistent with those proposed by OECD guidance (OECD ENV/EPOC/WMP (96)1, (97)2, 1996, 1997).

In Canada, the national legislation on waste and hazardous waste is regulated under the Canadian Environment Protection Act, 1988 (CEPA). Specific testing, criteria and protocols exist in the Canadian Transportation of Dangerous Goods Regulations (TDGR) for the hazard classes that are in most cases analogous to the Basel Annex III characteristic

identified. Canada controls all of Basel Annex I and Annex II wastes, all OECD amber and red listing, and a number of other wastes that do not have a corresponding Annex I or II entry. The more than 3000 listed wastes by Canadian regulations include a few hundred substances identified as being hazardous to the environment.

In the countries other than the USA and EU Member States the status of national legislation, which provides for definition of terms related to waste management is different, from more or less developed to almost none. In countries associated with the EU, in particular in candidates to the EU in the pre-accession stage, the national legislation on waste gradually adopt or harmonize national regulations with the EU legislation. For example, in Poland waste management is regulated by Waste Act of 27 April 2001. Polish terminological standards and legislation on waste in force are distinctly influenced by the EU regulations, in particular through the direct adoption of the EU list of wastes (Polish Waste Act, 2001). Poland adopts definition of wastes from Council Directive 91/156/EEC. Hazardous wastes are defined in Waste Act after Council Directive 91/689/EEC on hazardous waste. Poland adopted subsequently EWC and harmonized lists of wastes following Commission Decisions 2000/532/EC and 2001/118/EC, and incorporated the relevant lists of wastes also into subsequent national Directives of the Cabinet on charges for the use of the environment and for the disposal of waste (1993, 1998, 2001, 2003). According to the practical application of the definitions, waste has to be paid for disposal, but ceases being waste when it is actually within the "commercial cycle or chain of utility" and has "set and contractual relations between producer and user". This creates strong incentive for waste producers to look for customers or re-use technologies, based on the system of fees and penalties for the disposal of waste (Directives of the Cabinet, 1993, 1998, 2001, 2003; Waste Act, 2001; Environment Protection Act, 2001; see also Chapter II.1).

Simultaneously, lack of equivocal formulation and scope of the quoted definition of waste, hazardous waste and waste that are not hazardous but not inert, not only between the national and EU legal definitions, but within the national standards and regulations is symptomatic and reflects the difference in approaches within the regulatory bodies.

In many other countries of the world there is still no agreed definition of the term hazardous waste. The criteria for this definition consider either only the danger to human health or also the threat to the environment. Some national regulations define hazardous waste in terms of hazard characteristics (ignitability, reactivity), other give as criteria the "hazardous concentrations" of substances (UNEP, 1992). Significant and growing influence on the integration of national legislation of the participating parties is exerted by the Basel Convention due to its worldwide scope and activity. Gradually, the parties to the Basel Convention that had no national legal definition adopt the Basel Convention definitions and list for hazardous waste classification that makes worldwide national reporting and statistics much more clear and reliable. In many countries there are no other hazard criteria, categories of wastes to be controlled and categories of wastes requiring special consideration in addition to those listed in Annexes I and II of the Basel Convention (e.g. Albania, Benin, Bulgaria, Cyprus, Iran, Japan, Nigeria, Panama, Romania). Some countries incorporate definitions and lists of the Basel Convention into the national laws (e.g. Australia, Switzerland), or introduce additional categories of wastes requiring special consideration to those listed in Annexes I and II of the Basel Convention (e.g. Bolivia, Brazil, China, Indonesia, Republic of Macedonia, Saint Lucia, Sri Lanka,

Turkey). In Argentina the legal term hazardous wastes means "any waste that may cause damage, directly or indirectly, to living creatures or to pollute the soil, water, the atmosphere or the environment in general". This definition, which is broad and vague, became more specific by referring to wastes of categories listed in Annex I or having any of the characteristics of the Annex III of the Basel Convention (Hazardous Waste Law 24051-92. Article 2nd). In Russian Federation, the national definition of hazardous wastes is formulated by the Federal Law "On Wastes of Production and Consumption" of 26 June 1998. According to this definition hazardous waste is the waste containing harmful substances having hazardous properties (toxicity, explosivity, flammability, high-reaction ability) or containing the agents causing contagious diseases or that posing an immediate or potential threat to environment and human health either by themselves or on contact with other substances". Other former republics of the USSR, Kyrgyzstan and Uzbekistan have the national definitions of hazardous wastes close to that of Russian Federation, some other have their national legislation in preparation (Georgia, Moldova, Lithuania). A number of other countries have not yet national legislation on hazardous waste (e.g. Andorra, Senegal, Gambia) (SBC, 1999, 2000, 2001). Indian legal definition of hazardous wastes also differed substantially from this adopted by the Basel Convention. Indian national legislation on hazardous waste management was brought in line with the ratified Basel Convention through amendment its Hazardous Waste Rules (1989), which came into force in 2000 (Anonymous, 2001).

To harmonize the national legislation of the parties, which display exemplified different status, the "Revised Model National Legislation on the Management of Hazardous Wastes and other Wastes as well as on the Control of Transboundary Movements of Hazardous Wastes and their Disposal" (SBC, 1995), was adopted by the third meeting of the Conference of the Parties (COP3) to the Basel Convention and brought out in 1996 by the Secretariat of the Basel Convention (SBC). This model national law defines also relevant terms on waste, in conformity with the Convention (SBC, 1995, 1996).

I.1.6. Summary and conclusions

The brief review of the terminological issues shows clearly that still much is to be done for integration and harmonization of waste-related legal terms and definitions. The growing number of parallel national, regional and international regulations in force evokes problems with discrepancy of definitions of the basic terms related to waste in general and solid and hazardous waste in particular. This, in turn, exerts negative impact on environmentally safe and economically effective waste management in the national, regional and global scale. In the light of the current terminological problems and multitude of lists related to waste terminology, the focusing of efforts on the integration of the legislative arena directed to the development of well-thought and fully justified equivocal terminology with a reduced number of well-systemized lists and thorough analysis of consequences on environmental safety, economy and sustainable development of waste management system has now become a task of utmost priority. The importance and the weight of this task are difficult to overestimate. Beginning now, not the developing and enacting of new regulations, which multiply definitions for the same terms, but careful revision of the national, regional and international terminology by the competent

international body should be the first step towards the harmonized, integrated, environmentally and economically optimized waste management, worthy of the 21st century.

Appendix A

Excerpt from: Council Directive 91/156/EEC of 18 March 1991 amending Directive 75/443/EEC on waste *OJ L 078 26.03.1991, p. 32–37.*

Annex I

Categories of waste

Q1 Production or consumption residues not otherwise specified below
Q2 Off-specification products
Q3 Products whose date for appropriate use has expired
Q4 Materials spilled, lost or having undergone other mishap, including any materials, equipment, etc., contaminated as a result of the mishap
Q5 Materials contaminated or soiled as a result of planned actions (e.g. residues from cleaning operations, packing materials, containers, etc.)
Q6 Unusable parts (e.g. reject batteries, exhausted catalysts, etc.)
Q7 Substances, which no longer perform satisfactorily (e.g. contaminated acids, contaminated solvents, exhausted tempering salts, etc.)
Q8 Residues of industrial processes (e.g. slags, still bottoms, etc.)
Q9 Residues from pollution abatement processes (e.g. scrubber sludges, baghouse dusts, spent filters etc.)
Q10 Machining/finishing residues (e.g. lathe turnings, mill scales, etc.)
Q11 Residues from raw material extraction and processing (e.g. mining residues, oil field slops, etc.)
Q12 Adulterated materials (e.g. oils contaminated with PCBs, etc.)
Q13 Any materials, substances or products whose use has been banned by law
Q14 products for which the holder has no further use (e.g. agricultural, household, office, commercial and shop discards, etc.)
Q15 Contaminated materials, substances or products resulting from remedial action with respect to land
Q16 Any materials, substances or products, which are not contained in the above categories.

Annex IIA

Disposal operations

NB: This annex is intended to lit disposal operations such as they occur in practice. In accordance with Article 4, waste must be disposed of without endangering human health and without use of processes or methods likely to harm the environment

D1 Tipping above or underground (e.g. landfill, etc.)
D2 Land treatment (e.g. biodegradation of liquid or sludge discards in soils, etc.)
D3 Deep injection (e.g. injection of pumpable discards into wells, salt domes or naturally occurring repositories, etc.)
D4 Surface impoundment (e.g. placement of liquid or sludge discards into pits, ponds or lagoons, etc.)
D5 Specially engineered landfill (e.g. placement into lined discrete cells, which are capped and isolated from one another and the environment, etc.)
D6 Release of solid waste into a water body except seas/oceans
D7 Release into seas/oceans including seabed insertion
D8 Biological treatment not specified elsewhere in this Annex which results in final compounds or mixtures, which are disposed of by means of any of the operations in this Annex (e.g. evaporation, drying, calcination, etc.)
D9 Physico-chemical treatment not specified elsewhere in this Annex, which results in final compounds or mixtures, which are disposed of by means of any of the operations in this Annex (e.g. evaporation, drying, calcinations, etc.)
D10 Incineration on land
D11 Incineration at sea
D12 Permanent storage (e.g. emplacement of containers in a mine, etc.)
D13 Blending of mixture prior to submission to any of the operations in this Annex
D14 Repackaging prior to submission to any of the operations in this Annex
D15 Storage pending any of the operations in this Annex, excluding temporary storage, pending collection, on the site where it is produced.

Annex IIB

Operations, which may lead to recovery

NB: This Annex is intended to list recovery operations as they are carried out in practice. In accordance with Article 4, waste must be recovered without endangering human health and without the use of processes or methods likely to harm the environment

R1 Solvent reclamation/regeneration
R2 Recycling/reclamation of organic substances, which are not used as solvents
R3 Recycling/reclamation of metals and metal compounds
R4 Recycling/reclamation of other inorganic materials
R5 Regeneration of acids or bases
R6 Recovery of components used for pollution abatement
R7 Recovery of components from catalysts
R8 Oil re-refining or other re-uses of oil
R9 Use principally as a fuel or other means to generate energy
R10 Spreading on land resulting in benefit to agriculture or ecological improvement, including composting and other biological transformation processes, except in the case of waste excluded under Article 2 (1)(b)(iii)
R11 Use of wastes obtained from any of the operations numbered R1–R10
R12 Exchange of wastes for submission to any of the operations numbered R1–R11

R13 Storage of materials intended for submission to any operation in this Annex, excluding temporary storage, pending collection, on the site where it is produced.

Appendix B

Excerpt from: Doc. 391L0689, Council Directive 91/689/EEC of 12 December 1991 on hazardous waste, *OJ L 377 31.12.1991, p. 20; Amended by* **394L0031** *(OJ L 168 02.07.1994,* p. 28).

Annex I

Categories or generic types of hazardous waste listed according to their nature or the activity which generated them(*) *(waste may be liquid, sludge or solid in form)*

Annex I. A

Wastes displaying any of the properties listed in Annex III and which consist of

1. anatomical substances; hospital and other clinical wastes;
2. pharmaceuticals, medicines and veterinary compounds;
3. wood preservatives;
4. biocides and phyto-pharmaceutical substances;
5. residue from substances employed as solvents;
6. halogenated organic substances not employed as solvents excluding inert polymerized materials;
7. tempering salts containing cyanides;
8. mineral oils and oily substances (e. g. cutting sludges, etc);
9. oil/water, hydrocarbon/water mixtures, emulsions;
10. substances containing PCBs and/or PCTs (e. g. dielectrics etc);
11. tarry materials arising from refining, distillation and any pyrolytic treatment (e. g. still bottoms, etc);
12. inks, dyes, pigments, paints, lacquers, varnishes;
13. resins, latex, plasticizers, glues/adhesives;
14. chemical substances arising from research and development or teaching activities which are not identified and/or are new and whose effects on man and/or the environment are not known (e.g. laboratory residues, etc);
15. pyrotechnics and other explosive materials;
16. photographic chemicals and processing materials;
17. any material contaminated with any congener of polychlorinated dibenzo-furan;
18. any material contaminated with any congener of polychlorinated dibenzo-*p*-dioxin.

(*) Certain duplications of entries found in Annex II are intentional.

Annex I.B

Wastes which contain any of the constituents listed in Annex II and having any of the properties listed in Annex III and consisting of

19. animal or vegetable soaps, fats, waxes;
20. non-halogenated organic substances not employed as solvents;
21. inorganic substances without metals or metal compounds;
22. ashes and/or cinders;
23. soil, sand, clay including dredging spoils;
24. non-cyanidic tempering salts;
25. metallic dust, powder;
26. spent catalyst materials;
27. liquids or sludges containing metals or metal compounds;
28. residue from pollution control operations (e. g. baghouse dusts etc.) except (29), (30) and (33);
29. scrubber sludges;
30. sludges from water purification plants;
31. decarbonization residue;
32. ion-exchange column residue;
33. sewage sludges untreated or unsuitable for use in agriculture;
34. residue from cleaning of tanks and/or equipment;
35. contaminated equipment;
36. contaminated containers (e.g. packaging gas cylinders etc.) whose contents included one or more of the constituents listed in Annex II;
37. batteries and other electrical cells;
38. vegetable oils;
39. materials resulting from selective waste collections from households and which exhibit any of the characteristics listed in Annex III;
40. any other wastes which contain any of the constituents listed in Annex II and any of the properties listed in Annex III.

Annex II

Constituents of the wastes in Annex I.B which render them hazardous when they have the propertles described in Annex III(*)

Wastes having as constituents:

C1 beryllium; beryllium compounds;
C2 vanadium compounds
C3 chromium (VI) compounds;
C4 cobalt compounds;
C5 nickel compounds;
C6 copper compounds;

(*) Certain duplications of generic types of hazardous wastes listed in Annex I are intentional.

C7 zinc compounds;
C8 arsenic, arsenic compounds
C9 selenium; selenium compounds;
C10 silver compounds;
C11 cadmium; cadmium compounds;
C12 tin compounds;
C13 antimony; antimony compounds;
C14 tellurium, tellurium compounds;
C15 barium compounds; excluding barium sulfate;
C16 mercury; mercury compounds;
C17 thallium; thallium compounds;
C18 lead, lead compounds;
C19 inorganic sulfides;
C20 inorganic fluorine compounds, excluding calcium fluoride;
C21 inorganic cyanides
C22 the following alkaline or alkaline earth metals lithium, sodium, potassium, calcium, magnesium in uncombined form;
C23 acidic solutions or acids in solid form;
C24 basic solutions or bases in solid form;
C25 asbestos (dust and fibers);
C26 phosphorus: phosphorus compounds, excluding mineral phosphates;
C27 metal carbonyls;
C28 peroxides;
C29 chlorates;
C30 perchlorates;
C31 azides
C32 PCBs and/or PCTs;
C33 pharmaceutical or veterinary compounds;
C34 biocides and phyto-pharmaceutical substances (e.g. pesticides, etc.);
C35 infectious substances;
C36 creosotes;
C37 isocyanates; thiocyanates;
C38 organic cyanides (e.g. nitriles, etc);
C39 phenols; phenol compounds;
C40 halogenated solvents;
C41 organic solvents, excluding halogenated solvents;
C42 organohalogen compounds, excluding inert polymerized materials and other substances referred to in this Annex;
C43 aromatic compounds; polycyclic and heterocyclic organic compounds;
C44 aliphatic amines;
C45 aromatic amines
C46 ethers;
C47 substances of an explosive character, excluding those listed elsewhere in this Annex;
C48 sulfur organic compounds;
C49 any congener of polychlorinated dibenzo-furan;
C50 any congener of polychlorinated dibenzo-*p*-dioxin;

C51 hydrocarbons and their oxygen; nitrogen and/or sulfur compounds not otherwise taken into account in this Annex.

Annex III

Properties of wastes, which render them hazardous

H1 "Explosive": substances and preparations which may explode under the effect of flame or which are more sensitive to shocks or friction than dinitrobenzene.

H2 "Oxidizing": substances and preparations, which exhibit highly exothermic reactions when in contact with other substances, particularly flammable substances.

H3 -A "Highly flammable":
-liquid substances and preparations having a flash point below 21 °C (including extremely flammable liquids). or
-substances and preparations which may become hot and finally catch fire in contact with air at ambient temperature without any application of energy or
-solid substances and preparations which may readily catch fire after brief contact with a source of ignition and which continue to burn or to be consumed after removal of the source of ignition, or
-gaseous substances and preparations which are flammable in air at normal pressure, or
-substances and preparations which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities.

H3 -B "Flammable": liquid substances and preparations having a flash point equal to or greater than 21°C and less than or equal to 55°C.

H4 "Irritant": non-corrosive substances and preparations, which through immediate prolonged or repeated contact with the skin or mucous membrane can cause inflammation.

H5 "harmful": substances and preparations which, if they are inhaled or ingested or if they penetrate the skin may involve limited health risks.

H6 "Toxic": substances and preparations (including very toxic substances and preparations) which, if they are inhaled or ingested or if they penetrate the skin may involve serious acute or chronic health risks and even death.

H7 "Carcinogenic": substances and preparations which, if they are inhaled or ingested or if they penetrate the skin may induce cancer or increase its incidence.

H8 "Corrosive": substances and preparations, which may destroy living tissue on contacts.

H9 "Infectious": substances containing viable microorganisms or their toxins, which are known or reliably believed to cause disease in man or other living organisms.

H10 "Teratogenic": substances and preparations which, if they are inhaled or ingested or if they penetrate the skin may induce non-hereditary congenital malformations or increase their incidence.

H11 "Mutagenic": substances and preparations which, if they are inhaled or ingested or if they penetrate the skin may induce hereditary genetic defects or increase their incidence.

H12 Substances and preparations which release toxic or very toxic gases in contact with

water air or an acid.

H13 Substances and preparations capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics listed above.

H14 "Ecotoxic": substances and preparations, which present or may present immediate or delayed risks for one or more sectors of the environment.

Notes

1. Attribution of the hazard properties "toxic" (and "very toxic"), "harmful", "corrosive" and "irritant" is made on the basis of the criteria laid down by Annex VI, part I A and part II B of Council Directive 67/548/EEC of 27 June 1967 of the approximation of laws regulations and administrative provisions relating to the classification, packaging and labeling of dangerous substances[1] in the version as amended by Council Directive 79/831/EEC.[2]
2. With regard to attribution of the properties "carcinogenic" and "mutagenic", and reflecting the most recent findings, additional criteria are contained in the Guide to the classification and labeling of dangerous substances and preparations of Annex VI (part II D) to Directive 67/548/EEC in the version as amended by Commission Directive 83/467/EEC.[3]

Test methods

The test methods serve to give specific meaning to the definitions given in Annex III.

The methods to be used are those described in Annex V to Directive 67/548/EEC, in the version as amended by Council Directive 84/449/EEC,[4] or by subsequent Commission Directives adapting Directive 67/548/EEC to technical progress. These methods are themselves based on the work and recommendations of the competent international bodies, in particular the OECD.

Appendix C

Excerpt from: Doc. 300D052: Commission Decision 2000/532/EC of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of council Directive 91/689/EEC on hazardous waste (notified under document number C(2000)1147) (Text with EEA relevance), *OJ L226 06 09.2000, p. 3*

[1] OJ No I 196, 16.8.1967, p. 1.
[2] OJ No I 259, 15.10.1979, p. 10.
[3] OJ No I 257, 16.9.1983, p. 1.
[4] OJ No I 251, 19.9.1984, p. 1.

Amended by **301D0118** *OJ L 047 16.02.2001, p. 1)*
Amended by **301D0119** *(OJ L 047 16.02.2001, p. 32)*
Commission Decision of 16 January 2001 amending Decision 2000/532/EC as regards the list of wastes *(notified under document number C(2001)108) (2001/118/EC):*

Article 1
Decision 2000/532/EC is amended as follows:
1. Article 2 is replaced by the following:
   Article 2
   Wastes classified as hazardous are considered to display one or more of the properties listed in Annex III to Directive 91/689/EEC and, as regards H3 to H8, H10(*) and H11 of the said Annex, one or more of the following characteristics:

- flash point $\leq 55°C$,
- one or more substances classified(**) as very toxic at a total concentration $\geq 0.1\%$.
- one or more substances classified as toxic at a total concentration $\geq 3\%$.
- one or more substances classified as harmful at a total concentration $\geq 25\%$.
- one or more corrosive substances classified as R35 at a total concentration $\geq 1\%$.
- one or more corrosive substances classified as R34 at a total concentration $\geq 5\%$.
- one or more irritant substances classified as R41 at a total concentration $\geq 10\%$.
- one or more irritant substances classified as R36, R37, R38 at a total concentration $\geq 20\%$.
- one substance known to be carcinogenic of category 1 or 2 at a concentration $\geq 0.1\%$.
- one substance known to be carcinogenic of category 3 at a concentration $\geq 1\%$.
- one substance toxic for reproduction of category 1 or 2 classified as R60, R61 at a concentration $\geq 0.5\%$.
- one substance toxic for reproduction of category 3 classified as R62, R63 at a concentration $\geq 5\%$.
- one mutagenic substance of category 1 or 2 classified as R46 at a concentration $\geq 0.1\%$.
- one mutagenic substance of category 3 classified as R40 at a concentration $\geq 1\%$.

2. The Annex is replaced by the text in the Annex to this Decision.
   Article 2
   This Decision shall apply from January 2002
   Article 3
   This decision is addressed to the Member States.

(*) In Directive 92/32/EEC amending for the seventh time Directive 67/548/EEC the term "toxic for reproduction" was introduced. The term "Teratogenic" was replaced by a corresponding term toxic for reproduction. This term is considered to be in line with property H10 in Annex III to Directive 91/689/EEC.
(**) The classification as well as the R numbers refer to Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labeling of dangerous substances (O) L 196, 16.8.1967, p. 1) and its subsequent amendments. the concentration limits refer to those laid down in Directive 88/379/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labeling of dangerous preparations (O) L 187, 16.7.1988, p. 14) and its subsequent amendments.

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I.2
Solid waste origins: sources, trends, quality, quantity

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I.2.1. Introduction

Effective waste management in the local, regional and global scale, which has the protection of human health and the environment as an essential and ultimate objective, requires reliable and complete statistical data on waste sources, amounts generated, qualitative and quantitative structure, properties determining their long-term environmental behavior and changes in waste streams as a function of time. Unfortunately, the available data are extremely limited, in particular with regard to long-term waste stream changes and future trends, even in the USA and in the EU. One of the major reasons for this situation is the lack of harmonized terms and definitions, as well as of the uniform classification and organization of statistical data collection. The lack of reliable long-term and current qualitative and quantitative data is a serious obstacle to setting priorities for environmentally safe and economically sound waste management in the different parts of our world. The global and transboundary effects of waste transport and disposal in the last decades have been increasingly an international issue. This brings about the priority range of the transmission of information on the distribution of transboundary movement of hazardous wastes and other wastes, based on reliable statistical data. The notorious incompleteness and lack of reliability of the waste statistics in the EU was confirmed quite recently. Obtaining reliable waste statistics was considered particularly difficult due to the differences in the definitions of waste categories, apart from the physical collection of the data (Bontoux and Leone, 1997).

Efforts of the EC legislative bodies in the last decade of the 20th and the first years of the 21st century resulted in several decisions directed to the improvement of statistics on waste, which visibly improved the quality of statistical data. Among these initiatives of EC, the most important are:

- Establishing a harmonized list of wastes (Commission Decisions 2000/532/EC and 2001/118/EC).
- Laying down decisions concerning database systems, formats and questionnaires for the reporting obligations of Member States on the implementation of certain Directives relating to the environment in the waste sector (Council Directive 91/692/EEC, 1991 implemented by Commission Decisions 94/741/EC, 1994 and 97/622/EC, 1997). Reporting on hazardous waste is regulated by Commission Decisions 96/302/EC (1996) and 98/184/EC (1998).

- Enacting decisions concerning the reporting on shipment of waste within, into or out of the EC (Commission Decision 1999/412/EC); on the landfill of waste (Commission Decision 2000/738/EC); on specific kinds of waste, e.g. on packaging and packaging waste (Commission Decision 1997/138/EC) or end-of-life vehicles (Commission Decision 2001/753/EC).
- Laying down Regulation (EC) No. 2150/2002 of the European Parliament and of the Council of 25 November 2002 on waste statistics.

Significant progress in measuring, presenting and interpreting the data on waste generation and management shows the recent EUROSTAT works focused on the elaboration of indicators for sustainable development (EUROSTAT, 2001a, EUROSTAT Web site), though the situation in this area is still far from being satisfactory.

In the USA, despite a variety of sources and databases on solid and hazardous waste generation and management, there is no single comprehensive, exhaustive and current, continuously updated database. This situation that was described more than a decade ago (Dietz and Burns, 1989) has not changed significantly until now. The most comprehensive database for the generation of hazardous wastes is the National Biennial RCRA Hazardous Waste Report with the most recent data being for 1997 (US EPA, 1999).

Demographic changes evidenced by the rapid growth of population and accelerated industrial development in the developing countries along with simultaneous proliferation of new technologies, materials and chemicals in the developed countries, which are transmitted by the international companies to the developing regions, have contributed to an increase in both the amount and variety of solid wastes all over the world. Reliable statistical data on the sources and amounts of waste generation, structure of solid waste streams, their movement and management is thus a basic prerequisite for optimization of waste management strategies in a national and global scale. They are of particular importance for setting priorities in waste management practice and for providing an adequate regulatory framework and enforcement procedures for its implementation. New efforts being undertaken by international bodies (OECD, EUROSTAT, Secretariat of the Basel Convention), US EPA and statistical offices of many countries significantly contribute to better integration of waste statistics, improvement of its reliability and completeness. Currently, the most reliable source of objective and internationally comparable ecological information, which includes also waste generation data, is the OECD Environmental Compendium. This statistical information is published every 2 years pursuant to the OECD Council Decision and follow-up obligations of the OECD and EU member countries. The data discussed below come from publications of the EU Statistical Office EUROSTAT and OECD–EUROSTAT Questionnaire – "Environment Protection" being submitted obligatorily by the OECD members. This questionnaire is a basic instrument of the integrated system of the environmental information in the framework of the OECD and EU, published in the form of the environmental compendia and other statistical studies by OECD (1997), (1998), (1999), (2001) and (2002). Some data originate from the estimates of the OECD Secretariat and other reliable international databases (UN, FAO, etc.). The main goal of these environmental statistics is identification of priorities focused on the protection of the environment, efficient implementation of policies and practice, including waste management and the promotion of sustainable development in the national and international arena. Integrated waste

statistics are still not equally satisfactory, and there remain vast information gaps. The statistical information at the national and international level still shows significant margins of uncertainty. Comprehensive, regionally and globally harmonized waste statistics based on univocal terms, definitions and classification, which exclude misinterpretation, remains a goal for the future, though current progress resulting from the growing recognition of the urgent need of environmentally safe and economically sound waste management strategies is unquestionable (e.g. see EU Europa Web site).

A crucial milestone in the development of the European statistics was enactment in 2002 by the European Parliament and the Council of the Regulation on waste statistics that established a framework for Community statistics on the generation, recovery and disposal of waste that would guarantee complete and comparable results by means of following obligatory harmonized forms and terms of supply by the Member States. Within the Regulation, the EU statistics covers:

- Generation of waste;
- Recovery and disposal of waste;
- Import and export of waste.

Regular Community statistics creates the basis for monitoring the implementation of waste policy in compliance with the principles of maximization of waste recovery and safe disposal, as well as for assessing compliance with the principle of waste prevention. Another target is to establish a link between waste generation data and global, national and regional inventories of resource use. Low compatibility of statistical data due to difference in reporting between the EU Member States has been planned to be overcome during a transitional period when national statistical systems will undergo adaptation. A significant improvement of the EUROSTAT data may be anticipated, though the development of the harmonized statistical data in the global scale, which is a basic prerequisite of the global waste management strategy still needs much more concerted effort of the countries.

I.2.2. Waste generation in the OECD countries: amounts and sources

Data reported below are based on the official statistical sources (OECD, 1997, 1998, 1999, 2001, 2002; EUROSTAT, 2000a–c, 2001a,b) and national statistics, e.g. Central Statistical Office, 2001, 2002. The lack of complete data for every country and a long list of the explanatory footnotes reflect the current status of waste statistics and discrepancies in the definition of waste categories. In spite of these limitations, they give an approximate idea about the annual waste originating in the EU and OECD countries and the composition of waste streams with respect to the principal sources of solid waste generation (nuclear waste is excluded and not discussed here) (Tables I.2.1–I.2.7). The weakness of the estimated total current generation of solid waste in the OECD is due to the lack of incorporating complete source data on the major waste streams for the USA and Canada, and numerous statistical gaps for other countries with respect to several principal sources of waste. Shockingly high data on production waste in the USA or mining waste in Canada that appeared in the OECD Compendium (1997) have never reappeared again in the later OECD statistical reports (OECD, 1998, 1999, 2001, 2002). Apart from the production scale, the diversity between the data from the USA and the rest of the OECD

countries comes from the differences in the definitions of "solid waste", and "hazardous waste". The detailed definitions of these terms according to the European Community legislation have been given in the previous Chapter I.1, also in the form of excerpts from the relevant Council Directives (see Appendices A, B and C to the Chapter I.1). In this chapter, these definitions in accordance to the U.S. Code of Federal Regulations (Revised as in 1999) are quoted extensively in the Appendix A. The comparison of the legislative approaches confirms substantial divergences, despite of numerous similarities, which should have resulted in the weak compatibility of seemingly simple statistical data.

On the basis of available incomplete data (OECD, 1997, 1998, 1999; Central Statistical Office, 2000; EUROSTAT, 2000a,b) it has been estimated that in the OECD countries approximately 12,000 Mt (million tons) of solid waste are generated annually (3600 Mt without the USA and Canada). Of this, agricultural waste (23%), manufacturing/ production residues (21%), mining waste (16%) and municipal waste (16%) are the major constituents of the waste stream. The biggest waste generator among the 30 OECD member countries is the USA. Its documented contribution to the total waste stream (production, municipal, construction/demolition and other waste – see Tables I.2.1 and I.2.2) accounts for 63%, while the share of the next in line, France and Japan, is more than 10-fold less for each. In the EU countries, besides agricultural, production and mining waste, a high position is held by construction/demolition residues. The range of each type of waste generation is extremely wide, thus the structure of waste stream is different in every OECD and EU country (Table I.2.1).

Incomplete and inconsistent data on the generation of selected *recyclable waste* (OECD, 1998, 1999; Central Statistical Office, 2000; EUROSTAT, 2000a,b) show their differentiated proportions in the total amount, determined by the specifics of the economy of each OECD member country (Table I.2.2). The documented generation of six groups of waste accounted for 1098 Mt, of these five kinds of packaging waste comprised about 11.4%. The highest amount of construction and demolition waste, which significantly deviated from the other OECD participants, was generated in Germany (26%) and the USA (22%). Japan produced 67% of the total sewage sludge; the USA participated in 65% in the total amount of end-of-life vehicles, in 73% in rubber waste and generated 45% of the total packaging waste.

Data on the annual per capita generation of *municipal waste* in the OECD countries (OECD, 1998, 2002) were less variable and ranged from 300 to 360 kg (Greece, Mexico, Poland, Czech Republic, Poland, Slovakia, Korea) to 760 kg (USA), of this per capita generation of household waste varied from 190 to 580 kg (OECD, 2002) (Table I.2.3a). In most of the reported cases an increase of the municipal waste generation has been observed in the last two decades, from 8% (Japan) to 195% (Ireland). Individual consumption in almost the same period generally increased from 7.5% (Sweden) to 164.9% (Korea), and in one case showed a 7.1% decrease (Mexico) (OECD, 1998). Compared to 1980, in four countries the overall decrease of waste generation within two decades was recorded (Australia, Slovakia, Hungary and Korea). In the last decade, though, in four EU Member States (the UK, Finland, Luxembourg and Germany) a positive trend of decreasing municipal waste generation occurred (from -3.4 to -2% annually), at annual increase rates in other EU Member States ranging from 1.6% (Austria) to 9.5% (Spain) and mean value for the EU that accounted for 2.3%. In the countries that are candidates to the EU, the annual increase rate for municipal waste generation was

considerably lower, from 0.5% in Hungary to 1.7% in Czech Republic, with a mean value of 1.2% (Table I.2.3b). Despite large amounts of municipal waste produced in the OECD countries, it accounted for only 15.7% of the total documented waste stream (Table I.2.1).

Annual generation of *hazardous waste (HW)* in the OECD countries according to the available data for mid-1990s without Japan (OECD, 1998) appeared to be extremely variable and ranged from only 6 thousand tons (Island) to 213,620 thousand tons (USA) (Table I.2.4). In 1997, 20,316 large quantity generators (LQGs) in the USA reported that they generated 40.7 Mt of RCRA hazardous waste (US EPA, 1999). The value contained in the OECD report is approximately fivefold greater than that in the EPA report, which indicates the differences that exist in defining hazardous wastes and that can be found in the statistical reports. Total annual hazardous waste generation, recorded in accordance with the Basel Convention, accounts for 269,675 thousand tons (without Japan), that is 18% of the total industrial manufacturing/production waste generation. The OECD countries without the USA and Japan generate in total only 56,055 thousand tons, i.e. just 8.6% of the estimated total industrial manufacturing/production waste generated in these countries. Despite a relatively low proportion of these materials in the waste stream, hazardous waste is subject to a special concern due to the extent of threat posed to human health and the environment. The US share of the generation of HW is extremely high, both in mass units and as measured in kg per thousand US $ of GDP. According to the statistics, the amount of hazardous waste generation in the USA, also per US $1000 of GDP are 1–2 orders of magnitude higher than in other OECD countries. These statistical data differ significantly from the estimates based on the hazardous waste generated per US $1000 of GDP (named here HW factor) given in the UNEP study (UNEP, 1992). Hazardous waste in these estimates also includes high volume wastewater streams, which may somewhat deform the data. Nevertheless, the rationale behind these estimates was a clear relation between the level of industrialization and HW factor that was claimed to be as high as 75.0 for the USA, 10.0 for the former USSR, 5.0 for Western Europe and mature industrial countries, 2.0 for newly industrialized ones and 1.0 for developing countries (UNEP, 1992). This, though, was not confirmed in the analysis of statistical data for the OECD countries (Table I.2.4) (OECD, 1998). The sixfold higher HW factor for the USA reflects economical specifics rather than the level of industrialization. The OECD statistical data (Table I.2.4) display occurrence of the highest HW factors (besides the USA) for the countries with developed primary production (heavy industry and chemistry). HW factors >10 (in the range from 11.3 to 58.2) include Canada, Mexico, Portugal, Luxembourg, Poland, Czech Republic and Hungary. Within the range of the lowest HW factor <2, from 1.3 to 1.9, fall Island, Australia and the UK. Therefore, the direct relation between the level of industrialization and HW factor is rather doubtful.

HW generated in the USA dominates the total HW stream. The quantities and sources of HW in the USA were comprehensively analyzed by Dietz and Burns (1989) based on the data of the first national probability survey conducted for EPA by Westat Inc. in 1982 and 1983. In this survey, despite a large degree of uncertainty ($\pm 50\%$ for 95% confidence level), the best national estimate of the quantity of RCRA-regulated HW generated in 1981 was 264 Mt. This number included solid HW and associated wastewater since both are hazardous waste under RCRA (Dietz and Burns, 1989, see also Appendix A). The later data on HW generation in the USA reported for 1993 accounted for 213.6 Mt (OECD, 1998). That means 21% reduction of annual waste generated, partially due to changes in

Table I.2.1. Amounts and sources of solid waste generated annually in the EU and OECD countries (after OECD, 1997, 1998, 1999; Central Statistical Office, 2000; EUROSTAT, 2000a,b, 2001b)*.

Countries	Agriculture, forestry	Mining and quarrying	Manufacturing, production	Power generation	Water purification and supply	Construction, demolition	Other	Municipal	Total[a]
	in thousand tons								
Canada[b]	*14,000*	*1,052,990*	–	–	–	–	–	20,600	20,600[a]
Mexico	11,498	123,196	29,570	–	–	–	–	29,270	193,534
USA	–	–	*7,080,000*	–	–	–	–	190,200	190,200[a]
Japan[c]	74,950	30,790	139,030	57,290	9060	76,930	74,690	50,540	513,280
Korea[d]	–	–	36,540	690	4270	11,150	–	18,220	70,870
Australia	560	–	37,040	11,000	–	10	–	12,000	60,610
New Zealand[e]	–	–	1760	–	–	–	–	1270	3030
Austria[f]	–	**3**[4]	**14,284**[1]	**125**[4]	2300	**25,392**[1]	13,690	**5270**[1]	61,764
Belgium	–	**389**[2]	**13,734**[1,2,3]	**1072**[1,2]	–	**7718**[2]	–	**5307**	**28,220**
Czech Republic[g]	5460	5000	38,570	17,060	–	780	18,990	**3017**	88,877
Denmark[h]	–	–	**2736**[1]	**1775**	170	**3427**	810	**2951**	11,869
Finland[i]	22,000	**15,000**[8]	**15,500**	**1350**[8]	2400	**7000**[3]	–	**2100**[3]	65,350
France[g]	377,000	**75,000**[8]	**101,000**[2]	–	–	**13,700**[9]	–	**34,700**[2]	601,400
Germany[j]	–	**67,813**[4]	**65,119**[4]	**25,310**[4]	1870	**131,645**[4]	940	**43,486**[4,3]	336,983
Greece	7780	**3900**[2]	**6682**[1]	**9320**	–	**1800**[1]	–	**3900**	33,382
Hungary[k]	62,000	790	*6328*	1080	–	–	10	**4800**	75,008
Iceland	–	–	10	–	–	–	30	150	190
Ireland	31,000	**2200**[2]	**3781**[2]	**353**[2]	60	**1320**[2]	280	**2030**[2]	41,024
Italy[l]	–	–	22,210	1330	–	14,310	42,500	**26,605**	106,955
Luxembourg	–	–	**1440**[10]	–	–	–	–	**193**[6]	1633
The Netherlands[m]	17,000	**326**[1]	**8577**[1]	**1402**[1]	70	13,950	2640	**8782**[1]	52,747
Norway	18,000	7600	2880	–	–	3600	–	2720	34,800
Poland[n]	–	***49,480***	***58,176***	***18,009***	***1325***	***68***	***522***	***12,317***	***139,897***

Portugal[o]	–	**7120**	**10,989**	**569**	–	**7733**	–	**4313**[7]	30,724
Spain	114,000	**70,000**[4]	**13,800**[10]	–	10,000	**115**[2]	–	**15,307**[1]	223,222
Sweden	–	**47,000**[4]	**13,990**[4]	**600**[3]	–	**1500**[3]	–	**3200**[3]	66,290
Switzerland[p]	–	–	1500	–	40	3000	190	4280	9010
Turkey	–	–	28,110	8680	–	–	–	20,250	57,040
UK[o]	80,000	**74,000**[1]	**56,000**[2]	**13,000**[1]	35,000	**70,000**[1]	66,000	**28,000**[1]	422,000
Slovakia	4500	790	6720	2900	550	170	2480	**1700**	19,810
EU15[a]	648,780	362,751	351,342	56,206	51,870	299,610	126,860	186,144	2,083,563
%	31.14	17.41	16.86	2.70	2.49	14.38	6.09	8.93	100.00
OECD[a]	825,748	580,397	737,576	172,915	67,115	395,318	223,772	557,478	3,560,319
%	23.19	16.30	20.72	4.86	1.89	11.10	6.29	15.66	100.0

Sources: EUROSTAT, 2000a,b – 1997 data (**bold**); Central Statistical Office, 2000 – 1999 data (***italic bold***); OECD, 1999 (normal) and 1998 (*italic*) – data from the last available year in 1990s.

Data for: 1) 1996; 2) 1995; 3) 1994; 4) 1993; 5) 25,257 thousand tons collected during public waste collection according to the German Waste Act. 6) Without fractions collected separately. Data for: 7) 1998; 8)1992; 9) 1991; 10) 1990. * – Data related to the last available year in 1990s. Rounded total data may comprise estimates.

[a]The total estimates calculated by the authors are based on the available statistical data given in the respective column/row. Data after OECD (1997) for the USA and Canada (*italic*) were not considered.

[b]Data for municipal waste include waste from construction/demolition.

[c]Data on agriculture include waste from fishing. Data on other waste comprise waste from power generation and sewage sludge.

[d]Data on production activity comprise waste from agriculture, mining and quarrying, power generation and water purification and distribution.

[e]Data on municipal waste include only household waste.

[f]Valid classification does not relate to sectors but to groups of waste; data may not be comparable to other countries.

[g]Estimates comprise hazardous waste.

[h]Data comprise sewage sludge. Data on other waste include hazardous and other production waste. Total value does not include waste from agriculture, and mining and quarrying.

[i]Data on agriculture do not comprise waste from forestry.

[j]Data on other waste are related to hospital waste.

[k]Data do not include hazardous waste, lack of data from all privatized enterprises.

[l]Data on waste from production processes may comprise waste from mining and quarrying.

[m]Data on other waste include commercial waste and car scrapping.

[n]1999 data, comprise majority of industrial and power generation sources. Mining waste do not include overburden from opencast mines.

[o]Data comprise entirely hazardous waste (besides data on municipal waste).

[p]Data on other waste comprise sewage sludge.

Table I.2.2. Annual generation of some recyclable waste in the EU and OECD countries (after OECD, 1998, 1999; Central Statistical Office, 2000; EUROSTAT, 2000a,b)[*].

Countries[a]	Year	Construction, demolition	Excavation, dredging	Sewage sludge	Vehicles	Rubber	Packaging				
							Total[b]	Paper	Plastic	Glass	Metals
		in thousands tons/yr									
Canada	1996	4881	7450[c]	976	1000[d]	232[e]	6200	2400	1300	1400	1100
Mexico[f]	1994	–	–	–	–	223	*7174*	*4146*	*1290*	*1738*	–
USA[g]	1996	122,953	–	6700	12,500	10,110	56,809	34,909	7394	10,015	4491
Japan[h]	1995	60,238	–	180,490	–	92	–	–	–	–	–
Korea[i]	1996	11,145	–	6137	138	1844	12,146	5157	1102	840	5047
Australia	1992	1569	–	60,000	271	103	914	–	–	–	–
New Zealand[j]	1995	534	–	–	–	–	453	216	107	84	46
Austria[k]	1996/1997	6403	20,000	309	165	57	**1170[6]**	**710[6]**	**160[6]**	**203[6]**	**97[6]**
Belgium	1995	7294	819	88	154	153	**911**	**190[1]**	**143[1]**	**162[1]**	**87[1]**
Czech Republic[l]	1996	777	1062	176	–	27	446	4	33	409	–
Denmark[m]	1997	3427	–	162	107	41	**900[4]**	**409[4]**	**151[4]**	**176[4]**	**64[4]**
Finland[n]	1994	7000	3000	150	120	30	**420**	**84**	**99**	**52**	**30**
France[o]	1995	25,000	–	900	1400	350	**9300**	**4000**	**1500**	**3000**	**800**
Germany[p]	1993	142,252	–	4921	928	263	11,951	5080	1441	3290	699
Greece	1997	1800	–	59	4	43	**600**	**270**	**180**	**115**	**35**
Hungary	1996	–	–	84		50–55	700	305	140	195	62
Iceland	1995	–	–	0.18	–	–	45	20	16	5	4
Ireland	1995	–	785	29	–	–	–	–	–	–	–
Italy	1991	34,400	–	3400	1400	–	**7726**	**3342**	**1777**	**2248**	**459**
Luxembourg[q]	1997	3520	–	8	–	1	–	–	–	–	–
The Netherlands[r]	1996	13,950	36,382	600	257	87	**2710**	**1401**	**613**	**472**	**224**
Norway[s]	1996	3600	–	95	65	34	514	276	137	65	36
Poland[t]	1999	***68***	–	***1397***	–	–	***317***	***108***	***58***	***111***	***40***
Portugal[u]	1994	–	–	8	–	–	923	239	410	179	95

Spain[v]	1994	22,000	–	404	380	–	**2481**[4]	–	**776**[4]	**914**[4]	**422**[4]
Sweden	1994	1500	–	230	104	50	–	–	–	**84**	–
Switzerland[w]	1996	3000	–	190	97	41	556	174	45	309	28
Turkey		–	–	*2786*	–	–	–	–	–	–	–
UK	1996	70,000	51,000	1000	–	–	–	–	–	–	–
Slovakia	1997	371	138	89	52	10	–	–	–	–	–
EU15[a]		338,546	111,986	12,268	5019	1075	39,092	15,725	7250	10,895	3012
OECD[a]		547,682	120,635	271,388	19,142	13,846	125,366	63,440	18,872	26,066	13,866

Sources: EUROSTAT, 2000a,b – 1997 data (**bold**); Central Statistical Office, 2000 – 1999 data (***italic bold***); OECD, 1999 (normal) and 1998 (*italic*) – data from the last available year in 1990s.

* – Data related to the last available year. 1) Data for Walloon only. Data for: 2) 1995; 3) 1997 (if different from the indicated year).

[a]Total estimates calculated by the authors are based on the sums of available data given in the respective column.

[b]Data may comprise selected kinds of packaging waste.

[c]Data for 1988.

[d]Data for 1992.

[e]Data include only used tires and are related to 1994.

[f]Data on municipal waste are related only to used tires.

[g]Data on construction waste do not comprise road and bridge construction waste and waste from soil cleaning. Data on car scrapping are related to 1997. Data on packaging are related entirely to the municipal waste.

[h]Data on sewage sludge are related to 1993 and rubber waste to 1991.

[i]Data on car scrapping are related to 1995.

[j]Data on packaging are related to 1994.

[k]Data on vehicle scrapping are related only to the end-of-life cars and tires. Data on packaging are related to 1993 and comprise only household waste.

[l]Estimated data comprise hazardous waste. Data on sewage sludge are of 1997.

[m]Data on sewage sludge are for 1996, and packaging waste for 1995 (reused glass is not considered).

[n]Data on rubber waste comprise only used tires and are related to 1995.

[o]Data on construction waste are for 1992, and for vehicle scrapping for 1991. Data on packaging are related to household only and are of 1994.

[p]Data on sludge and packaging are of 1995.

[q]Data on rubber waste comprise entirely used tires.

[r]Data on soil excavation are of 1995 and are expressed da in m^3. Data on rubber waste are of 1995 and comprise only used tires. Data on vehicle scrapping are related to 1997.

[s]Data on construction waste are related to 1993, waste from vehicle scrapping to 1997 and rubber waste – to 1992 and comprise only used tires.

[t]Data on packaging waste are related to 1999 and estimated from volumetric units. Data on construction waste do not comprise demolition.

[u]Data on sludge are related to 1991.

[v]Data on construction waste are of 1990.

[w]Data on rubber waste are of 1994, and on packaging waste – of 1995.

Table I.2.3a. Amounts and trends of municipal waste generation vs. consumption per capita in the EC and OECD countries (after OECD, 1998, 2002).

Countries	Waste generation (2000)					Consumption (1995)[a]	
	Total, thousands tons	From households, thousands tons	In kilograms per capita	% change since 1980[b] per capita	From households in kg per capita	In thousands US $ GDP per capita	% change since 1980 per capita
Canada[c]	18,110[1]	9926	640[1]	25[1]	330	11.0	18.3
Mexico	30,733	25,714	310	24[2]	260	3.5	−7.1
USA[d]	208,520	125,112	760	27	460	16.8	31.6
Japan[d]	51,446	33,968	410	8	270	11.0	47.5
Korea[e]	16,950	14,375	360	−30	300	6.3	164.9
Australia[f]	12,000[1]	7000[1]	690[1]	−2[1]	–	10.4	29.3
New Zealand[g]	–	1450	–	–	380	8.9	18.3
Austria[d]	4496	3096	560	33[2]	380	10.1	32.3
Belgium[h]	5588	4574	550	52	450	11.0	21.7
Czech Republic[i]	3434	2600	330	32	250[1]	5.1	–
Denmark[j]	3546	3084	660	65	580	9.7	27.4
Finland[k]	2400	960	460	12[2]	190	7.5	21.6
France[l]	30,744	22,041	510	13[2]	360	10.7	23.5
Germany[m]	44,094	35,177	540	0[2]	300[1]	10.4	27.5
Greece[n]	4550	–	300	15[2]	–	7.4	28.4
Hungary	4552	2674	450	−15[2]	270	4.0	–
Iceland	198	74	710	14[2]	260	9.7	13.0
Ireland[o]	2057	1221	560	195	330	8.3	40.1
Italy	29,000	–	500	100	–	11.1	33.5
Luxembourg[p]	278	221	640	82	510	16.5	36.3
The Netherlands [q]	9691	8495	610	24	530	10.5	18.6
Norway[r]	2755	1452	620	14	330	9.2	30.2
Poland[s]	12,226	8480	320	14.	220	2.9	–
Portugal[t]	4531	–	450	125	–	6.8	43.9
Spain	26,505	20,664	670	–	520	7.8	28.8
Sweden[u]	4000	3229	450	50	–	8.3	7.5
Switzerland	4681	2851	650	48	450	12.0	8.2
Turkey[v]	24,945	–	390	44	–	3.3	12.5

UK[d]	33,200	28,460	560	19[2]	480	10.6	41.5
Slovakia[w]	1706	1093	320	−14	200	–	–
Russian Fed[x]	50,000	–	340	112	–	–	–
North America	265,000	–	660	–	–	*10.4*	*14.3*
EU15	188,000	–	520	–	–	*9.8*	*28.8*
OECD-Europe	220,000	–	500	–	–	–	–
OECD[y]	551,000	–	560	–	–	*9.3*	*30.7*

Sources: OECD 1998: data for 1980 and 1995 related to consumption per capita.

* – Data for 1990 and 2000 are related to 1992 and 1998.

[a]The *estimates (italic)* based on sums and average values of consumption per capita were calculated by the authors on the basis of available OECD (1998) data for 1980 and 1995 related to consumption per capita.

[b]% changes of total municipal waste generation per capita in 2000 compared to 1980 were calculated by the authors on the basis of available data of OECD (2002) for these or other years specified in reference marks c) – y) below; 1) If data for 2000 were not available, % changes were calculated for the decade 1980–1990. 2) If data for 1980 were not available, % changes were calculated for the decade 1990–2000.

[c]Data for 1990 and 2000 are related to 1992 and 1998.

[d]Data for 2000 are related to 1999.

[e]Data for 1980 are related to 1985.

[f]Data for 1980 and 1990 are related to 1978 and 1992.

[g]Data for 1980, 1990 and 2000 are related to 1982, average of 1986–1991 and 1999, respectively.

[h]Estimate.

[i]Data for 1990 and 2000 are related to 1987 and 1996.

[j]Data for 1990 are related to 1995. Data on household waste for 1980 are related to 1985.

[k]Data for 1990 are related to 1994. Estimates on household waste.

[l]Data for 1990 and 2000 are related to 1989 and 1999.

[m]Data for 1998.

[n]Data for 2000 are related to 2001.

[o]Data for 1990 are related to 1995; data for 2000 are related to 1998.

[p]Data for 1990 are related to 1992; data for 2000 are related to 1999.

[q]Data for 1980 are related to 1981.

[r]Data for 1990 are related to 1992.

[s]Data are related to collected waste; data for 1985 comprise liquid waste from containers and other tanks.

[t]Data are related also to Azores and Madera Islands.

[u]Data for 2000 are related to 1998.

[v]Data for 1990 and 2000 are related to 1989 and 1998.

[w]Data for 1980 and 1990 are related to 1987 and 1992, respectively.

[x]Estimates based on studies of different towns.

[y]Data do not comprise former GDR, Czech Republic, Slovakia, Hungary, Poland and Korea.

Table I.2.3b. Annual amounts and trends of municipal waste generation in the EC and associated/candidate European countries in the last decade (after Central Statistical Office, 2001, 2002; EUROSTAT, 2001a,b).

Countries	Waste generation, thousand tons				Annual % change[a]	In kilograms per capita[b]
	1990 and the closest available		2000 – the closest available			
	Year	Total	Year	Total		
EU15						
Austria[c]	1990	4782	1996	5270	1.6	654
Belgium	1991	4294	1999	5462	3.1	535
Denmark	1994	2803	1998	3141	2.9	593
Finland	1990	3100	1997	2510	−3.0	489
France	1993	33,700	1998	37,800	2.3	644
Germany[d]	1990	50,183	1996	44,390	−2.0	543
Greece	1990	3000	1997	3900	3.8	372
Ireland	1995	1550	1998	1933	7.6	523
Italy	1990	20,000	1998	26,846	3.7	466
Luxembourg[e]	1990	224	1998	184	−2.4	434
The Netherlands	1991	7470	1999	9359	2.9	594
Portugal	1990	3000	1999	4364	4.6	433
Spain	1990	12,546	1999	24,470	9.5	670
Sweden	1990	3200	1998	4000	2.8	452
UK[f]	1989	35,000	1999	30,000	−3.4	508
Associated countries						
Island	1992	159	1999	–	–	516
Norway	1990	2000	1999	2650	3.2	596
Switzerland	1990	4090	1999	4555	1.2	639
Candidates to the EU						
Czech Republic	1996	3200	1999	3365	1.7	327
Cyprus	1993	368	–	–	–	516
Estonia	1995	533	1999	569	1.6	394
Hungary	1990	4171	1999	4376	0.5	434
Poland	1990	11,098	1999	12,317	1.2	319
			2000	**12,226**	1.0	317
Slovenia	1995	1024				515
EU15		*178,852*		*203,623*	*2.3*	*527*
Associated-3		*6249*		*7205*	*2.2*	*584*
Candidate-6		*20,394*		*20,536*	*1.2*	*417*

Central Statistical Office, 2002–2000 data for Poland (**bold**).

Note: *Total and mean values (italic)* are estimated by the authors on the basis of available statistical data given in the respective columns.

[a]Annual increase rate is based on the data for the oldest and the latest available year from the last decade.

[b]Data are referred to the last available year.

[c]Data comprise construction waste.

[d]Preliminary data for 1996.

[e]Preliminary data.

[f]1999 data are for England and Wales.

Table I.2.4. Annual generation of industrial manufacturing/production waste and hazardous waste in the EU and OECD countries in mid-1990s (after OECD, 1998).

Countries	Generation of production/ manufacturing wastes[a]		Generation of hazardous waste[b]				
	Total in thousand tons	In kg/US $1000 GDP	Year	Generation		In thousand tons	
				Total in thousand tons	In kg/US $1000 GDP	Export–import	Amount for utilization
Canada		–	1991	5896	11.3	87.9	5808
Mexico[c]	29,570	60	1995	8000	16.1	−152.8	8153
USA		–	1993	213,620	428.7	142.7	191,091
Japan	143,710	60	1995	–	–	2.0	–
Korea	27,010	50	1995	1622	3.1	–	1622
Australia[d]	37,040	130	1992	426	1.5	3.0	423
New Zealand[e]		–	1993	110	2.3	10.5	100
Austria[f]	10,470	80	1994	513	3.6	10.9	502
Belgium[g]	13,730	8	1994	776	4.44	−317.0	1093
Czech Republic	19,770	230	1994	1867	21.9	−4.9	1872
Denmark[h]	2560	30	1995	250	2.6	−34.0	284
Finland[f]	11,500	140	1992	559	7.5	16.6	542
France[f]	105,000	100	1990	7000	6.8	−447.6	
Germany[f]	64,860	50	1993	9100	6.6	522.6	8557
Greece[i]	510	10	1992	450	4.5	0.1	450
Hungary	6330	100	1994	3537	58.2	9.6	3527
Iceland[j]	10	–	1994	6	1.3	0.8	5
Ireland[f]	3780	70	1995	248	4.6	16.4	231
Italy	22,210	20	1991	3387	3.5	13.0	3374
Luxembourg[f]	1440	160	1995	180	15.7	180.0	
The Netherlands	7920	30	1993	1520	6.0	−73.5	1593

(*continued*)

Table I.2.4. Continued.

Countries	Generation of production/ manufacturing wastes[a]		Generation of hazardous waste[b]				
	Total in thousand tons	In kg/US $1000 GDP	Year	Generation		In thousand tons	
				Total in thousand tons	In kg/US $1000 GDP	Export–import	Amount for utilization
Norway	3290	40	1994	500	5.7	28.4	472
Poland[k]	22,610	120	1995	3866	20.0		
Portugal		–	1994	1356	13.2	−6.2	1363
Spain	13,800	30	1987	1708	4.0	−75.0	1783
Sweden	13,990	100	1985	500	3.8	30.0	470
Switzerland	1350	10	1995	834	5.6	96.0	738
Turkey	25,040	80	1995	–	–	–	–
UK[l]	56,000	60	1993/1994	1844	1.9	−68.0	1912
EU15	*32,770*	*63***		*29,391*	*5.9***	*−231.7*	*22,154*
OECD	1,500,000*,n	90**,n		*269,675*	*24.6***	*−8.5*	*235,965*

Note: *Total and mean values* for EU15 and OECD (except Secretariat estimates) calculated by the authors are based on the available data given in the respective columns; n – Secretariat estimates; * – without the USA; ** – mean.

[a]Data for mid-1990s.

[b]Waste controlled in accordance with the Basel Convention.

[c]Data on production of hazardous waste are for the year 1994.

[d]Data on industrial waste comprise region Queensland only, and on hazardous waste entirely Victoria region.

[e]Data on hazardous waste generation are for the year 1990.

[f]Data on hazardous waste are collected in accordance with the national legislation.

[g]Data related to export and import comprise entirely the region of Flanders and Walloon.

[h]Hazardous waste in accordance with the European Waste Catalogue.

[i]Export is related only to some kinds of wastes.

[j]Data on hazardous wastes do not comprise households and small enterprises.

[k]Not all hazardous wastes are classified in accordance with the Basel Convention.

[l]Data on hazardous waste are only for England and Wales.

the RCRA hazardous-waste management system. The structure of HW sources shows predominance (71%) of the chemical and petroleum industries as generators of HW. These industries may be responsible for as much as 85% of the total quantity of HW generated. Metal-related industries generate 22% of HW, while share of other industries accounts for 7%. Most of the waste comprises spent solvents, process wastewater and sludge and other waste from the listed industries. Reactive waste accounts for 52%, corrosive waste for 35%, toxic waste for 10%, ignitable waste for 1% and unspecified ones for 1–5% (some waste falls into two or more categories) (Dietz and Burns, 1989).

I.2.3. Waste arisings and structure of the waste stream in the EU States and candidate countries

Until recently, the estimate of the quantity and source structure of the waste stream in the EU Member States and the European Union as a whole was based on the combined data from different national and international sources and displayed a high degree of uncertainty due to the lack of consolidated information. Also, at present the statistical data show wide confidence intervals and a lack of completeness. Much support for the generation of waste statistics was provided by the EWC – European Waste Catalogue (1994), though its adoption by the Member States was voluntary. The situation in the statistical arena has improved considerably after establishing a harmonized list of wastes (Commission Decision 2000/532/EC, amended by Commission Decision 2001/118/EC). Wastes included in the list, which replaced the European Waste Catalogue and a list of hazardous waste, are fully defined by the six-digit code for the waste and the respective two-digit and four-digit headings. The list is preceded by the description of steps that should be taken to identify a waste. Most of the countries – candidates to the EU and South-East European Countries have adopted the EWC and the list of hazardous wastes pursuant to the EC Council Directives, and replacing them the harmonized list of wastes (Commission Decision 2000/532/EC, amended in 2001).

A better resolution of uncertainties arising from the national differences and disharmony in the waste definitions in the EU member states is anticipated also after approval in 2003 of the European Standards EN 13965-1 and EN 13965-2 "Characterization of waste – Terminology" (CEN, 2003a,b). European standards have the status of national standards for CEN (European Committee for Standardization) members without any alteration, and are adopted also by the candidates to the EU.

Distinct improvement in completeness and time relevancy of statistical data in recent years demonstrates the EU and candidates' status on HW statistics and comparison of data for mid-1990s (Tables I.2.4 and I.2.5). Completeness and compatibility of recent statistical data on HW for candidates to the EU are particularly striking. Comparison of data on hazardous waste generation in mid-1990s and in 1998 for candidate countries that are also OECD members indicates significant differences that originate from shifting to the European list of wastes from the national regulations.

Data for the EU15 Member States show a general trend to increase the amount of generated hazardous waste since 1992–1995, though in Finland, Portugal and Luxembourg some decrease also occurred (Austria, Belgium and Spain) (Table I.2.5, after EUROSTAT, 2000a–c, 2001a). Of the total amount 28.8 Mt in 1994/1995 and over

Table I.2.5. Annual generation and management of hazardous waste in the EC, associated and candidate countries in 1994–1998 (after EUROSTAT, 2000a–c, 2001a; Central Statistical Office, 2001).

Countries	Hazardous waste (thousand tons)											
	Generation				Management							
	Year	Total	Year	Total	Year	Incinerated	Disposed	Total	Year	Incinerated	Disposed	Total
EU15												
Austria	1994	513	1998	868	1994	99	–	*99*	1996	106	–	*106*
Belgium	1994	776	***1997***	***1625***[a]	1994	75	530	*605*	1998	113	636	*749*
Denmark	1994	194	1998	281	1994	–	62	*62*	1998	156	57	*213*
Finland	***1992***	***559***	1997	485	1994	–	–	–	1997	101	234	*335*
France[b]	***1990***	***7000***	***1990***	***7000***	1994	1210	728	*1938*	1998	1361	803	*2164*
Germany[c]	***1993***	***9100***	1996	17,421	***1993***	***2034***	***3253***	*5287*	1996	–	–	–
Greece	1995	350	1997	–	1995	–	–	–	1997	1	226	*227*
Ireland	1995	248	1998	370	1995	50	5	*55*	1998	71	41	*112*
Italy	1995	2708	1997	3401	1995	112	643	*755*	1997	374	791	*1165*
Luxembourg[d]	1995	200	1997	143	1995	–	17	*17*	1997	–	–	–
The Netherlands	1994	885	1998	1448	1994	165	204	*269*	1998	244	370	*614*
Portugal	1995	668	1997	595	1995	–	–	–	1997	–	–	–
Spain	1995	3394	1998	–	1996	918	–	*918*	1998	–	–	–
Sweden	1994	139	1998	801	1994	–	–	–	1998	–	–	–
UK	***1993***	***2077***	1998	–	***1993***	***185***	***931***	*1116*	1998	–	–	–
Associated countries												
Island	1994	6	1998	8	1996	–	–	–	1998	–	–	–
Norway	1994	640	1998	655	1994	–	–	–	1998	119	–	–
Switzerland	1994	854	1998	1043	1994	295	201	*496*	1998	371	219	*590*
Candidates to the EU												
Czech Republic	1995	6005	1998	3399	1995	33	176	*209*	1998	16	406	*422*
Cyprus	1994	68	1997	52	1994	–	–	–	1997	–	–	–

Estonia	1995	7273	1998	6272	1995	–	6517	*6517*	1998	–	6050	*6050*
Hungary	1994	3338	1998	3915	1994	1517	1424	*2941*	1996	1110	1035	*2145*
Poland	1994	3188	1998	1105[e]								
			1999	**1601**					**1999**	–	**96**	
Slovenia	1995	170	1998	–	1995	–	–	–	1998	–	–	
EU15		*28,811*		*34,438*		*4848*	*6373*	*11,221*		*2527*[f]	*3158*[f]	*5685*[f]
Associate-3		*1500*		*1706*		*295*	*201*	*496*		*490*	*219*	*590*
Candidate-6		*20,042*		*15,239*		*1550*	*8117*	*9667*		*1126*	*7587*	*8713*

Italic bold – data after EUROSTAT 2000a–c; **Bold** – data after Central Statistical Office (2001).

Note: *Total values (italic)* are estimated by the authors on the basis of available statistical data given in the respective columns. In case of lacking recent data for waste generation, the latest available data were used (France, Greece, Spain and UK).

[a]Flanders only; data for 1997.

[b]Data for incineration and disposal do not comprise internal management.

[c]Preliminary data for 1996.

[d]Preliminary data. Data for 1994 for disposal comprise also waste other than hazardous.

[e]Disparity of data for 1994 and 1998 results from the changes in waste classification.

[f]Incomplete data, without Germany, UK and four other Member States.

34 Mt in 1997/1998 (incomplete data, without Spain, UK and Greece, and old data from France) that is about 9–10% of production waste, 4.8 Mt (17%) were incinerated and 6.4 Mt (22%) disposed in 1994/1995 (data on waste management for 1997/1998 were incomplete). Of the EU Member States, the highest amounts of HW were generated in Germany and in France, while the highest amounts of HW generation per capita were in Luxembourg and Belgium. Hazardous waste generation per capita ranged in the EU countries from 16 to 341 kg/year (mean 103 kg/year).

In six countries – candidates to the EU – total amounts of HW generated in 1998 (15 Mt) showed deep decrease (for 24%) in comparison with 1994/1995 that was partly due to alteration of production profile (Czech Republic), but also resulted from the changes in waste classification (Poland) (Table I.2.5). Values of HW generation per capita (from 15 to 625 kg/year without Estonia) were comparable to those recorded for the EU countries (EUROSTAT, 2000a,b, 2001a). The highest HW generation among candidate countries was from Estonia and Czech Republic, within the range recorded for Germany and France. This resulted in extremely high amount of HW per capita in 1977 in small Estonia (5049 kg/year), and elevated value for Czech Republic (625 kg/year). Candidate countries disposed of about 30% more and incinerate three times less HW than EU countries (Table I.2.5).

Currently, the most reliable statistics on waste generation are provided by the reports of OECD and publications of the EUROSTAT. Tables I.2.1–I.2.7 illustrate the degree of uncertainty of the statistical data based on different, even relatively harmonized sources. In Table I.2.3a, two sets of parallel data for 1997 for the EU Member States originated from reports of OECD (1998), (1999) and EUROSTAT (2000a,b) show lesser or bigger divergence and incompleteness. It results in wide confidence intervals and significant differences both in estimates of the total amounts of waste generated and in the source structure of the waste stream in the particular Member States and the European Union as a whole.

As estimate still plays a considerable role in evaluation of the actual status and long-term prognosis for waste generation, it can be of interest to compare the UNEP (1992) estimate after Haines (1988) and a decade later EUROSTAT (2000a,b) statistical data (Table I.2.6). UNEP estimated total annual waste generation in the EU as approximately 2162 Mt. Of this, the major components of the waste stream were reported to be agricultural waste (44%), sewage sludge (14%) and extractive/mining waste (12%). EUROSTAT data for 1997, completed by OECD (1999) and national sources (Bontoux and Leone, 1997), at almost the same total amount, show lesser percentile of agricultural waste (33%), though their share can be higher, as the data on agricultural waste are the least complete. The amounts of industrial and construction/demolition waste appeared to be almost two times higher, while the amount of sewage sludge (OECD, 1999 data) was 24-fold less than the UNEP estimate.

To summarize, the biggest principal sources of waste in the EU appeared to be agriculture (32.7%), mining waste (17.0%), industrial manufacturing/production waste (16.4%) and construction/demolition waste (14.0%) (Table I.2.7). According to these data assembled from the available statistical sources including OECD (1999) and EUROSTAT (2000a,b) and national statistics (Bontoux and Leone, 1997), in the EU the biggest waste generators are France, Germany and the UK. They contribute 65% to the total waste generation. Their share in the source-related waste streams of the EU ranged from 60 to

Table I.2.6. Comparison of estimated and statistical data for annual waste generation in the European Community – principal sources (UNEP, 1992; OECD, 1999; EUROSTAT, 2000a).

Kind of waste	Million tons/yr		%	
	UNEP estimate[a]	Statistics 1997[b]	UNEP estimate[a]	Statistics 1997[b]
Household and consumer wastes	132	186	6	9
Agricultural wastes	950	698	44	33
Industrial wastes	160	350	7	16
Sewage sludge	300	12.3[c]	14	0.6
Extractive (mining) wastes	250	362	12	17
Demolition and construction wastes	170	300	8	14
Other wastes (litter, etc.)	200	225[d]	9	10.4
Total	2162	2133	100	100

[a]UNEP, 1992 (adapted from Haines, 1988).
[b]EUROSTAT, 2000a.
[c]After OECD, 1999.
[d]Together with power generation waste and waste from water purification and supply.

Table I.2.7. Amounts and percentile structure of waste generated in the EU (Mt/yr and % of the total for a country) (after Bontoux and Leone, 1997; OECD, 1999; EUROSTAT, 2000a,b)*.

Country	Million tons/yr (% of the total for the country)							
	Agriculture	Mining	Industrial	Construction	Other[a]	Municipal	Total[b]	Hazardous[c]
Austria[d]	*0.8 (1.28)*	**0.003**[4] (0.005)	**14.28**[1] (22.82)	**25.39**[1] (40.57)	16.84 (26.90)	**5.27**[1] (8.42)	62.58 (100.0)	**0.61**[1] (0.97)
Belgium	–	**0.39**[2] (1.38)	**13.73**[1,2,3] (48.65)	**7.72**[2] (27.36)	1.07 (3.79)	**5.31** (18.82)	28.22 (100.0)	**1.63** (5.78)
Denmark[e]	–	–	**2.74**[1] (20.81)	**3.43** (28.90)	3.02 (25.44)	**2.95** (24.85)	11.87 (100.0)	**0.25** (2.11)
Finland[f]	22.0 (33.66)	**15.00**[8] (22.95)	**15.50** (23.72)	**7.00**[3] (10.71)	3.75 (5.74)	**2.100**[3] (3.21)	65.35 (100.0)	**0.56**[8] (0.86)
France[g]	377.0 (62.69)	**75.00**[8] (12.47)	**101.00**[2] (16.79)	**13.70**[9] (2.28)	–	**34.70**[2] (5.77)	601.40 (100.0)	**7.00**[10] (1.16)
Germany[h]	27.9 (7.65)	**67.81**[4] (18.58)	**65.12**[4] (17.85)	**131.64**[4] (36.08)	28.92 (7.93)	**43.49** (11.92)	364.88 (100.0)	**9.10**[4] (2.49)
Greece	7.78 (23.31)	**3.90**[2] (10.78)	**6.68**[1] (20.01)	**1.80**[1] (5.39)	9.62 (28.82)	**3.90** (11.68)	33.38 (100.0)	**0.35**[1] (1.05)
Ireland	31.00 (75.57)	**2.20**[2] (5,36)	**3.78**[2] (9.22)	**1.32**[2] (3.22)	0.69 (1.68)	**2.03**[2] (4.95)	41.02 (100.0)	**0.25**[2] (0.61)
Italy[h]	–	–	22.21 (20.77)	14.31 (13.38)	43.83 (40.98)	**26.60** (24.87)	106.95 (100.0)	3.39[9] (3.17)
Luxembourg[i]	–	–	**1.44**[10] (88.34)	–	–	**0.19**[6] (11.66)	1.63 (100.0)	**0.14** (8.59)
The Netherlands[j]	17.00 (32.23)	**0.33**[1] (0.63)	**8.58**[1] (16.27)	13.95 (26.45)	4.11 (7.79)	**8.78**[1] (16.64)	52.75 (100.0)	**0.93**[1] (1.76)
Portugal[k]	–	**7.12** (23.18)	**10.99** (35.77)	**7.73** (25.16)	0.57 (1.86)	**4.31**[7] (14.03)	30.72 (100.0)	**0.56** (3.13)
Spain	114.0 (51.07)	**70.00**[4] (31.36)	**13.80**[10] (6.18)	**0.11**[2] (0.05)	10.0 (4.48)	**15.31**[1] (6.86)	223.22 (100.0)	**3.39**[2] (1.52)
Sweden	*21 (24.06)*	**47.00**[4] (53.84)	**13.99**[4] (16.03)	**1.50**[3] (1.72)	0.60 (0.69)	**3.20**[3] (3.67)	87.23 (100.0)	**0.14**[3] (0.16)
UK[l]	**80.0** (18.96)	**74.00**[1] (17.54)	**56.00**[2] (13.27)	**70.00**[1] (16.59)	114.0 (27.01)	**28.00**[1] (6.64)	422.00 (100.0)	**2.08**[4] (0.49)

Total[l]	698.48 (32.74)	362.45 (16.99)	349.57 (16.39)	299.60 (14.04)	237.02 (11.58)	**186.14** (8.26)	2133.26 (100.0)	30.78 (1.44)
Total max[l]	484.90 (34.93)	216.81 (15.62)	222.12 (16.00)	215.34 (15.51)	142.92 (10.29)	106.19 (7.65)	1388.28 (100.0)	18.18 (1.31)

Sources: National statistical sources 1993–1997, after Bontoux and Leone, ITPS, 1997 *(italic)*; OECD, 1999 (normal); EUROSTAT, 2000a,b (**bold**).

* – Data related to 1997 or the last available year in 1990s. Rounded total data may comprise estimates. Data for: 1) 1996; 2) 1995; 3) 1994; 4) 1993; 5) 25,257 thousand tons collected during public waste collection according to the German Waste Act. 6) Without fractions collected separately. Data for: 7) 1998; 8)1992; 9) 1991; 10) 1990. Data for three largest contributors are underlined.

Note: Total values were calculated by the authors on the basis of available data given in the respective columns/rows.

[a]Data comprise also waste from power generation, and water purification and supply.

[b]Total includes entirely sums of available data given in the column; also data on agricultural waste from national statistical sources 1993–1997 *(italic)*.

[c]Waste controlled in accordance with the national legislation.

[d]Valid classification does not relate to sectors but to groups of waste; data may not be comparable to other countries.

[e]Data comprise sewage sludge. Data on other waste include hazardous and other production waste. Total value does not include waste from agriculture, and mining and quarrying.

[f]Data on agriculture do not comprise waste from forestry.

[g]Estimates comprise hazardous waste.

[h]Data on other waste are related to hospital waste.

[i]The latest statistical data on production waste are for 1990; no contemporary data are available.

[j]Data on other waste include commercial waste and car scrapping.

[k]Data comprise entirely hazardous waste (besides data on municipal waste).

[l]Data on other waste comprise sewage sludge.

[m]Amounts and percentile comprise entirely sums of available data given in the column, also data on agricultural waste from national statistical sources 1993–1997 *(italic)*.

over 70%: they generated 72% of construction/demolition waste, 69% of agricultural waste, 64% of industrial manufacturing/production waste, 60% of mining and "other" residues and 57% of municipal waste. Besides these waste generators in the European Union, a high position with respect to the amount of agricultural and mining waste (second and third, respectively) also is held by Spain. Hazardous waste generation in the EU accounted for only 1.44% of the documented total annual waste generation. The HW produced in the three EU Member States – the biggest waste generators – constituted 59% of the total annual HW. The biggest generator of hazardous waste appeared to be Germany. Its share of the HW generation was estimated to be 30%. The next in line were France, Italy and Spain, which were responsible for generation of 23, 11 and 11%, respectively, of the total HW. The percentile structure of waste for each EU Member State differed considerably from the total for the EU and reflected the specifics of their economy. The proportion of agricultural waste (over 50%) was the highest for Ireland, France and Spain. Mining waste dominated in Sweden (54%), while a high amount of construction/demolition waste was specific for Austria and Germany. The percentile of hazardous waste ranged from 0.16% (Sweden) to 8.59% (Luxembourg).

Potentially recyclable waste generated in the EU accounted for 24% of the total registered waste generation. The bulk of this waste is construction/demolition (67%) and dredging (22%) material. Ultimately recyclable packaging waste accounted for no more than 7.7%. In the OECD Member States beside construction (50%) and dredging waste (11%), the proportion of sewage sludge (25%) was significant. Packaging waste accounted for 11%. Therefore, the structure of the recyclable waste in the EU and OECD as a whole is somewhat different (Table I.2.2).

There is still substantial degree of uncertainty in the European statistics, as both the OECD and EUROSTAT data suffer from being incomplete, and related to different years for some member countries that also often randomly merge various kinds of waste (e.g. compare OECD, 1999 and EUROSTAT, 2000a–c data for construction waste – Tables I.2.2 and I.2.7). Nevertheless, due to harmonization of statistical methods and of nomenclature based on the EWC (1994) these data are considered the most reliable. It is anticipated that enactment of the harmonized single European List of Wastes (2000) and Regulation on waste statistics (2002) and the adoption of this list by all the EU Member States and by the candidate and South-East European countries along with the establishing uniform questionnaire and reporting obligation due to implementation of the Regulation on waste statistics (2002) will greatly improve the status of the European statistics on waste in general. The recent progress in elaboration of clear and comparable indicators for sustainable development proposed by EUROSTAT (2001a) should considerably increase the application of statistics as an indispensable tool for the actualization of the sustainable development and auditing the efficiency of the undertaken measures. The inconsistency and incompleteness of data on waste generation in other OECD countries is much higher, and ways to overcome this problem are much more complicated. Especially problematic is lack of terminological and statistical compatibility between North America and the EU. A significant effort should be put into the harmonization area, in particular for the univocal interpretation of statistical data from the USA, which is the world's biggest generator of waste. Excluding these data from the statistics undermines reliability of all the comparative analysis for the OECD (see Table I.2.1). In turn, taking them into consideration in their present status would cause no lesser misinterpretation.

The preceding analysis clearly shows that the inconsistency of the statistical data concerning major waste streams, their structure and amounts in the OECD, the EU and at the national levels is still high. The need for harmonization and unification of the national and international waste statistics based at present on the equivocal definitions and lists is urgent. In this field, closer cooperation of the US EPA and other national statistical offices, and international bodies (OECD, EC and SBC) is required.

I.2.4. Waste generation in new countries of the former USSR

If the waste statistics in the OECD (including the USA) and the EU Member States is still incomplete and inconsistent, there was almost no reliable or even any data on solid waste generation and control in most of the states of the former USSR (except Baltic states) until statistical data on the total amount of hazardous wastes in 1999 as reported by Parties by 10 October 2001 were issued by the Secretariat of the Basel Convention (SBC). Among 36 Parties that submitted numerical data on HW generation in that year, were Russian Federation, Uzbekistan, Kyrgyzstan and Moldova.

The huge amounts of solid and hazardous waste generated and disposed in the area of the former USSR in an uncontrolled manner can be only guessed, considering the historically strong pressure on the development of primary process industries, which generate the bulk of solid and hazardous wastes. In particular, these industries – high volume and hazardous waste generators – comprise the mineral and metal processing industries, chemical and engineering industries, as well as oil spills and crude oil processing. The reported amount of HW generated in Russian Federation in 1999 can be compared only with the scale of HW generation in the USA (108,070 thousand tons, that is about 50% of HW generated in the USA) and comprised 54% of the total HW that is 200,556 thousand tons, as reported by 36 Parties. Along with Uzbekistan, the second in size HW generator, it comprised 67.7% of the total, while other two former republics of the USSR contributed to the total reported HW generation to a lesser extent (SBC, 2001b).

Some rough idea about the scale of waste generation in the former USSR can provide also statistical data for the Central European candidate (three of them are OECD Members) that used to be within the influence of the USSR economy (Tables I.2.4 and I.2.5). These countries (Poland, Hungary and Czech Republic) display particularly high solid waste (SW) and HW generation per US $1000, i.e. high SW and HW factors (100–230 and 20–58 kg, respectively) (Table I.2.4). For the former USSR countries, substantially higher SW and HW factors are anticipated.

Baltic states (Estonia, Latvia and Lithuania) – candidates to the EU and former republics of the USSR that are covered by the recent EU statistical report (EUROSTAT, 2000c, 2001a) are not typical for the whole country due to the small size and late annexing to the USSR. Nevertheless, on the background of Latvia and Lithuania where primary process industries were not particularly developed, HW generation in Estonia was reported to be extremely high (7361 thousand tons in 1997 and 6272 in 1998 that is comparable to France). The HW generation per capita in this small country accounted for 5049 kg that is 15 times higher than the highest value for the EU Member States (341 kg in Luxembourg). Of the generated HW, 89.6–96.5%, i.e. 6512–6050 thousand tons was disposed, which

was about equal to the total HW amount disposed by all 15 EU Member States (EU15) (Table I.2.5, after EUROSTAT, 2001a). These data give rough idea about the probable size of HW generation in the majority of the new countries of the former USSR.

I.2.5. Waste generation in the developing countries

The data on solid waste generation and control in the developing countries are scarce. The governments of these countries have given a low priority to the development of controls over solid waste generation and safe disposal, often because of a failure to understand the threat, which inadequate management could pose to human health and the environment.

Even a very rough estimate of waste amounts and source structure, as well as composition of waste in the developing countries is extremely difficult. The notion of "developing countries" is eclectic due to considerable differences between regions and the particular developing countries with respect to the degree of urbanization, level and structure of the industrial development, and intensity and structure of agriculture, as well as cultural development, traditions, habits and a common life style. Though, according to Down To Earth Magazine (Anonymous, 2001a) based on UNEP (2000) data, the municipal solid waste (MSW) structure only to a limited extent depends on factors like geographical location, energy sources and the climate, being related mainly to the income per capita. The comparison of average MSW composition of low-income Asian countries (the latter data referring to India and China) with high- and middle-income countries reveals that ash is one of the main components of garbage that constitutes the "other" category in low-income countries, while in high- and middle-income countries the share of this category is about four times lower. In turn, the middle- and low-income countries have a high compostable organic content in their municipal wastes, while in MSW generated in the high-income countries the organic fraction is significantly smaller. In low-income countries, the fractional share of recyclable material is the lowest (Fig. I.2.1, after UNEP, 2000; Anonymous, 2001a).

The same sources consider also the direct relation between the income per capita and MSW generation, and assume waste generation per capita to increase from 1.6 to 2.74 times by 2025 in all three types of countries (in high-income countries the increase being the highest), in parallel with a growth of the income per capita from 30% to 2.4 times (in high-income countries being relatively the lowest) (Fig. I.2.2, after UNEP, 2000; Anonymous, 2001a). This prognosis, though, in view of the present status and trends (see Tables I.2.3a and I.2.3b), is based on the simplified assumptions and does not seem correct with respect to high-income countries where MSW generation strongly depends on the life style and though still growing, shows distinct trends to slowing down due to the implementation of waste management strategies focused on waste minimization, restrictive regulations and growing public awareness. Progressively increasing costs of landfilling, e.g. reported increase of landfill fee in Oregon, USA, from US $18 to $68 per ton between 1988 and 1991, and lack of new land for landfill siting also contribute to limitation of waste generation (Anonymous, 2000). Most likely, the municipal waste generation in the developing low- and middle-income countries will grow and its structure will change in the longer time span in parallel with growing income until both factors reach the actual level of developed countries; if by that time waste management,

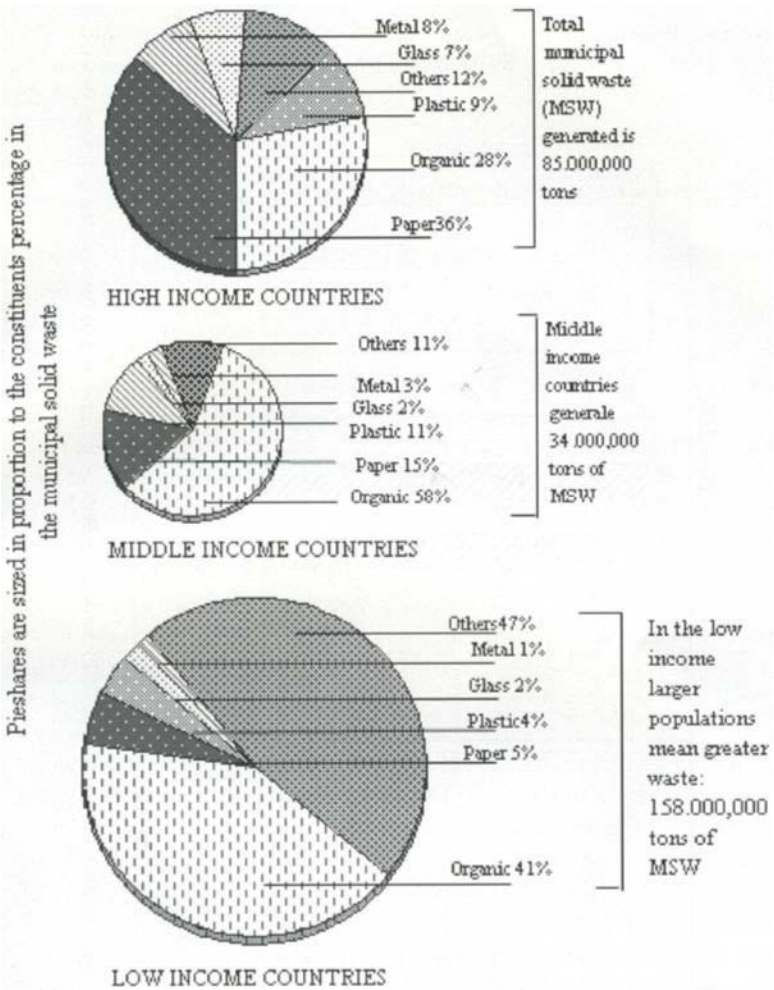


Figure I.2.1. MSW composition vs. average income (after UNEP, 2000; Anonymous, 2001a). Ash is one of the main components constituting the "other" category in low-income countries, especially in India and China. The middle- and low-income countries have high amount of compostable organic content in their MSW.

legislation and public awareness in these countries also adequately improve, the increasing trends will cease.

The status of the reporting on HW in developing countries can be exemplified in Indian statistics (Anonymous, 2001b). Officially, there has never been an effort to secure a national inventory of such wastes. The State Pollution Control Boards (SPCBs) recently furnished data based on estimates from which could be concluded that the 13,011 units in the country generated approximately 4.4 Mt of hazardous waste per year, classified in three categories: recyclable, incinerable and disposable. At the same time, from the data given by the Secretary of Ministry of Environment and Forest (MoEF) appeared that

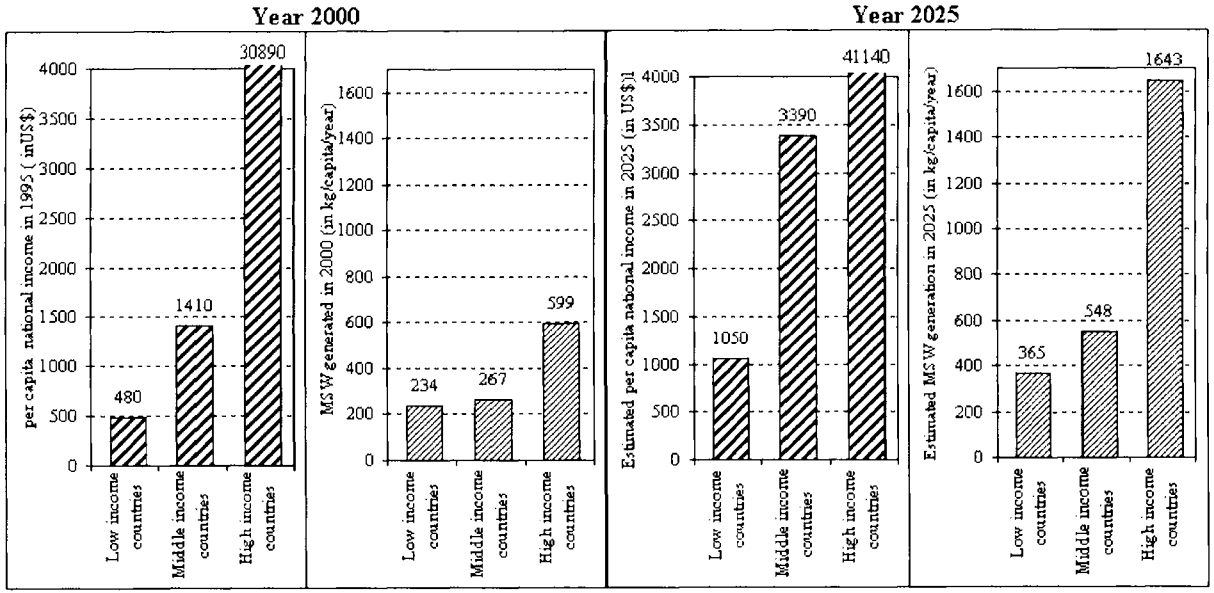


Figure I.2.2. Average MSW generation vs. income per capita in 2000 and prognosis of UNEP for MSW generation increase in 2025 based on the income growth (after UNEP, 2000; Anonymous, 2001a).

the quantity of HW generated was merely 0.7 Mt. The reason for discrepancies of such magnitude was that the inventories made by SPCBs were based on the definition of HW provided in the unamended Hazardous waste Rules, 1989, which led to the inclusion of large quantities of high volume, low-toxic wastes such as phosphogypsum, red mud, slag from iron and steel and ferro alloy industries, etc. These wastes are now excluded from the category of hazardous waste due to amendments of 06.01.2000 to the HW Rules in order to comply with ratified Basel Convention. Currently, not even a preliminary figure of total hazardous waste quantities is available as per this amendment and will not be available for some more time. The unreliable statistical data in India originate thus from weak legislation and incompatible classification of HW. This example reflects an overall status on solid and hazardous waste statistics in developing countries; in many of them hardly any statistics in this field exists.

The increasing population and industrialization in these countries results in the increase of quantities and changing structure of solid and hazardous waste that intensifies threat to human health and the environment. Besides national economies, there is an already high and still growing influence on the amounts and structure of waste generation in these countries exerted by the activity of large international companies siting their plants close to resources, cheap manpower and liberal environmental regulations. In many cases, this enables avoidance of restrictions imposed by the Basel Convention on transboundary movement of hazardous waste.

I.2.6. Transboundary movement of hazardous waste

For these "white spot" regions the only reliable source of data is transmission of information under the Basel Convention on HW transboundary movement. Recently, SBC – Secretariat of the Basel Convention – pays much attention to reporting and transmission of information on generation and transboundary movement of hazardous and other wastes (SBC, 1999a–c). These data comprise the total HW transboundary movement, which is also covered by the OECD statistics for the OECD countries (Table I.2.4). The amount of HW annually exported from the OECD Member countries varied in a wide range, from 0.1 thousand tons (Greece) to 522.6 thousand tons (Germany). The biggest HW exporters ($\geq$ 100 thousand tons annually) were consecutively Germany, Luxembourg, the USA and Switzerland. The annual import of HW reported by eight OECD Member States ranged from 4.9 (Czech Republic) to 447.6 thousand tons (France). Besides France, the biggest HW importers were Belgium and Mexico. The total export–import balance of HW in the OECD is almost 0 (export 1170.5 thousand tons, import 1174.1 thousand tons). Of this, the EU is the predominant importer/exporter, with a considerable excess of import (1021.3 thousand tons) over export (789.6 thousand tons) (OECD, 1998).

The structure of transboundary movement in 1993–1999 of HW and other wastes by Y-codes of Basel Convention lists, according to categories, generic types or constituents that render them hazardous, was also analyzed and presented by the SBC – Secretariat of the Basel Convention (1996), (1999a–c), (2000) and (2001a,b) (For explanation of Y-codes of the Basel Convention see Chapter II.2, Appendix A, Annexes I and II). The first

analysis of 1996 was based on the data provided by the Parties of the Basel Convention to the Secretariat for the year 1993, in accordance with Article 13 of the Convention. The data were reported in a form required by SBC by 18 of 101 Parties, among them by 10 OECD Member countries. The precision of these data, however, have to be considered with great caution due to the limited number of the Parties participating in the survey, as well as due to the differences in national definitions of hazardous waste and the difficulties in obtaining accurate data. This remark, underlined by SBC (1996), illustrates and confirms the most unsatisfactory state of statistical information on waste that time.

During the following years, a continuous trend in improving national reporting by the Parties to the Secretariat and in transmission of information under the Basel Convention has been observed. By 10 October 2001, the SBC prepared 87 Country Fact Sheets for the year 1999 containing the information on the generation and transboundary movement of hazardous and other wastes as reported by Parties (SBC, 2001a). Of this number, the data on amount of HW generation were submitted by 36 reporting Parties, among them by 14 OECD countries. Amounts of "other wastes" that cover wastes under Annex II: Y46–Y47 of the Basel Convention were reported by 24 Parties, among them 11 OECD countries. Of 200,556 thousand tons HW and 92,554 thousand tons of other wastes generated by the reporting Parties that give grand total 293,110 thousand tons, total amount of HW and other wastes by Y-codes generated in 1999 as reported by Parties was 26,738 thousand tons, i.e. covered only 9% of total reported amount (SBC, 2001b). This still shows the weakness and limitation of the SBC statistics despite of constantly growing number of the participating Parties.

The highest percent of total amount generated was made up by wastes collected from the households Y46 (39%), wastes having as constituents copper compounds Y22 (20%), and in descending quantities by four other wastes: basic solutions or bases in solid form Y35 (6%), waste oils/water, hydrocarbons/water mixtures, emulsions Y9 (<6%), residues arising from industrial waste disposal operations (>4%) and residues arising from the incineration of household wastes Y47 (<4%). Other wastes by Y-codes comprised 21% of reported grand total.

The SBC data on transboundary movement in 1999 of HW and other wastes by Y-codes among all reporting Parties (Fig. I.2.3a) and non-OECD reporting parties (Fig. I.2.3b), display significant predominance of wastes without Y-codes over other wastes, and much higher reported export than import, particularly among non-OECD reporting parties.

The precision of these data, however, have to be considered with great caution due to the still limited number of the Parties participating in the survey, as well as due to the differences in national definitions of hazardous waste and the difficulties in obtaining accurate data, in particular in the developing countries. This remark, underlined by SBC in 1996, illustrates and confirms the unsatisfactory state of statistical information on waste that time, and inadequate improvement in this field until now.

I.2.7. Conclusion

The concerted international systematic efforts focused on harmonization of waste terminological standards and on integrated waste and hazardous waste catalogue instead

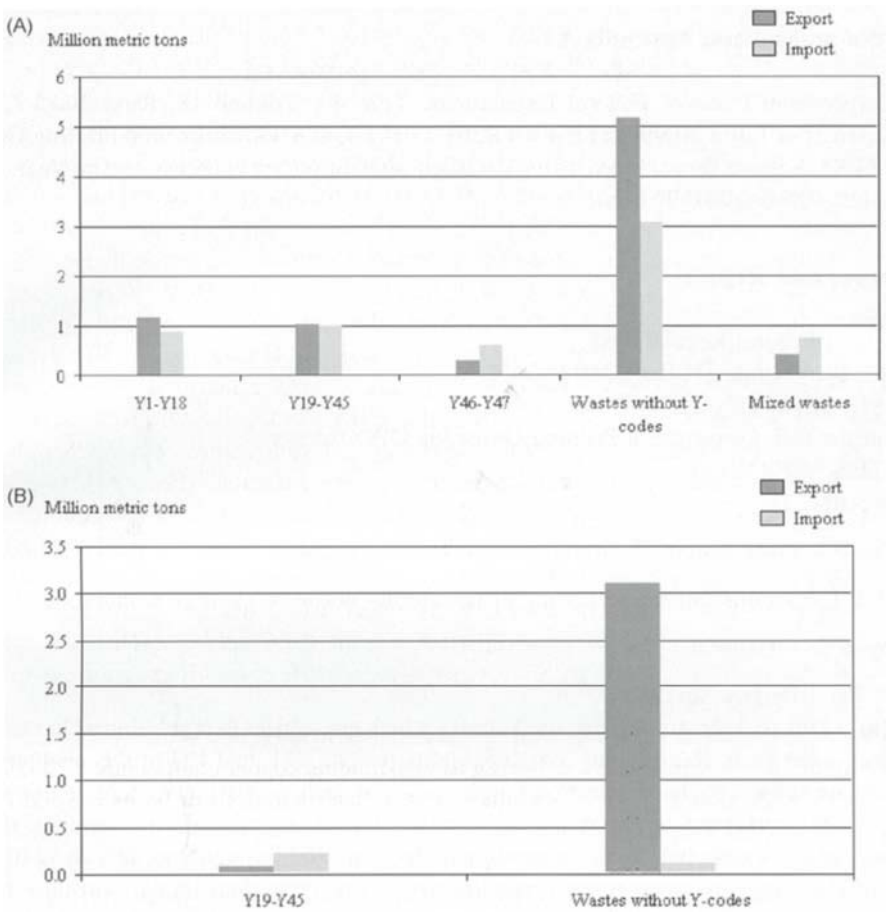


Figure I.2.3. Transboundary movement of hazardous wastes and other wastes by Y-codes in 1999 (after SBC, 2001b). Explanation of Y-codes used in Figure I.2.3 – (Ref. Annex 1 of the Basel Convention – See Chapter II.2, Appendix A). Y1–Y18 – waste streams; Y19–Y45 – wastes having as constituents; Y46–Y47 – wastes requiring special consideration. a – transboundary movement among all reporting Parties. Total amount exported: 8,104,960 tons. Total amount imported: 6,338,474 tons. b – transboundary movement among non-OECD reporting Parties. Total amount exported: 3,203,289 tons. Total amount imported: 335,473 tons. The amount of Y1–Y18 exported was negligible (1400 tons). There was no import of Y1–Y18; there was no export and no import of Y46–Y47; the amount of mixed wastes exported was negligible (4561 tons); there was no import of mixed wastes.

of multiplication of waste lists by different international and national bodies, is an urgent task of the first priority on the way to complete and reliable regional and global waste statistics. It is obvious, that reliable information is an indispensable instrument and a prerequisite to sound and sustainable waste management strategies. Hence, much more attention should be paid to the improvement of the regional and global statistics on solid waste and hazardous waste generation, disposal of and transboundary movement.

List of appendices: Appendix A

Excerpts from Code of Federal Regulations, Title 40, Volume 18, Parts 260 to 265, Revised as of July 1, 1999, CITE 40CFR261.1–261.4, U.S. Governmental Printing Office via GPO Access, downloaded from the Web site: http://www.access.gpo.gov/nara/cfr/waisidx_99/40cfr261_99.html.

Purpose and Scope

[Code of Federal Regulations]
[Title 40, Volume 18, Parts 260 to 265]
[Revised as of July 1, 1999]
From the U.S. Government Printing Office via GPO Access
[CITE: 40CFR261.1]
[Page 30–31]

Title 40 – Protection of Environment Agency (continued)

Part 261 – Identification and Listing of Hazardous Waste – Table of Contents

Subpart A – General

Sec. 261.1 Purpose and scope.

(a) This part identifies those solid wastes which are subject to regulation as hazardous wastes under parts 262 through 265, 268, and parts 270, 271, and 124 of this chapter and which are subject to the notification requirements of section 3010 of RCRA. In this part:

(1) Subpart A defines the terms "solid waste" and "hazardous waste", identifies those wastes which are excluded from regulation under parts 262 through 266, 268 and 270 and establishes special management requirements for hazardous waste produced by conditionally exempt small quantity generators and hazardous waste which is recycled.

(2) Subpart B sets forth the criteria used by EPA to identify characteristics of hazardous waste and to list particular hazardous wastes.

(3) Subpart C identifies characteristics of hazardous waste.

(4) Subpart D lists particular hazardous wastes.

(b)(1) The definition of solid waste contained in this part applies only to wastes that also are hazardous for purposes of the regulations implementing subtitle C of RCRA. For example, it does not apply to materials (such as non-hazardous scrap, paper, textiles, or rubber) that are not otherwise hazardous wastes and that are recycled.

(2) This part identifies only some of the materials which are solid wastes and hazardous wastes under sections 3007, 3013, and 7003 of RCRA. A material which is not defined as a solid waste in this part, or is not a hazardous waste identified or listed in this part, is still a solid waste and a hazardous waste for purposes of these sections if:

(i) In the case of sections 3007 and 3013, EPA has reason to believe that the material may be a solid waste within the meaning of section 1004(27) of RCRA and a hazardous waste within the meaning of section 1004(5) of RCRA; or

(ii) In the case of section 7003, the statutory elements are established.

(c) For the purposes of Secs. 261.2 and 261.6:

(1) A "spent material" is any material that has been used and as a result of contamination can no longer serve the purpose for which it was produced without processing;

(2) "Sludge" has the same meaning used in Sec. 260.10 of this chapter;

(3) A "by-product" is a material that is not one of the primary products of a production process and is not solely or separately produced by the production process. Examples are process residues such as slags or distillation column bottoms. The term does not include a co-product that is produced for the general public's use and is ordinarily used in the form it is produced by the process.

(4) A material is "reclaimed" if it is processed to recover a usable product, or if it is regenerated. Examples are recovery of lead values from spent batteries and regeneration of spent solvents.

(5) A material is "used or reused" if it is either:

(i) Employed as an ingredient (including use as an intermediate) in an industrial process to make a product (for example, distillation bottoms from one process used as feedstock in another process). However, a material will not satisfy this condition if distinct components of the material are recovered as separate end products (as when metals are recovered from metal-containing secondary materials); or

(ii) Employed in a particular function or application as an effective substitute for a commercial product (for example, spent pickle liquor used as phosphorous precipitant and sludge conditioner in wastewater treatment).

(6) "Scrap metal" is bits and pieces of metal parts (e.g.,) bars, turnings, rods, sheets, wire) or metal pieces that may be combined together with bolts or soldering (e.g., radiators, scrap automobiles, railroad box cars), which when worn or superfluous can be recycled.

(7) A material is "recycled" if it is used, reused, or reclaimed.

(8) A material is "accumulated speculatively" if it is accumulated before being recycled. A material is not accumulated speculatively, however, if the person accumulating it can show that the material is potentially recyclable and has a feasible means of being recycled; and that – during the calendar year (commencing on January 1) – the amount of material that is recycled, or transferred to a different site for recycling, equals at least 75 percent by weight or volume of the amount of that material accumulated at the beginning of the period. In calculating the percentage of turnover, the 75 percent requirement is to be applied to each material of the same type (e.g., slags from a single smelting process) that is recycled in the same way (i.e., from which the same material is recovered or that is used in the same way). Materials accumulating in units that would be exempt from regulation under Sec. 261.4(c) are not to be included in making the calculation. (Materials that are already defined as solid wastes also are not to be included in making the calculation.) Materials are no longer in this category once they are removed from accumulation for recycling, however.

(9) "Excluded scrap metal" is processed scrap metal, unprocessed home scrap metal, and unprocessed prompt scrap metal.

(10) "Processed scrap metal" is scrap metal which has been manually or physically altered to either separate it into distinct materials to enhance economic value or to improve the handling of materials. Processed scrap metal includes, but is not limited to scrap metal which has been baled, shredded, sheared, chopped, crushed, flattened, cut, melted, or separated by metal type (i.e., sorted), and, fines, drosses and related materials

which have been agglomerated. (Note: shredded circuit boards being sent for recycling are not considered processed scrap metal. They are covered under the exclusion from the definition of solid waste for shredded circuit boards being recycled (Sec. 261.4(a)(13)).

(11) "Home scrap metal" is scrap metal as generated by steel mills, foundries, and refineries such as turnings, cuttings, punchings, and borings.

(12) "Prompt scrap metal" is scrap metal as generated by the metal working/fabrication industries and includes such scrap metal as turnings, cuttings, punchings, and borings. Prompt scrap is also known as industrial or new scrap metal.

[45 FR 33119, May 19, 1980, as amended at 48 FR 14293, Apr. 1, 1983; 50 FR 663, Jan. 4, 1985; 51 FR 10174, Mar. 24, 1986; 51 FR 40636, Nov. 7, 1986; 62 FR 26018, May 12, 1997]

Solid Waste

[Code of Federal Regulations]
[Title 40, Volume 18, Parts 260 to 265]
[Revised as of July 1, 1999]
From the U.S. Government Printing Office via GPO Access
[CITE: 40CFR261.2]

Title 40 – Protection of Environment Agency (continued)

Part 261 – Identification and Listing of Hazardous Waste – Table of Contents

Subpart A – General

Sec. 261.2 Definition of solid waste.

(a)(1) A solid waste is any discarded material that is not excluded by Sec. 261.4(a) or that is not excluded by variance granted under Secs. 260.30 and 260.31.

(2) A discarded material is any material which is:

(i) Abandoned, as explained in paragraph (b) of this section; or

(ii) Recycled, as explained in paragraph (c) of this section; or

(iii) Considered inherently waste-like, as explained in paragraph (d) of this section; or

(iv) A military munition identified as a solid waste in 40 CFR 266.202.

(b) Materials are solid waste if they are abandoned by being:

(1) Disposed of; or

(2) Burned or incinerated; or

(3) Accumulated, stored, or treated (but not recycled) before or in lieu of being abandoned by being disposed of, burned, or incinerated.

(c) Materials are solid wastes if they are recycled – or accumulated, stored, or treated before recycling – as specified in paragraphs (c)(1) through (4) of this section.

(1) Used in a manner constituting disposal. (i) Materials noted with a "*" in Column 1 of Table 1 are solid wastes when they are:

(A) Applied to or placed on the land in a manner that constitutes disposal; or

(B) Used to produce products that are applied to or placed on the land or are otherwise contained in products that are applied to or placed on the land (in which cases the product itself remains a solid waste).

Table 1

	Use constituting disposal (Sec. 261.2(c)(1))	Energy recovery/fuel (Sec. 261.2(c)(2))	Reclamation (Sec. 261.2(c)(3)) (except as provided in 261.4(a)(17) for mineral processing secondary materials)	Speculative accumulation (Sec. 261.2(c)(4))
	1	*2*	*3*	*4*
Spent materials	(*)	(*)	(*)	(*)
Sludges (listed in 40 CFR Part 261.31 or 261.32...	(*)	(*)	(*)	(*)
Sludges exhibiting a characteristic of hazardous waste	(*)	(*)	–	(*)
By-products (listed in 40 CFR 261.31 or 261.32)...	(*)	(*)	(*)	(*)
By-products exhibiting a characteristic of hazardous waste	(*)	(*)	–	(*)
Commercial chemical products listed in 40 CFR 261.33...	(*)	(*)	–	–
Scrap metal other than excluded scrap metal (see 261.1(c)(9))...	(*)	(*)	(*)	(*)

Note: The terms "spent materials," "sludges," "by-products," and "scrap metal" and "processed scrap metal" are defined in Sec. 261.1.

(ii) However, commercial chemical products listed in Sec. 261.33 are not solid wastes if they are applied to the land and that is their ordinary manner of use.

(2) Burning for energy recovery. (i) Materials noted with a "*" in column 2 of Table 1 are solid wastes when they are:

(A) Burned to recover energy;

(B) Used to produce a fuel or are otherwise contained in fuels (in which cases the fuel itself remains a solid waste).

(ii) However, commercial chemical products listed in Sec. 261.33 are not solid wastes if they are themselves fuels.

(3) Reclaimed. Materials noted with a "*" in column 3 of Table 1 are solid wastes when reclaimed (except as provided under 40 CF R261.4(a)(17)). Materials noted with a "–" in column 3 of Table 1 are not solid wastes when reclaimed (except as provided under 40 CFR 261.4(a)(17)).

(4) Accumulated speculatively. Materials noted with a "*" in column 4 of Table 1 are solid wastes when accumulated speculatively.

(d) Inherently waste-like materials. The following materials are solid wastes when they are recycled in any manner:

(1) Hazardous Waste Nos. F020, F021 (unless used as an ingredient to make a product at the site of generation), F022, F023, F026, and F028.

(2) Secondary materials fed to a halogen acid furnace that exhibit a characteristic of a hazardous waste or are listed as a hazardous waste as defined in subparts C or D of this part, except for brominated material that meets the following criteria:

(i) The material must contain a bromine concentration of at least 45%; and

(ii) The material must contain less than a total of 1% of toxic organic compounds listed in Appendix VIII; and

(iii) The material is processed continually on-site in the halogen acid furnace via direct conveyance (hard piping).

(3) The Administrator will use the following criteria to add wastes to that list:

(i)(A) The materials are ordinarily disposed of, burned, or incinerated; or

(B) The materials contain toxic constituents listed in Appendix VIII of part 261 and these constituents are not ordinarily found in raw materials or products for which the materials substitute (or are found in raw materials or products in smaller concentrations) and are not used or reused during the recycling process; and

(ii) The material may pose a substantial hazard to human health and the environment when recycled.

(e) Materials that are not solid waste when recycled. (1) Materials are not solid wastes when they can be shown to be recycled by being:

(i) Used or reused as ingredients in an industrial process to make a product, provided the materials are not being reclaimed; or

(ii) Used or reused as effective substitutes for commercial products; or

(iii) Returned to the original process from which they are generated, without first being reclaimed or land disposed. The material must be returned as a substitute for feedstock materials. In cases where the original process to which the material is returned is a secondary process, the materials must be managed such that there is no placement on the land. In cases where the materials are generated and reclaimed within the primary mineral

processing industry, the conditions of the exclusion found at Sec. 261.4(a)(17) apply rather than this paragraph.

(2) The following materials are solid wastes, even if the recycling involves use, reuse, or return to the original process (described in paragraphs (e)(1) (i) through (iii) of this section):

(i) Materials used in a manner constituting disposal, or used to produce products that are applied to the land; or

(ii) Materials burned for energy recovery, used to produce a fuel, or contained in fuels; or

(iii) Materials accumulated speculatively; or

(iv) Materials listed in paragraphs (d)(1) and (d)(2) of this section.

(f) Documentation of claims that materials are not solid wastes or are conditionally exempt from regulation. Respondents in actions to enforce regulations implementing subtitle C of RCRA who raise a claim that a certain material is not a solid waste, or is conditionally exempt from regulation, must demonstrate that there is a known market or disposition for the material, and that they meet the terms of the exclusion or exemption. In doing so, they must provide appropriate documentation (such as contracts showing that a second person uses the material as an ingredient in a production process) to demonstrate that the material is not a waste, or is exempt from regulation. In addition, owners or operators of facilities claiming that they actually are recycling materials must show that they have the necessary equipment to do so.

[50 FR 664, Jan. 4, 1985, as amended at 50 FR 33542, Aug. 20, 1985; 56 FR 7206, Feb. 21, 1991; 56 FR 32688, July 17, 1991; 56 FR 42512, Aug. 27, 1991; 57 FR 38564, Aug. 25, 1992; 59 FR 48042, Sept. 19, 1994; 62 FR 6651, Feb. 12, 1997; 62 FR 26019, May 12, 1997; 63 FR 28636, May 26, 1998; 64 FR 24513, May 11, 1999]

Hazardous Waste

[Code of Federal Regulations]
[Title 40, Volume 18, Parts 260 to 265]
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Title 40 – Protection of Environment Agency (continued)

Part 261 – Identification and Listing of Hazardous Waste – Table of Contents

Subpart A – General

Sec. 261.3 Definition of hazardous waste.

(a) A solid waste, as defined in Sec. 261.2, is a hazardous waste if:

(1) It is not excluded from regulation as a hazardous waste under Sec. 261.4(b); and

(2) It meets any of the following criteria:

(i) It exhibits any of the characteristics of hazardous waste identified in subpart C of this part. However, any mixture of a waste from the extraction, beneficiation, and processing of ores and minerals excluded under Sec. 261.4(b)(7) and any other solid

waste exhibiting a characteristic of hazardous waste under subpart C is a hazardous waste only if it exhibits a characteristic that would not have been exhibited by the excluded waste alone if such mixture had not occurred, or if it continues to exhibit any of the characteristics exhibited by the non-excluded wastes prior to mixture. Further, for the purposes of applying the Toxicity Characteristic to such mixtures, the mixture is also a hazardous waste if it exceeds the maximum concentration for any contaminant listed in table I to Sec. 261.24 that would not have been exceeded by the excluded waste alone if the mixture had not occurred or if it continues to exceed the maximum concentration for any contaminant exceeded by the nonexempt waste prior to mixture.

(ii) It is listed in subpart D of this part and has not been excluded from the lists in subpart D of this part under Secs. 260.20 and 260.22 of this chapter.

(iii) It is a mixture of a solid waste and a hazardous waste that is listed in subpart D of this part solely because it exhibits one or more of the characteristics of hazardous waste identified in subpart C of this part, unless the resultant mixture no longer exhibits any characteristic of hazardous waste identified in subpart C of this part, or unless the solid waste is excluded from regulation under Sec. 261.4(b)(7) and the resultant mixture no longer exhibits any characteristic of hazardous waste identified in subpart C of this part for which the hazardous waste listed in subpart D of this part was listed. (However, nonwastewater mixtures are still subject to the requirements of part 268 of this chapter, even if they no longer exhibit a characteristic at the point of land disposal.)

(iv) It is a mixture of solid waste and one or more hazardous wastes listed in subpart D of this part and has not been excluded from paragraph (a)(2) of this section under Secs. 260.20 and 260.22 of this chapter; however, the following mixtures of solid wastes and hazardous wastes listed in subpart D of this part are not hazardous wastes (except by application of paragraph (a)(2) (i) or (ii) of this section) if the generator can demonstrate that the mixture consists of wastewater the discharge of which is subject to regulation under either section 402 or section 307(b) of the Clean Water Act (including wastewater at facilities which have eliminated the discharge of wastewater) and:

(A) One or more of the following solvents listed in Sec. 261.31 – carbon tetrachloride, tetrachloroethylene, trichloroethylene – provided, that the maximum total weekly usage of these solvents (other than the amounts that can be demonstrated not to be discharged to wastewater) divided by the average weekly flow of wastewater into the headworks of the facility's wastewater treatment or pre-treatment system does not exceed 1 part per million; or

(B) One or more of the following spent solvents listed in Sec. 261.31 – methylene chloride, 1,1,1-trichloroethane, chlorobenzene, o-dichlorobenzene, cresols, cresylic acid, nitrobenzene, toluene, methyl ethyl ketone, carbon disulfide, isobutanol, pyridine, spent chlorofluorocarbon solvents – provided that the maximum total weekly usage of these solvents (other than the amounts that can be demonstrated not to be discharged to wastewater) divided by the average weekly flow of wastewater into the headworks of the facility's wastewater treatment or pre-treatment system does not exceed 25 parts per million; or

(C) One of the following wastes listed in Sec. 261.32, provided that the wastes are discharged to the refinery oil recovery sewer before primary oil/water/solids separation – heat exchanger bundle cleaning sludge from the petroleum refining industry (EPA Hazardous Waste No. K050), crude oil storage tank sediment from petroleum refining operations (EPA Hazardous Waste No. K169), clarified slurry oil tank sediment and/or in-line filter/separation solids from petroleum refining operations (EPA Hazardous Waste No. K170), spent hydrotreating catalyst (EPA Hazardous Waste No. K171), and spent hydrorefining catalyst (EPA Hazardous Waste No. K172); or

(D) A discarded commercial chemical product, or chemical intermediate listed in Sec. 261.33, arising from de minimis losses of these materials from manufacturing operations in which these materials are used as raw materials or are produced in the manufacturing process. For purposes of this paragraph (a)(2)(iv)(D), "de minimis" losses include those from normal material handling operations (e.g., spills from the unloading or transfer of materials from bins or other containers, leaks from pipes, valves or other devices used to transfer materials); minor leaks of process equipment, storage tanks or containers; leaks from well maintained pump packings and seals; sample purgings; relief device discharges; discharges from safety showers and rinsing and cleaning of personal safety equipment; and reinstate from empty containers or from containers that are rendered empty by that rinsing; or

(E) Wastewater resulting from laboratory operations containing toxic (T) wastes listed in subpart D of this part, Provided, That the annualized average flow of laboratory wastewater does not exceed one percent of total wastewater flow into the headworks of the facility's wastewater treatment or pre-treatment system or provided the wastes, combined annualized average concentration does not exceed one part per million in the headworks of the facility's wastewater treatment or pre-treatment facility. Toxic (T) wastes used in laboratories that are demonstrated not to be discharged to wastewater are not to be included in this calculation; or

(F) One or more of the following wastes listed in Sec. 261.32 – wastewaters from the production of carbamates and carbamoyl oximes (EPA Hazardous Waste No. K157) – Provided that the maximum weekly usage of formaldehyde, methyl chloride, methylene chloride, and triethylamine (including all amounts that can not be demonstrated to be reacted in the process, destroyed through treatment, or is recovered, i.e., what is discharged or volatilized) divided by the average weekly flow of process wastewater prior to any dilutions into the headworks of the facility's wastewater treatment system does not exceed a total of 5 parts per million by weight; or

(G) Wastewaters derived from the treatment of one or more of the following wastes listed in Sec. 261.32 – organic waste (including heavy ends, still bottoms, light ends, spent solvents, filtrates, and decantates) from the production of carbamates and carbamoyl oximes (EPA Hazardous Waste No. K156) – Provided, that the maximum concentration of formaldehyde, methyl chloride, methylene chloride, and triethylamine prior to any dilutions into the headworks of the facility's wastewater treatment system does not exceed a total of 5 milligrams per liter.

(v) Rebuttable presumption for used oil. Used oil containing more than 1000 ppm total halogens is presumed to be a hazardous waste because it has been mixed with halogenated hazardous waste listed in subpart D of part 261 of this chapter. Persons may rebut this presumption by demonstrating that the used oil does not contain hazardous waste

(for example, by using an analytical method from SW-846, Third Edition, to show that the used oil does not contain significant concentrations of halogenated hazardous constituents listed in Appendix VIII of part 261 of this chapter). EPA Publication SW-846, Third Edition, is available for the cost of $110.00 from the Government Printing Office, Superintendent of Documents, PO Box 371954, Pittsburgh, PA 15250-7954. 202-512-1800 (document number 955-001-00000-1).

(A) The rebuttable presumption does not apply to metalworking oils/fluids containing chlorinated paraffins, if they are processed, through a tolling agreement, to reclaim metalworking oils/fluids. The presumption does apply to metalworking oils/fluids if such oils/fluids are recycled in any other manner, or disposed.

(B) The rebuttable presumption does not apply to used oils contaminated with chlorofluorocarbons (CFCs) removed from refrigeration units where the CFCs are destined for reclamation. The rebuttable presumption does apply to used oils contaminated with CFCs that have been mixed with used oil from sources other than refrigeration units.

(b) A solid waste which is not excluded from regulation under paragraph (a)(1) of this section becomes a hazardous waste when any of the following events occur:

(1) In the case of a waste listed in subpart D of this part, when the waste first meets the listing description set forth in subpart D of this part.

(2) In the case of a mixture of solid waste and one or more listed hazardous wastes, when a hazardous waste listed in subpart D is first added to the solid waste.

(3) In the case of any other waste (including a waste mixture), when the waste exhibits any of the characteristics identified in subpart C of this part.

(c) Unless and until it meets the criteria of paragraph (d) of this section:

(1) A hazardous waste will remain a hazardous waste.

(2)(i) Except as otherwise provided in paragraph (c)(2)(ii) of this section, any solid waste generated from the treatment, storage, or disposal of a hazardous waste, including any sludge, spill residue, ash, emission control dust, or leachate (but not including precipitation run-off) is a hazardous waste. (However, materials that are reclaimed from solid wastes and that are used beneficially are not solid wastes and hence are not hazardous wastes under this provision unless the reclaimed material is burned for energy recovery or used in a manner constituting disposal.)

(ii) The following solid wastes are not hazardous even though they are generated from the treatment, storage, or disposal of a hazardous waste, unless they exhibit one or more of the characteristics of hazardous waste:

(A) Waste pickle liquor sludge generated by lime stabilization of spent pickle liquor from the iron and steel industry (SIC Codes 331 and 332).

(B) Waste from burning any of the materials exempted from regulation by Sec. 261.6(a)(3)(iii) and (iv).

(C)(1) Nonwastewater residues, such as slag, resulting from high temperature metals recovery (HTMR) processing of K061, K062 or F006 waste, in units identified as rotary kilns, flame reactors, electric furnaces, plasma arc furnaces, slag reactors, rotary hearth furnace/electric furnace combinations or industrial furnaces (as defined in paragraphs (6), (7), and (13) of the definition for "Industrial furnace" in 40 CFR 260.10), that are disposed in subtitle D units, provided that these residues meet the generic exclusion levels identified in the tables in this paragraph for all constituents,

and exhibit no characteristics of hazardous waste. Testing requirements must be incorporated in a facility's waste analysis plan or a generator's self-implementing waste analysis plan; at a minimum, composite samples of residues must be collected and analyzed quarterly and/or when the process or operation generating the waste changes. Persons claiming this exclusion in an enforcement action will have the burden of proving by clear and convincing evidence that the material meets all of the exclusion requirements.

Constituent	Maximum for any single composite sample – TCLP (mg/l)
Generic exclusion levels for K061 and K062 non-wastewater HTMR residues	
Antimony...	0.10
Arsenic...	0.50
Barium...	7.6
Beryllium...	0.010
Cadmium...	0.050
Chromium (total)...	0.33
Lead...	0.15
Mercury...	0.009
Nickel...	1.0
Selenium...	0.16
Silver...	0.30
Thallium...	0.020
Zinc...	70
Generic exclusion levels for F006 non-wastewater HTMR residues	
Antimony...	0.10
Arsenic...	0.50
Barium...	7.6
Beryllium...	0.010
Cadmium...	0.050
Chromium (total)...	0.33
Cyanide (total) (mg/kg)...	1.8
Lead...	0.15
Mercury...	0.009
Nickel...	1.0
Selenium...	0.16
Silver...	0.30
Thallium...	0.020
Zinc...	70

(2) A one-time notification and certification must be placed in the facility's files and sent to the EPA region or authorized state for K061, K062 or F006 HTMR residues that meet the generic exclusion levels for all constituents and do not exhibit any characteristics that are sent to subtitle D units. The notification and certification that is placed in the

generators or treaters files must be updated if the process or operation generating the waste changes and/or if the subtitle D unit receiving the waste changes. However, the generator or treater need only notify the EPA region or an authorized state on an annual basis if such changes occur. Such notification and certification should be sent to the EPA region or authorized state by the end of the calendar year, but no later than December 31. The notification must include the following information: The name and address of the subtitle D unit receiving the waste shipments; the EPA Hazardous Waste Number(s) and treatability group(s) at the initial point of generation; and, the treatment standards applicable to the waste at the initial point of generation. The certification must be signed by an authorized representative and must state as follows: "I certify under penalty of law that the generic exclusion levels for all constituents have been met without impermissible dilution and that no characteristic of hazardous waste is exhibited. I am aware that there are significant penalties for submitting a false certification, including the possibility of fine and imprisonment."

(D) Biological treatment sludge from the treatment of one of the following wastes listed in Sec. 261.32 – organic waste (including heavy ends, still bottoms, light ends, spent solvents, filtrates, and decantates) from the production of carbamates and carbamoyl oximes (EPA Hazardous Waste No. K156), and wastewaters from the production of carbamates and carbamoyl oximes (EPA Hazardous Waste No. K157).

(E) Catalyst inert support media separated from one of the following wastes listed in Sec. 261.32 – Spent hydrotreating catalyst (EPA Hazardous Waste No. K171), and Spent hydrorefining catalyst (EPA Hazardous Waste No. K172).

(d) Any solid waste described in paragraph (c) of this section is not a hazardous waste if it meets the following criteria:

(1) In the case of any solid waste, it does not exhibit any of the characteristics of hazardous waste identified in subpart C of this part. (However, wastes that exhibit a characteristic at the point of generation may still be subject to the requirements of part 268, even if they no longer exhibit a characteristic at the point of land disposal.)

(2) In the case of a waste which is a listed waste under subpart D of this part, contains a waste listed under subpart D of this part or is derived from a waste listed in subpart D of this part, it also has been excluded from paragraph (c) of this section under Secs. 260.20 and 260.22 of this chapter.

(e) [Reserved]

(f) Notwithstanding paragraphs (a) through (d) of this section and provided the debris as defined in part 268 of this chapter does not exhibit a characteristic identified at subpart C of this part, the following materials are not subject to regulation under 40 CFR parts 260, 261 to 266, 268, or 270:

(1) Hazardous debris as defined in part 268 of this chapter that has been treated using one of the required extraction or destruction technologies specified in Table 1 of Sec. 268.45 of this chapter; persons claiming this exclusion in an enforcement action will have the burden of proving by clear and convincing evidence that the material meets all of the exclusion requirements; or

(2) Debris as defined in part 268 of this chapter that the Regional Administrator, considering the extent of contamination, has determined is no longer contaminated with hazardous waste.

[57 FR 7632, Mar. 3, 1992; 57 FR 23063, June 1, 1992, as amended at 57 FR 37263, Aug. 18, 1992; 57 FR 41611, Sept. 10, 1992; 57 FR 49279, Oct. 30, 1992; 59 FR 38545, July 28, 1994; 60 FR 7848, Feb. 9, 1995; 63 FR 28637, May 26, 1998; 63 FR 42184, Aug. 6, 1998]

Exclusions

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Title 40 – Protection of Environment Agency (continued)

Part 261 – Identification and Listing of Hazardous Waste – Table of Contents

Subpart A – General

Sec. 261.4 Exclusions.

(a) Materials which are not solid wastes. The following materials are not solid wastes for the purpose of this part:

(1)(i) Domestic sewage; and

(ii) Any mixture of domestic sewage and other wastes that passes through a sewer system to a publicly-owned treatment works for treatment. "Domestic sewage" means untreated sanitary wastes that pass through a sewer system.

(2) Industrial wastewater discharges that are point source discharges subject to regulation under section 402 of the Clean Water Act, as amended. [Comment: This exclusion applies only to the actual point source discharge. It does not exclude industrial wastewaters while they are being collected, stored or treated before discharge, nor does it exclude sludges that are generated by industrial wastewater treatment.]

(3) Irrigation return flows.

(4) Source, special nuclear or by-product material as defined by the Atomic Energy Act of 1954, as amended, 42 U.S.C. 2011 et seq.

(5) Materials subjected to in-situ mining techniques, which are not removed from the ground as part of the extraction process.

(6) Pulping liquors (i.e., black liquor) that are reclaimed in a pulping liquor recovery furnace and then reused in the pulping process, unless it is accumulated speculatively as defined in Sec. 261.1(c) of this chapter.

(7) Spent sulfuric acid used to produce virgin sulfuric acid, unless it is accumulated speculatively as defined in Sec. 261.1(c) of this chapter.

(8) Secondary materials that are reclaimed and returned to the original process or processes in which they were generated where they are reused in the production process provided:

(i) Only tank storage is involved, and the entire process through completion of reclamation is closed by being entirely connected with pipes or other comparable enclosed means of conveyance;

(ii) Reclamation does not involve controlled flame combustion (such as occurs in boilers, industrial furnaces, or incinerators);

(iii) The secondary materials are never accumulated in such tanks for over twelve months without being reclaimed; and

(iv) The reclaimed material is not used to produce a fuel, or used to produce products that are used in a manner constituting disposal.

(9)(i) Spent wood preserving solutions that have been reclaimed and are reused for their original intended purpose; and

(ii) Wastewaters from the wood preserving process that have been reclaimed and are reused to treat wood.

(iii) Prior to reuse, the wood preserving wastewaters and spent wood preserving solutions described in paragraphs (a)(9)(i) and (a)(9)(ii) of this section, so long as they meet all of the following conditions:

(A) The wood preserving wastewaters and spent wood preserving solutions are reused on-site at water borne plants in the production process for their original intended purpose;

(B) Prior to reuse, the wastewaters and spent wood preserving solutions are managed to prevent release to either land or groundwater or both;

(C) Any unit used to manage wastewaters and/or spent wood preserving solutions prior to reuse can be visually or otherwise determined to prevent such releases;

(D) Any drip pad used to manage the wastewaters and/or spent wood preserving solutions prior to reuse complies with the standards in part 265, subpart W of this chapter, regardless of whether the plant generates a total of less than 100 kg/month of hazardous waste; and

(E) Prior to operating pursuant to this exclusion, the plant owner or operator submits to the appropriate Regional Administrator or State Director a one-time notification stating that the plant intends to claim the exclusion, giving the date on which the plant intends to begin operating under the exclusion, and containing the following language: "I have read the applicable regulation establishing an exclusion for wood preserving wastewaters and spent wood preserving solutions and understand it requires me to comply at all times with the conditions set out in the regulation." The plant must maintain a copy of that document in its on-site records for a period of no less than 3 years from the date specified in the notice. The exclusion applies only so long as the plant meets all of the conditions. If the plant goes out of compliance with any condition, it may apply to the appropriate Regional Administrator or State Director for reinstatement. The Regional Administrator or State Director may reinstate the exclusion upon finding that the plant has returned to compliance with all conditions and that violations are not likely to recur.

(10) EPA Hazardous Waste Nos. K060, K087, K141, K142, K143, K144, K145, K147, and K148, and any wastes from the coke by-products processes that are hazardous only because they exhibit the Toxicity Characteristic (TC) specified in section 261.24 of this part when, subsequent to generation, these materials are recycled to coke ovens, to the tar recovery process as a feedstock to produce coal tar, or mixed with coal tar prior to the tar's sale or refining. This exclusion is conditioned on there being no land disposal of the wastes from the point they are generated to the point they are recycled to coke ovens or tar recovery or refining processes, or mixed with coal tar.

(11) Nonwastewater splash condenser dross residue from the treatment of K061 in high temperature metals recovery units, provided it is shipped in drums (if shipped) and not land disposed before recovery.

(12)(i) Oil-bearing hazardous secondary materials (i.e., sludges, byproducts, or spent materials) that are generated at a petroleum refinery (SIC code 2911) and are inserted into the petroleum refining process (SIC code 2911 – including, but not limited to, distillation, catalytic cracking, fractionation, or thermal cracking units (i.e., cokers)) unless the material is placed on the land, or speculatively accumulated before being so recycled. Materials inserted into thermal cracking units are excluded under this paragraph, provided that the coke product also does not exhibit a characteristic of hazardous waste. Oil-bearing hazardous secondary materials may be inserted into the same petroleum refinery where they are generated, or sent directly to another petroleum refinery, and still be excluded under this provision. Except as provided in paragraph (a)(12)(ii) of this section, oil-bearing hazardous secondary materials generated elsewhere in the petroleum industry (i.e., from sources other than petroleum refineries) are not excluded under this section. Residuals generated from processing or recycling materials excluded under this paragraph (a)(12)(i), where such materials as generated would have otherwise met a listing under subpart D of this part, are designated as F037 listed wastes when disposed of or intended for disposal.

(ii) Recovered oil that is recycled in the same manner and with the same conditions as described in paragraph (a)(12)(i) of this section. Recovered oil is oil that has been reclaimed from secondary materials (including wastewater) generated from normal petroleum industry practices, including refining, exploration and production, bulk storage, and transportation incident thereto (SIC codes 1311, 1321, 1381, 1382, 1389, 2911, 4612, 4613, 4922, 4923, 4789, 5171, and 5172.) Recovered oil does not include oil-bearing hazardous wastes listed in subpart D of this part; however, oil recovered from such wastes may be considered recovered oil. Recovered oil does not include used oil as defined in 40 CFR 279.1.

(13) Excluded scrap metal (processed scrap metal, unprocessed home scrap metal, and unprocessed prompt scrap metal) being recycled.

(14) Shredded circuit boards being recycled provided that they are:

(i) Stored in containers sufficient to prevent a release to the environment prior to recovery; and

(ii) Free of mercury switches, mercury relays and nickel-cadmium batteries and lithium batteries.

(15) Condensates derived from the overhead gases from kraft mill steam strippers that are used to comply with 40 CFR 63.446(e). The exemption applies only to combustion at the mill generating the condensates.

(16) Comparable fuels or comparable syngas fuels (i.e., comparable/syngas fuels) that meet the requirements of Sec. 261.38.

(17) Secondary materials (i.e., sludges, by-products, and spent materials as defined in Sec. 261.1) (other than hazardous wastes listed in subpart D of this part) generated within the primary mineral processing industry from which minerals, acids, cyanide, water or other values are recovered by mineral processing or by beneficiation, provided that:

(i) The secondary material is legitimately recycled to recover minerals, acids, cyanide, water or other values;

(ii) The secondary material is not accumulated speculatively;

(iii) Except as provided in paragraph (a)(15)(iv) of this section, the secondary material is stored in tanks, containers, or buildings meeting the following minimum integrity standards: a building must be an engineered structure with a floor, walls, and

a roof all of which are made of non-earthen materials providing structural support (except smelter buildings may have partially earthen floors provided the secondary material is stored on the non-earthen portion), and have a roof suitable for diverting rainwater away from the foundation; a tank must be free standing, not be a surface impoundment (as defined in 40 CFR 260.10), and be manufactured of a material suitable for containment of its contents; a container must be free standing and be manufactured of a material suitable for containment of its contents. If tanks or containers contain any particulate which may be subject to wind dispersal, the owner/operator must operate these units in a manner which controls fugitive dust. Tanks, containers, and buildings must be designed, constructed and operated to prevent significant releases to the environment of these materials.

(iv) The Regional Administrator or the State Director may make a site-specific determination, after public review and comment, that only solid mineral processing secondary materials may be placed on pads, rather than in tanks, containers, or buildings. Solid mineral processing secondary materials do not contain any free liquid. The decision-maker must affirm that pads are designed, constructed and operated to prevent significant releases of the secondary material into the environment. Pads must provide the same degree of containment afforded by the non-RCRA tanks, containers and buildings eligible for exclusion.

(A) The decision-maker must also consider if storage on pads poses the potential for significant releases via groundwater, surface water, and air exposure pathways. Factors to be considered for assessing the groundwater, surface water, air exposure pathways are: the volume and physical and chemical properties of the secondary material, including its potential for migration off the pad; the potential for human or environmental exposure to hazardous constituents migrating from the pad via each exposure pathway, and the possibility and extent of harm to human and environmental receptors via each exposure pathway.

(B) Pads must meet the following minimum standards: be designed of non-earthen material that is compatible with the chemical nature of the mineral processing secondary material, capable of withstanding physical stresses associated with placement and removal, have run on/runoff controls, be operated in a manner which controls fugitive dust, and have integrity assurance through inspections and maintenance programs.

(C) Before making a determination under this paragraph, the Regional Administrator or State Director must provide notice and the opportunity for comment to all persons potentially interested in the determination. This can be accomplished by placing notice of this action in major local newspapers, or broadcasting notice over local radio stations.

(v) The owner or operator provides a notice to the Regional Administrator or State Director, identifying the following information: the types of materials to be recycled; the type and location of the storage units and recycling processes; and the annual quantities expected to be placed in non land-based units. This notification must be updated when there is a change in the type of materials recycled or the location of the recycling process.

(vi) For purposes of Sec. 261.4(b)(7), mineral processing secondary materials must be the result of mineral processing and may not include any listed hazardous wastes. Listed hazardous wastes and characteristic hazardous wastes generated by non-mineral processing industries are not eligible for the conditional exclusion from the definition of solid waste.

(18) Petrochemical recovered oil from an associated organic chemical manufacturing facility, where the oil is to be inserted into the petroleum refining process (SIC code 2911) along with normal petroleum refinery process streams, provided:

(i) The oil is hazardous only because it exhibits the characteristic of ignitability (as defined in Sec. 261.21) and/or toxicity for benzene (Sec. 261.24, waste code D018); and

(ii) The oil generated by the organic chemical manufacturing facility is not placed on the land, or speculatively accumulated before being recycled into the petroleum refining process. An "associated organic chemical manufacturing facility" is a facility where the primary SIC code is 2869, but where operations may also include SIC codes 2821, 2822, and 2865; and is physically co-located with a petroleum refinery; and where the petroleum refinery to which the oil being recycled is returned also provides hydrocarbon feedstocks to the organic chemical manufacturing facility. "Petrochemical recovered oil" is oil that has been reclaimed from secondary materials (i.e., sludges, byproducts, or spent materials, including wastewater) from normal organic chemical manufacturing operations, as well as oil recovered from organic chemical manufacturing processes.

(19) Spent caustic solutions from petroleum refining liquid treating processes used as a feedstock to produce cresylic or naphthenic acid unless the material is placed on the land, or accumulated speculatively as defined in Sec. 261.1(c).

(b) Solid wastes which are not hazardous wastes. The following solid wastes are not hazardous wastes:

(1) Household waste, including household waste that has been collected, transported, stored, treated, disposed, recovered (e.g., refuse-derived fuel) or reused. "Household waste" means any material (including garbage, trash and sanitary wastes in septic tanks) derived from households (including single and multiple residences, hotels and motels, bunkhouses, ranger stations, crew quarters, campgrounds, picnic grounds and day-use recreation areas). A resource recovery facility managing MSW shall not be deemed to be treating, storing, disposing of, or otherwise managing hazardous wastes for the purposes of regulation under this subtitle, if such facility:

(i) Receives and burns only

(A) Household waste (from single and multiple dwellings, hotels, motels, and other residential sources) and

(B) Solid waste from commercial or industrial sources that does not contain hazardous waste; and

(ii) Such facility does not accept hazardous wastes and the owner or operator of such facility has established contractual requirements or other appropriate notification or inspection procedures to assure that hazardous wastes are not received at or burned in such facility.

(2) Solid wastes generated by any of the following and which are returned to the soils as fertilizers:

(i) The growing and harvesting of agricultural crops.

(ii) The raising of animals, including animal manures.

(3) Mining overburden returned to the mine site.

(4) Fly ash waste, bottom ash waste, slag waste, and flue gas emission control waste, generated primarily from the combustion of coal or other fossil fuels, except as provided by Sec. 266.112 of this chapter for facilities that burn or process hazardous waste.

(5) Drilling fluids, produced waters, and other wastes associated with the exploration, development, or production of crude oil, natural gas or geothermal energy.

(6)(i) Wastes which fail the test for the Toxicity Characteristic because chromium is present or are listed in subpart D due to the presence of chromium, which do not fail the test for the Toxicity Characteristic for any other constituent or are not listed due to the presence of any other constituent, and which do not fail the test for any other characteristic, if it is shown by a waste generator or by waste generators that:

(A) The chromium in the waste is exclusively (or nearly exclusively) trivalent chromium; and

(B) The waste is generated from an industrial process which uses trivalent chromium exclusively (or nearly exclusively) and the process does not generate hexavalent chromium; and

(C) The waste is typically and frequently managed in non-oxidizing environments.

(ii) Specific waste which meet the standard in paragraphs (b)(6)(i) (A), (B), and (C) (so long as they do not fail the test for the toxicity characteristic for any other constituent, and do not exhibit any other characteristic) are:

(A) Chrome (blue) trimmings generated by the following subcategories of the leather tanning and finishing industry; hair pulp/chrome tan/retan/wet finish; hair save/chrome tan/retan/wet finish; retan/wet finish; no beamhouse; through-the-blue; and shearling.

(B) Chrome (blue) shavings generated by the following subcategories of the leather tanning and finishing industry: Hair pulp/chrome tan/retan/wet finish; hair save/chrome tan/retan/wet finish; retan/wet finish; no beamhouse; through-the-blue; and shearling.

(C) Buffing dust generated by the following subcategories of the leather tanning and finishing industry; hair pulp/chrome tan/retan/wet finish; hair save/chrome tan/retan/wet finish; retan/wet finish; no beamhouse; through-the-blue.

(D) Sewer screenings generated by the following subcategories of the leather tanning and finishing industry: Hair pulp/crome tan/retan/wet finish; hair save/chrome tan/retan/wet finish; retan/wet finish; no beamhouse; through-the-blue; and shearling.

(E) Wastewater treatment sludges generated by the following subcategories of the leather tanning and finishing industry: Hair pulp/chrome tan/retan/wet finish; hair save/chrome tan/retan/wet finish; retan/wet finish; no beamhouse; through-the-blue; and shearling.

(F) Wastewater treatment sludges generated by the following subcategories of the leather tanning and finishing industry: Hair pulp/chrome tan/retan/wet finish; hair save/chrometan/retan/wet finish; and through-the-blue.

(G) Waste scrap leather from the leather tanning industry, the shoe manufacturing industry, and other leather product manufacturing industries.

(H) Wastewater treatment sludges from the production of TiO_2 pigment using chromium-bearing ores by the chloride process.

(7) Solid waste from the extraction, beneficiation, and processing of ores and minerals (including coal, phosphate rock, and overburden from the mining of uranium ore), except as provided by Sec. 266.112 of this chapter for facilities that burn or process hazardous waste.

(i) For purposes of Sec. 261.4(b)(7) beneficiation of ores and minerals is restricted to the following activities; crushing; grinding; washing; dissolution; crystallization;

filtration; sorting; sizing; drying; sintering; pelletizing; briquetting; calcining to remove water and/or carbon dioxide; roasting, autoclaving, and/or chlorination in preparation for leaching (except where the roasting (and/or autoclaving and/or chlorination)/leaching sequence produces a final or intermediate product that does not undergo further beneficiation or processing); gravity concentration; magnetic separation; electrostatic separation; flotation; ion exchange; solvent extraction; electrowinning; precipitation; amalgamation; and heap, dump, vat, tank, and in situ leaching.

(ii) For the purposes of Sec. 261.4(b)(7), solid waste from the processing of ores and minerals includes only the following wastes as generated:

(A) Slag from primary copper processing;

(B) Slag from primary lead processing;

(C) Red and brown muds from bauxite refining;

(D) Phosphogypsum from phosphoric acid production;

(E) Slag from elemental phosphorus production;

(F) Gasifier ash from coal gasification;

(G) Process wastewater from coal gasification;

(H) Calcium sulfate wastewater treatment plant sludge from primary copper processing;

(I) Slag tailings from primary copper processing;

(J) Fluorogypsum from hydrofluoric acid production;

(K) Process wastewater from hydrofluoric acid production;

(L) Air pollution control dust/sludge from iron blast furnaces;

(M) Iron blast furnace slag;

(N) Treated residue from roasting/leaching of chrome ore;

(O) Process wastewater from primary magnesium processing by the anhydrous process;

(P) Process wastewater from phosphoric acid production;

(Q) Basic oxygen furnace and open hearth furnace air pollution control dust/sludge from carbon steel production;

(R) Basic oxygen furnace and open hearth furnace slag from carbon steel production;

(S) Chloride process waste solids from titanium tetrachloride production;

(T) Slag from primary zinc processing.

(iii) A residue derived from co-processing mineral processing secondary materials with normal beneficiation raw materials or with normal mineral processing raw materials remains excluded under paragraph (b) of this section if the owner or operator:

(A) Processes at least 50 percent by weight normal beneficiation raw materials or normal mineral processing raw materials; and,

(B) Legitimately reclaims the secondary mineral processing materials.

(8) Cement kiln dust waste, except as provided by Sec. 266.112 of this chapter for facilities that burn or process hazardous waste.

(9) Solid waste which consists of discarded arsenical-treated wood or wood products which fails the test for the Toxicity Characteristic for Hazardous Waste Codes D004 through D017 and which is not a hazardous waste for any other reason if the waste is generated by persons who utilize the arsenical-treated wood and wood product for these materials' intended end use.

(10) Petroleum-contaminated media and debris that fail the test for the Toxicity Characteristic of Sec. 261.24 (Hazardous Waste Codes D018 through D043 only) and are subject to the corrective action regulations under part 280 of this chapter.

(11) Injected groundwater that is hazardous only because it exhibits the Toxicity Characteristic (Hazardous Waste Codes D018 through D043 only) in Sec. 261.24 of this part that is reinjected through an underground injection well pursuant to free phase hydrocarbon recovery operations undertaken at petroleum refineries, petroleum marketing terminals, petroleum bulk plants, petroleum pipelines, and petroleum transportation spill sites until January 25, 1993. This extension applies to recovery operations in existence, or for which contracts have been issued, on or before March 25, 1991. For groundwater returned through infiltration galleries from such operations at petroleum refineries, marketing terminals, and bulk plants, until [insert date six months after publication]. New operations involving injection wells (beginning after March 25, 1991) will qualify for this compliance date extension (until January 25, 1993) only if:

(i) Operations are performed pursuant to a written state agreement that includes a provision to assess the groundwater and the need for further remediation once the free phase recovery is completed; and

(ii) A copy of the written agreement has been submitted to: Characteristics Section (OS-333), U.S. Environmental Protection Agency, 401 M Street, SW., Washington, DC 20460.

(12) Used chlorofluorocarbon refrigerants from totally enclosed heat transfer equipment, including mobile air conditioning systems, mobile refrigeration, and commercial and industrial air conditioning and refrigeration systems that use chlorofluorocarbons as the heat transfer fluid in a refrigeration cycle, provided the refrigerant is reclaimed for further use.

(13) Non-terne plated used oil filters that are not mixed with wastes listed in subpart D of this part if these oil filters have been gravity hot-drained using one of the following methods:

(i) Puncturing the filter anti-drain back valve or the filter dome end and hot-draining;

(ii) Hot-draining and crushing;

(iii) Dismantling and hot-draining; or

(iv) Any other equivalent hot-draining method that will remove used oil.

(14) Used oil re-refining distillation bottoms that are used as feedstock to manufacture asphalt products.

(15) Leachate or gas condensate collected from landfills where certain solid wastes have been disposed, provided that:

(i) The solid wastes disposed would meet one or more of the listing descriptions for Hazardous Waste Codes K169, K170, K171, and K172 if these wastes had been generated after the effective date of the listing (February 8, 1999);

(ii) The solid wastes described in paragraph (b)(15)(i) of this section were disposed prior to the effective date of the listing;

(iii) The leachate or gas condensate do not exhibit any characteristic of hazardous waste nor are derived from any other listed hazardous waste;

(iv) Discharge of the leachate or gas condensate, including leachate or gas condensate transferred from the landfill to a POTW by truck, rail, or dedicated pipe, is subject to regulation under sections 307(b) or 402 of the Clean Water Act.

(v) After February 13, 2001, leachate or gas condensate will no longer be exempt if it is stored or managed in a surface impoundment prior to discharge. There is one exception: if the surface impoundment is used to temporarily store leachate or gas condensate in response to an emergency situation (e.g., shutdown of wastewater treatment system), provided the impoundment has a double liner, and provided the leachate or gas condensate is removed from the impoundment and continues to be managed in compliance with the conditions of this paragraph after the emergency ends.

(c) Hazardous wastes which are exempted from certain regulations. A hazardous waste which is generated in a product or raw material storage tank, a product or raw material transport vehicle or vessel, a product or raw material pipeline, or in a manufacturing process unit or an associated non-waste-treatment-manufacturing unit, is not subject to regulation under parts 262 through 265, 268, 270, 271 and 124 of this chapter or to the notification requirements of section 3010 of RCRA until it exits the unit in which it was generated, unless the unit is a surface impoundment, or unless the hazardous waste remains in the unit more than 90 days after the unit ceases to be operated for manufacturing, or for storage or transportation of product or raw materials.

(d) Samples. (1) Except as provided in paragraph (d)(2) of this section, a sample of solid waste or a sample of water, soil, or air, which is collected for the sole purpose of testing to determine its characteristics or composition, is not subject to any requirements of this part or parts 262 through 268 or part 270 or part 124 of this chapter or to the notification requirements of section 3010 of RCRA, when:

(i) The sample is being transported to a laboratory for the purpose of testing; or

(ii) The sample is being transported back to the sample collector after testing; or

(iii) The sample is being stored by the sample collector before transport to a laboratory for testing; or

(iv) The sample is being stored in a laboratory before testing; or

(v) The sample is being stored in a laboratory after testing but before it is returned to the sample collector; or

(vi) The sample is being stored temporarily in the laboratory after testing for a specific purpose (for example, until conclusion of a court case or enforcement action where further testing of the sample may be necessary).

(2) In order to qualify for the exemption in paragraphs (d)(1) (i) and (ii) of this section, a sample collector shipping samples to a laboratory and a laboratory returning samples to a sample collector must:

(i) Comply with U.S. Department of Transportation (DOT), U.S. Postal Service (USPS), or any other applicable shipping requirements; or

(ii) Comply with the following requirements if the sample collector determines that DOT, USPS, or other shipping requirements do not apply to the shipment of the sample:

(A) Assure that the following information accompanies the sample:

(1) The sample collector's name, mailing address, and telephone number;

(2) The laboratory's name, mailing address, and telephone number;

(3) The quantity of the sample;

(4) The date of shipment; and

(5) A description of the sample.

(B) Package the sample so that it does not leak, spill, or vaporize from its packaging.

(3) This exemption does not apply if the laboratory determines that the waste is hazardous but the laboratory is no longer meeting any of the conditions stated in paragraph (d)(1) of this section.

(e) Treatability Study Samples. (1) Except as provided in paragraph (e)(2) of this section, persons who generate or collect samples for the purpose of conducting treatability studies as defined in section 260.10, are not subject to any requirement of parts 261 through 263 of this chapter or to the notification requirements of Section 3010 of RCRA, nor are such samples included in the quantity determinations of Sec. 261.5 and Sec. 262.34(d) when:

(i) The sample is being collected and prepared for transportation by the generator or sample collector; or

(ii) The sample is being accumulated or stored by the generator or sample collector prior to transportation to a laboratory or testing facility; or

(iii) The sample is being transported to the laboratory or testing facility for the purpose of conducting a treatability study.

(2) The exemption in paragraph (e)(1) of this section is applicable to samples of hazardous waste being collected and shipped for the purpose of conducting treatability studies provided that:

(i) The generator or sample collector uses (in "treatability studies") no more than 10,000 kg of media contaminated with non-acute hazardous waste, 1000 kg of non-acute hazardous waste other than contaminated media, 1 kg of acute hazardous waste, 2500 kg of media contaminated with acute hazardous waste for each process being evaluated for each generated waste stream; and

(ii) The mass of each sample shipment does not exceed 10,000 kg; the 10,000 kg quantity may be all media contaminated with non-acute hazardous waste, or may include 2500 kg of media contaminated with acute hazardous waste, 1000 kg of hazardous waste, and 1 kg of acute hazardous waste; and

(iii) The sample must be packaged so that it will not leak, spill, or vaporize from its packaging during shipment and the requirements of paragraph A or B of this subparagraph are met.

(A) The transportation of each sample shipment complies with U.S. Department of Transportation (DOT), U.S. Postal Service (USPS), or any other applicable shipping requirements; or

(B) If the DOT, USPS, or other shipping requirements do not apply to the shipment of the sample, the following information must accompany the sample:

(1) The name, mailing address, and telephone number of the originator of the sample;

(2) The name, address, and telephone number of the facility that will perform the treatability study;

(3) The quantity of the sample;

(4) The date of shipment; and

(5) A description of the sample, including its EPA Hazardous Waste Number.

(iv) The sample is shipped to a laboratory or testing facility which is exempt under Sec. 261.4(f) or has an appropriate RCRA permit or interim status.

(v) The generator or sample collector maintains the following records for a period ending 3 years after completion of the treatability study:

(A) Copies of the shipping documents;

(B) A copy of the contract with the facility conducting the treatability study;

(C) Documentation showing:

(1) The amount of waste shipped under this exemption;

(2) The name, address, and EPA identification number of the laboratory or testing facility that received the waste;

(3) The date the shipment was made; and

(4) Whether or not unused samples and residues were returned to the generator.

(vi) The generator reports the information required under paragraph (e)(v)(C) of this section in its biennial report.

(3) The Regional Administrator may grant requests on a case-by-case basis for up to an additional two years for treatability studies involving bioremediation. The Regional Administrator may grant requests on a case-by-case basis for quantity limits in excess of those specified in paragraphs (e)(2) (i) and (ii) and (f)(4) of this section, for up to an additional 5000 kg of media contaminated with non-acute hazardous waste, 500 kg of non-acute hazardous waste, 2500 kg of media contaminated with acute hazardous waste and 1 kg of acute hazardous waste:

(i) In response to requests for authorization to ship, store and conduct treatability studies on additional quantities in advance of commencing treatability studies. Factors to be considered in reviewing such requests include the nature of the technology, the type of process (e.g., batch versus continuous), size of the unit undergoing testing (particularly in relation to scale-up considerations), the time/quantity of material required to reach steady state operating conditions, or test design considerations such as mass balance calculations.

(ii) In response to requests for authorization to ship, store and conduct treatability studies on additional quantities after initiation or completion of initial treatability studies, when: There has been an equipment or mechanical failure during the conduct of a treatability study; there is a need to verify the results of a previously conducted treatability study; there is a need to study and analyze alternative techniques within a previously evaluated treatment process; or there is a need to do further evaluation of an ongoing treatability study to determine final specifications for treatment.

(iii) The additional quantities and timeframes allowed in paragraph (e)(3) (i) and (ii) of this section are subject to all the provisions in paragraphs (e)(1) and (e)(2) (iii) through (vi) of this section. The generator or sample collector must apply to the Regional Administrator in the Region where the sample is collected and provide in writing the following information:

(A) The reason why the generator or sample collector requires additional time or quantity of sample for treatability study evaluation and the additional time or quantity needed;

(B) Documentation accounting for all samples of hazardous waste from the waste stream which have been sent for or undergone treatability studies including the date each previous sample from the waste stream was shipped, the quantity of each previous shipment, the laboratory or testing facility to which it was shipped, what treatability study processes were conducted on each sample shipped, and the available results on each treatability study;

(C) A description of the technical modifications or change in specifications which will be evaluated and the expected results;

(D) If such further study is being required due to equipment or mechanical failure, the applicant must include information regarding the reason for the failure or breakdown and also include what procedures or equipment improvements have been made to protect against further breakdowns; and

(E) Such other information that the Regional Administrator considers necessary.

(F) Samples Undergoing Treatability Studies at Laboratories and Testing Facilities. Samples undergoing treatability studies and the laboratory or testing facility conducting such treatability studies (to the extent such facilities are not otherwise subject to RCRA requirements) are not subject to any requirement of this part, part 124, parts 262-266, 268, and 270, or to the notification requirements of Section 3010 of RCRA provided that the conditions of paragraphs (f) (1) through (11) of this section are met. A mobile treatment unit (MTU) may qualify as a testing facility subject to paragraphs (f) (1) through (11) of this section. Where a group of MTUs are located at the same site, the limitations specified in (f) (1) through (11) of this section apply to the entire group of MTUs collectively as if the group were one MTU.

(1) No less than 45 days before conducting treatability studies, the facility notifies the Regional Administrator, or State Director (if located in an authorized State), in writing that it intends to conduct treatability studies under this paragraph.

(2) The laboratory or testing facility conducting the treatability study has an EPA identification number.

(3) No more than a total of 10,000 kg of "as received" media contaminated with non-acute hazardous waste, 2500 kg of media contaminated with acute hazardous waste or 250 kg of other "as received" hazardous waste is subject to initiation of treatment in all treatability studies in any single day.

"As received" waste refers to the waste as received in the shipment from the generator or sample collector.

(4) The quantity of "as received" hazardous waste stored at the facility for the purpose of evaluation in treatability studies does not exceed 10,000 kg, the total of which can include 10,000 kg of media contaminated with non-acute hazardous waste, 2500 kg of media contaminated with acute hazardous waste, 1000 kg of non-acute hazardous wastes other than contaminated media, and 1 kg of acute hazardous waste. This quantity limitation does not include treatment materials (including nonhazardous solid waste) added to "as received" hazardous waste.

(5) No more than 90 days have elapsed since the treatability study for the sample was completed, or no more than one year (two years for treatability studies involving bioremediation) have elapsed since the generator or sample collector shipped the sample to the laboratory or testing facility, whichever date first occurs. Up to 500 kg of treated material from a particular waste stream from treatability studies may be archived for future evaluation up to five years from the date of initial receipt. Quantities of materials archived are counted against the total storage limit for the facility.

(6) The treatability study does not involve the placement of hazardous waste on the land or open burning of hazardous waste.

(7) The facility maintains records for 3 years following completion of each study that show compliance with the treatment rate limits and the storage time and quantity limits. The following specific information must be included for each treatability study conducted:

(i) The name, address, and EPA identification number of the generator or sample collector of each waste sample;

(ii) The date the shipment was received;

(iii) The quantity of waste accepted;

(iv) The quantity of "as received" waste in storage each day;

(v) The date the treatment study was initiated and the amount of "as received" waste introduced to treatment each day;

(vi) The date the treatability study was concluded;

(vii) The date any unused sample or residues generated from the treatability study were returned to the generator or sample collector or, if sent to a designated facility, the name of the facility and the EPA identification number.

(8) The facility keeps, on-site, a copy of the treatability study contract and all shipping papers associated with the transport of treatability study samples to and from the facility for a period ending 3 years from the completion date of each treatability study.

(9) The facility prepares and submits a report to the Regional Administrator, or State Director (if located in an authorized State), by March 15 of each year that estimates the number of studies and the amount of waste expected to be used in treatability studies during the current year, and includes the following information for the previous calendar year:

(i) The name, address, and EPA identification number of the facility conducting the treatability studies;

(ii) The types (by process) of treatability studies conducted;

(iii) The names and addresses of persons for whom studies have been conducted (including their EPA identification numbers);

(iv) The total quantity of waste in storage each day;

(v) The quantity and types of waste subjected to treatability studies;

(vi) When each treatability study was conducted;

(vii) The final disposition of residues and unused sample from each treatability study.

(10) The facility determines whether any unused sample or residues generated by the treatability study are hazardous waste under Sec. 261.3 and, if so, are subject to parts 261 through 268, and part 270 of this chapter, unless the residues and unused samples are returned to the sample originator under the Sec. 261.4(e) exemption.

(11) The facility notifies the Regional Administrator, or State Director (if located in an authorized State), by letter when the facility is no longer planning to conduct any treatability studies at the site.

(g) Dredged material that is not a hazardous waste. Dredged material that is subject to the requirements of a permit that has been issued under 404 of the Federal Water Pollution Control Act (33 U.S.C.1344) or section 103 of the Marine Protection, Research, and Sanctuaries Act of 1972 (33 U.S.C. 1413) is not a hazardous waste. For this paragraph (g), the following definitions apply:

(1) The term dredged material has the same meaning as defined in 40 CFR 232.2;

(2) The term permit means:

(i) A permit issued by the U.S. Army Corps of Engineers (Corps) or an approved State under section 404 of the Federal Water Pollution Control Act (33 U.S.C. 1344);

(ii) A permit issued by the Corps under section 103 of the Marine Protection, Research, and Sanctuaries Act of 1972 (33 U.S.C. 1413); or

(iii) In the case of Corps civil works projects, the administrative equivalent of the permits referred to in paragraphs (g)(2)(i) and (ii) of this section, as provided for in Corps regulations (for example, see 33 CFR 336.1, 336.2, and 337.6).

[45 FR 33119, May 19, 1980]

Editorial Note: For Federal Register citations affecting Sec. 261.4, see the List of CFR Sections Affected in the Finding Aids section of this volume.

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PART II

Legislation, regulations and management strategies

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II.1
Regulatory frameworks as an instrument of waste management strategies

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II.1.1. Introduction

Though over 25 years have passed since enactment of the first regulations on waste, the attempts to develop regionally and internationally harmonized waste management policies are still in progress. It is now clear that establishing a comprehensive system and creating adequate incentives for preventive management and proper cleanup worldwide have not yet been achieved. The best indicator of the quality of legislation is its efficiency. Law that has no proper or any enforcement mechanism is not worth the paper it is printed on. Such "paper law" can be exemplified in the environmental legislation of the former USSR and the countries under its influence. It can be summarized by a well-known sentence: "We have the best regulations in the world, unfortunately they do not work." The legislation that does not work is for sure the worst one and results in much greater harm than lack of regulations. Another imperfection of a waste legislation, common for the developed countries, comes from the too strong belief in the high level of public awareness as an instrument of proper control of waste disposal. This can result in "out of sight, out of mind" or "not in my backyard" practice, which leads to abortive solutions from the environmental and/or economic point of view. Nevertheless, public awareness is an extremely efficient support for safe waste management strategies.

This chapter is focused on the features and qualities of the legislation on waste and its efficiency, on efforts to reach this goal and results of these efforts.

II.1.2. Waste management practice in industrially developed countries

II.1.2.1. Terminology

The definition of "solid waste management" is similar in the US and EU legislation. According to RCRA (1976, 1984), this term means "the systematic administration of activities which provide for the collection, source separation, storage, transportation, transfer, processing, treatment and disposal of solid waste. The terms *solid waste planning, solid waste management* and *comprehensive planning* include planning or management

respecting resource recovery and resource conservation." Council Directive 91/156/EEC defines "waste management" as "collection, transport, recovery and disposal of waste, including the supervision of such operations and after-care of disposal sites."

Most of the basic legal terms related to solid waste management have been given in Chapter I and in the Appendices to that chapter, which provide excerpts from the EU and US legislation. A more detailed discussion of the European, OECD and Basel Convention terminology is based on the assumption, that in general, the US Federal laws and regulations are widely known, as they are discussed in numerous reference sources that are readily available for the reader outside USA. Some other legal terms related to waste management practice not defined in the previous chapters need to be given here, in particular the terms "solid waste management facility", "open dump", "landfill", "underground storage" and "treatment" being an integral part of the waste disposal practices.

The first two terms are defined in the RCRA (1976, 1984). The term *solid waste management facility* includes (A) any resource recovery system or component thereof, (B) any system, program, or facility for resource conservation, and (C) any facility for the collection, source separation, storage, transportation, transfer, processing, treatment or disposal of solid wastes, including hazardous wastes (HWs), whether such facility is associated with facilities generating such wastes or otherwise." The EU legal terminology relevant to this term comprises the major term "management" and derived terms "disposal", "recovery" and "collection" along with the lists of disposal operations and operations which may lead to recovery (Council Directive 91/156/EEC amending Directive 75/442/EEC on waste, Article I d, e, f, g, Annex IIA and IIB). These terms are given in Chapter I.1 and Appendix A to that chapter.

The term "open dump" means "any facility or site where solid waste is disposed off which is not a *sanitary landfill* which meets the criteria promulgated under section 4004 and which is not a facility for disposal of hazardous waste" (RCRA, 1976, 1984). This term is thus related entirely to solid wastes that are not HW and not a municipal waste.

In the EU legislation, the term "landfill" is of a more general character and is relevant to any solid waste, including HW and municipal waste, and to any form of storage, i.e. both onto or into land. According to the Council Directive 1999/31/EC (1999) on the landfill of waste, "*landfill* means a waste disposal site for the deposit of waste onto or into land (i.e. underground), including:

- internal waste disposal sites (i.e. landfill where a producer of waste is carrying out his own waste disposal at the place of production), and
- a permanent site (i.e. more than one year) which is used for temporary storage of waste but excluding:
  - facilities where waste is unloaded in order to permit its preparation for further transport for recovery, treatment or disposal elsewhere, and
  - storage of waste prior to recovery or treatment for a period less than three years as a general rule, or
  - storage of waste prior to disposal for a period less than one year."

According to the same Directive, the term "underground storage" means "a permanent waste storage facility in a deep geological cavity such as salt or potassium mine".

The term "treatment" means "the physical, thermal, chemical or biological processes, including sorting, that change the characteristics of the waste in order to reduce its volume or hazardous nature, facilitate its handling or enhance recovery".

II.1.2.2. General prerequisites, existing status of waste management and its efficiency

National, regional and global waste management strategies should be based on the harmonized, integrated and effective regulatory and legislative framework that addresses environmental safety and public health as a first priority and considers all the alternatives of waste stream minimization. There are three major prerequisites to ensure the implementation of legislation: (i) an effective enforcement procedure consisting of a sound, well-balanced system of charges, penalties and incentives; (ii) thorough legal liability of producer or holder for waste management in an environmentally safe way; and (iii) precise instruments of verification and effective audit of waste management practice, followed by execution of a law in a way that makes any attempts of evading or desisting from the juridical obligations highly unprofitable.

The legislation itself has to be clear, use unequivocal definitions and leave no doors open to differences in interpretation or to exemptions from the rule. Experience shows that producers will readily use any legislative gap to avoid extra costs of waste management. Quite often, the administration and legislative organs succumb to a massive pressure from industry and soften the regulations, e.g. by excluding some groups of potentially reusable waste materials from the category of "waste" simply by defining them as "secondary raw materials". An example of the consequences that can cause such playing on words was given in the introductory Chapter I.1 under the title "*Recyclable Waste* or *Secondary Raw Material*?". Artificial methods of reducing waste streams by just changing definitions are particularly popular in countries with a weak, unbalanced economy and a traditional low priority given to control of waste disposal practices. This approach is caused by a lack of recognition by governmental decision-makers and legislative bodies of the harm that inadequate management could cause to the human health and environment. In the Russian federation, Ukraine and other new states of the former USSR, the practice of constructing gigantic disposal sites and tailing waste ponds for open dumping of mining and ore processing waste has a long history. Despite numerous instances of severe pollution of surface and groundwater resources (Zoteev et al., 1999), the major standardization efforts are focused predominantly on the safety of these constructions from the standpoint of hydraulic engineering (Aksenov et al., 1999). The high-volume waste disposed off in huge unprotected sites is termed by the authors of national standards as "technogenic deposits". This tricky term is being applied to a high-volume disused waste potentially suitable for partial reuse and therefore considered as "non-waste" (Streltsov et al., 1999). Such a "terminological" way of waste stream minimization, though extremely cost-effective, bears many negative consequences to the environment and usually results in contamination of unprotected aquifers. This way of handling waste management problems is a rather adverse example of the legislative activity.

Pollution control in the different compartments of the environment works as connected vessels. Solution of a problem in one compartment immediately creates a new problem in another one. This requires an instant legislative reaction to a new situation, to get

a positive balance of pollution control in the environment as a whole. According to Congressional findings (RCRA, 1976, 1984), as a result of the Clean Air Act, the Water Pollution Control Act and other Federal and State Laws in the USA respecting public health and the environment, greater amounts of solid waste (in the form of sludge and other pollution treatment residues) have been generated. Similarly, inadequate and environmentally unsound practices for the disposal or use of solid waste have created greater amounts of air and water pollution and other problems for the environment and health. The same problems have been faced in the EU, other OECD member states and countries all over the world. In the past decades, as total and annual waste quantities increase, the availability of new disposal sites decrease and the cost of new disposal areas has risen significantly. Requirements for siting, constructing and managing disposal areas in the developed countries have become more stringent leading to a shortage of dumping sites and high costs of open dumping.

Consequently, open dumping has been recognized to be particularly harmful to health due to contamination of drinking water from underground and surface supplies and pollution of the air and land. A number of non-hazardous wastes were found to be sources of detrimental environmental impact lasting for decades. Land disposal, particularly landfill and surface impoundment, was found to be the least favored method for managing wastes, in particular hazardous ones, and also for waste that cannot be defined as inert. Simultaneously, solid waste was found to represent a potential source of usable material and/or energy. These findings gave rise to the enactment of RCRA (1976, 1984) and European Directives and Decisions on waste (EUR-Lex, 2003a,b), the objectives of which were to provide a legislative and regulatory basis for solid waste management strategies. This legislation, along with the already existing national one in developed countries, has created a framework within which enforcement procedures could be implemented. In view of the ultimate objectives of waste management strategies, besides safe solid waste disposal, minimization of HW generation, reducing the volume of waste stream and the volumes of waste requiring disposal should be ensured. The regulations on waste management should promote and enforce an application of the recovery and recycling of solid waste and environmentally safe disposal of the non-recoverable residues.

The available statistical data for the EU (EUROSTAT, 1997, 2000a,b,c, 2001a,b) and OECD (1998, 1999, 2001, 2002), though still incomplete and inconsistent, reflect the efficiency of these enforcement procedures, at least in waste recycling, municipal waste management, operating and capital costs of waste management and public opinion. These data show, on the one hand, general positive trends, and on the other hand an extreme diversity of efficiency of waste management strategies within the particular OECD and EU member countries, and the EU as a whole.

II.1.2.2.1. The EU waste management strategy

Facing the growth of waste generation by 10% a year, the EU has defined and is pursuing a general strategy aimed to reverse this trend, which has been addressed in the Council Resolution (1997), as well as in the document issued by the European Commission, Directorate General on Environment, Nuclear Safety and Civil Protection, and in other working and legislative documents focused on the most problematic issues concerning waste (EC DG ENV, 1999; EC-Environment; EUR-Lex, 2003a,b). In the EC DG ENV

(1999) document on EU waste management strategy, the major "P-principles" have been formulated, upon which EU approach to waste management is based: prevention, producer responsibility and polluter pays, precaution, and proximity. Based on these principles, the EU general strategy set out in 1996 a preferred hierarchy of waste management operations:

- prevention of waste (minimization and avoidance),
- recycling and reuse,
- optimum final disposal and improved monitoring.

The EU strategy has also stressed the need for:

- reduced waste movements and improved waste transport regulation;
- new and better waste management tools such as:
  - regulatory and economic instruments;
  - reliable and comparable statistics on waste;
  - waste management plans;
  - proper enforcement of legislation.

From the above, it can be seen that regulatory and economic instruments along with the reliable statistics on waste are considered of special importance in the EU waste management practice.

Waste prevention and minimization should receive the top priority in waste management plans. Complete or partial recycling (e.g. composting of municipal waste) has been found to be the way of waste reduction and conservation of natural resources. Recovering energy from waste material by using it as a fuel might also be considered as a solution. Neither waste landfilling nor incineration as the main alternative disposal method to landfill was found to be a perfect management option, both being potentially harmful to the environment and health. Recycling/composting also bears potential risks to human health and the environment (Table II.1.1). Therefore, the best option is to reduce the total amount of waste generated.

As particularly problematic waste in the European Community, the European Commission defined municipal waste, and also several constantly growing specific waste streams that require receiving special attention, among them packaging waste; end-of-life vehicles; batteries, electrical and electronic waste and hazardous household waste (EC DG ENV, 1999).

Packaging waste is estimated to form up to 50% of municipal waste in the EU, of this a relatively high total rate of 52.6% (for 11 of 15 EU member states, excluding Greece, Ireland, Luxembourg and Portugal) is being recovered. The EC Packaging Directive (1994) set the target recovery rate for this waste to 50–65% by weight, and recycling of 25–45%. The minimum recycling target aim, set for 12 EU member states to be fulfilled by 2001, was already exceeded in 1997 by 11 states, while the minimum recovery target of 50% was not yet achieved by Italy, Spain and UK (Table II.1.2). Nevertheless, packaging waste recycling/recovery rate in the EU-11 can be considered high compared to other OECD countries, as well as to three other EU member states (Greece, Ireland and Portugal) (Table II.1.3, Fig. II.1.1). This success was mainly due to high recycling rates for paper/cardboard and glass packaging, while recycling/recovery of other packaging waste such as plastics or metals was considerably lower for the majority of EU member states, at a similar waste generation per capita (Table II.1.4), among others due to difficulties with

Table II.1.1. Environmental impact of waste management options (after EC DG ENV, (1999).

Environmental compartment	Waste management option				
	Landfill	Incineration[a]	Recycling	Composting	Transportation
Air	Emission of CH_4, CO_2, odors	Emission of SO_2, NO_x, HCl, HF, NMVOC, CO, CO_2, N_2O, dioxins, dibenzofurans, heavy metals (Zn, Pb, Cu, As, etc.)	Emissions of dust	Emission of CH_4, CO_2, odors	Emissions of dust, NO_x, SO_2, release of hazardous substances from accidental spills
Water	Leaching of salts, heavy metals, biodegradable and persistent organics to groundwater	Deposition of hazardous substances on surface water	Waste water discharges		Risk of surface water and groundwater contamination from accidental spills
Soil	Accumulation of hazardous substances in soil	Landfilling of slags, fly ash and scrap	Landfilling of final residues		Risk of soil contamination from accidental spills
Landscape	Soil occupancy, restriction on other land uses	Visual intrusion, restriction on other land uses	Visual intrusion	Soil occupancy, restriction on other land uses	Traffic

Ecosystems	Contamination and accumulation of toxic substances in the food chain	Contamination and accumulation of toxic substances in the food chain		Contamination and accumulation of toxic substances in the food chain	Risk of contamination from accidental spills
Urban areas	Exposure to hazardous substances	Exposure to hazardous substances	Noise		Risk of exposure to hazardous substances from accidental spills, traffic

[a]Emissions from high-performance incinerators are reduced to the environmentally safe level.

Table II.1.2. Total packaging consumption and achieved recycling and recovery rates in member states in 1997, including exports for recycling/recovery (after EC DGXI.E.3 (2001)).

Member state	Packaging put on the market		Recovery (%)			Targets (%)	
	1,000 t	kg/capita	Recycling	Energy recovery	Total	Recycling	Recovery
Austria	1.113	138.0	64.8	4.8	69.6	25	50
Belgium	1.356	133.0	62.3	n.a.	62.3	50	80[a]
Denmark[b]	971	184.0	48.7	38.0	86.7		
Finland[b]	417	81.2	41.8	12.2	54.1	42	61
France	11.069	189.2	41.0	14.5	55.5	25–45	50–65
							75[c]
Germany[d]	13.731	167.4	78.3	2.3	80.5	45	65
Greece[e]	780	74.4	n.a.	n.a.	n.a.		
Ireland[f]	683	186.9	n.a.	n.a.	14.8	25–45	50–65
Italy[g]	9.529	165.8	29.6	2.2	31.8	25–45	50–65
Luxembourg[h]	39	93.2	n.a.	n.a.	n.a.	45	55
Netherlands	2.745	176.3	55.2	22.4	77.6	45[i]	65
						65[j]	
Portugal[e]	1.012	101.9	n.a.	n.a.	n.a.		25[k]
						25[l]	50[l]
Spain	5.879	149.6	34.4	1.6		25–45	50–65
Sweden	923	104.4	57.9	7.2	36.0		
UK	7.755	131.7	31.3	3.2	65.1		58
EU-11 total	55.487	158.9	46.3	6.3	52.6		
EU-15 total	58.001	155.2					

n.a., data not available.

[a]Targets have to be achieved by 1999.

[b]Report contains no figures on energy recovery; the figures given in the table are calculated as difference between total recovery and total recycling.

[c]Target for household packaging waste to be achieved by the end of 2002.

[d]Data on energy recovery of paper/cardboard and plastic packaging are not available; data on exports of tinplate and paper/cardboard packaging are not or only partially available.

[e]Total consumption estimated on the basis of information from CEPI, APME, FEVE and own assumptions.

[f]National waste data report; data refer to 1998.

[g]Data on exported wood packaging not available.

[h]ECO Counsel Agency; data refer to 1996.

[i]Mandatory target to be achieved in 1998 defined in the packaging and packaging waste decree.

[j]Voluntary target defined in the Covenant II to be achieved by 2001.

[k]Target to be reached by 2002.

[l]Target to be reached by 2006.

identifying the markets for recovered/recycled materials. According to the EC DGXI.E.3 (2001) report, recycling/recovery rates were the lowest in those countries where landfilling was the predominant waste management option, while waste management strategies and enforcement instruments aiming at separate collection and recycling hardly existed. The achievement of high recycling/recovery rate thus appears to be based on the development

Table II.1.3. Rate of waste paper and glass recycling in the OECD and EU member states in 1980–1997* (after OECD, 1998; EUROSTAT, 2000a,b,c).

Countries	Paper (%)					Glass (%)				
	1980	1985	1990	1996[a]	Change since 1980	1980	1985	1990	1996[a]	Change since 1980
Canada[b]	20	23	28	33	13	12	12	–	17	5
Mexico[c]	–	–	2	2	–	–	–	4	4	–
USA[c]	27	27	34	35	8	5	8	20	24	20
Japan[d]	48	50	50	51	4	35	47	48	56	21
Korea	37	–	44	53	16	–	–	46	57	–
Australia	–	36	51	–	–	–	–	–	42	–
New Zealand	17	19	20	27	10	–	–	–	–	–
Austria	30	37	37	65 (***71***)	35 (***41***)	20	38	60	76 (***76***)	56
Belgium[e]	15	14	–	12 (***38***)	−3 (***18***)	33	42	55	66 (***66***)	33
Czech Republic	–	–	–	40	–	–	–	–	–	–
Denmark	26	31	35	44 (***52***)	18 (***26***)	8	19	35	66 (***71***)	58 (***63***)
Finland	35	39	41	57 (***39***)	22 (***4***)	10	21	36	63 (***63***)	53
France	30	35	34	38 (***41***)	8 (***11***)	20	26	29	50 (***50***)	30
Germany[f]	34	43	44	67 (***71***)	–	23	43	54	79 (***79***)	–
Greece[g]	22	25	28	19 (***31***)	−3 (***9***)	15	15	15	20 (***25***)	5 (***10***)
Hungary	33	42	53	49	16	–	–	–	–	–
Iceland	–	–	–	36	–	–	–	70	75	–
Ireland	–	10	–	12 (***17***)	–	8	7	23	46 (***29***)	38 (***21***)
Italy	–	25	27	29 (***31***)	–	20	25	48	53 (***53***)	33
Luxembourg	–	–	–		–	–	–	–	–	–
The Netherlands	46	50	50	77 (***69***)	32 (***23***)	17	49	67	81 (***81***)	64
Norway	22	21	25	41	20	–	–	22	75	–
Poland	34	34	46	13	−20	–	–	–	–	–
Portugal	38	37	41	37 (***39***)	−1 (***1***)	–	10	27	42 (***42***)	–
Spain	47	57	51	52 (***41***)	5 (− ***6***)	–	13	27	35 (***35***)	–
Sweden	34	–	43	54 (***66***)	20 (***32***)	–	20	44	72 (***72***)	–
Switzerland	35	39	49	67	32	36	46	65	89	53
Turkey	–	–	27	34	–	–	33	31	13	–
United Kingdom	32	29	35	37 (***40***)	5 (***8***)	5	12	21	22 (***27***)	17 (***22***)
EU mean[h]	31.5	33	37	43 (***46***)	13 (***15***)	18	24	38.5	55 (***55***)	39 (***39***)
OECD mean[h]	32	33	39	40	12	16	26	39	51	35

Data for 1996 reported by EUROSTAT (2000a,b,c) are ***bold italic***; *ratio of the amount recycled to the amount used (total production in the country + import − export).

[a]Or the last year for which the data are available.

[b]Data only for glass packaging.

[c]Recycling rates are based on the amounts of waste generated.

[d]Data for glass do not include returnable bottles.

[e]Including estimates.

[f]Data for the years 1980–1990 do not include the former GDR. Recycling rate is based on the total sales.

[g]Data do not include import and export.

[h]Estimates based on the available statistical data given in the respective columns (calculated by the authors).

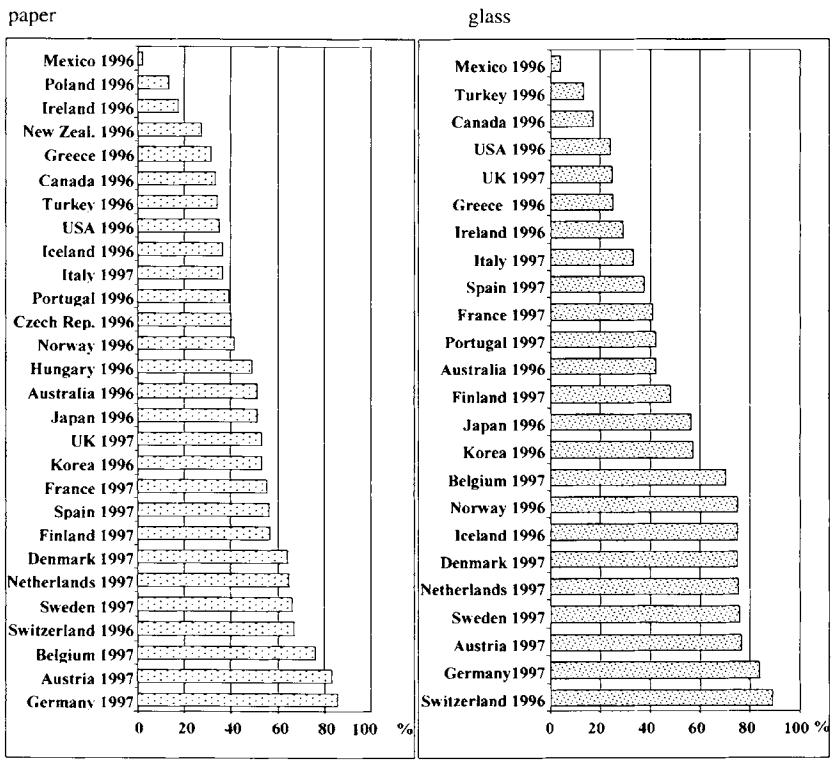


Figure II.1.1. Recycling of waste paper and glass in the OECD member states in 1996–1997, (after OECD, 1998 and EC DGXI.E.3, 2001).

of sound national (and internationally harmonized) waste management strategies that provide a legislative and regulatory framework within which efficient enforcement procedures can be implemented.

The study on the evaluation of costs and benefits for the achievement of reuse and recycling targets for the packaging materials has been recently subject to public discussion. Main elements of the working documents on waste batteries, as well as on electrical and electronic equipment include reduction of hazardous substances used in these products, establishment/improvement of collection and recovery/recycling systems and encouraging the producers' involvement in the recycling activity.

Proposals for the new EU legislation on waste management and disposal operations that reflect actual state of the art and technical progress, formulated by the European Commission in 1996–1999, and follow-up extensive regulatory activity resulted in the enactment of new updated Council Directives and Commission Decisions, among them Council Directive 1999/31/EC on the landfill of waste, Directive 2000/76/EC of the European Parliament on the incineration of waste; Directive 2000/53/EC on end-of-life vehicles (2000); Directives on waste electrical and electronic equipment 2002/95/EC and 2002/96/EC (2003), a number of additional recent regulations relevant to the EU packaging Directive adopted in 1994 and Council Directive on batteries and accumulators

Table II.1.4. Consumption of major kinds of packaging (kg/capita) and achieved recycling and recovery rates in member states and the EU in 1997* (after EC DGXI.E.3, 2001).

Member state	Cons. (kg/capita)	Paper/cardboard recovery (%)				Cons. (kg/capita)	Glass recovery (%)				Cons. (kg/capita)	Plastics recovery (%)				Cons. (kg/capita)	Metal recovery (%)				
		RC	ER	TR	Tg		RC	ER	TR	Tg		RC	ER	TR	Tg		RC	ER	TR	Tg	
																				Steel	Al
Austria	65.8	83.4	0.9	84.4	90	32.2	76.5	0.0	76.5	93	22.3	20.0	25.6	45.6	40	10.5	34.1	0.0	34.1	95	98
Belgium	53.8	76.0	n.a.	76.0		30.5	70.1	0.0	70.1		20.5	25.3	n.a.	25.3		11.8	70.3	0.0	70.3		
Denmark	87.8	64.1	30.9[a]	95.0	55	38.4	75.1	0.0	75.1	65	34.8	8.1	89.8[b]	97.9	15	11.0	15.8	0.0	15.8	15	15
Finland	47.4	56.5	16.4[a]	72.9	53	10.1	47.9	0.0	47.9	48	17.5	10.2	12.2[b]	22.4	45[c]	6.0	8.4	0.0	8.4	25	25
France	65.8	55.1	18.5	73.6		56.3	40.9	0.0	40.9		26.9	5.2	27.1	32.3		11.6	44.4	0.5	45.0		
Germany	66.4	85.5	n.a.	85.5	70[d]	45.7	83.9	0.0	83.9	75[d]	18.3	48.6[e]	n.a.	48.6	60[d]	13.7	82.0	n.a	82.0	70[d]	60[d]
Greece	30.2	n.a.	n.a.	n.a.		14.7	n.a.	n.a.	n.a.		20.9	n.a.	n.a.	n.a.		8.6	n.a.	n.a.	n.a.		
Ireland	82.2	n.a.	n.a.	14.9[f]	31	30.5	n.a.	n.a.	32.3[f]	45	46.2	n.a.	n.a.	2.6[f]	10	11.3	n.a.	n.a.	n.a.	5	25
Italy	56.5	36.3	3.1	39.4		39.1	33.4	0.0	33.4		30.9	9.6	6.1	15.6		7.9	5.5	0.0	5.5		
Luxembourg	28.6	n.a.	n.a.	n.a.		41.4	n.a.	n.a.	n.a.		16.7	n.a.	n.a.	n.a.		6.5	n.a.	n.a.	n.a.		
Netherlands	93.1	64.9	20.1	85.0	85[g]	30.1	75.5	0.0	75.5	90[g]	39.2	12.4	52.9	65.3	35[g]	13.9	67.1	0.0	67.1	80[g]	
Portugal	43.9	n.a.	n.a.	n.a		26.8	n.a.	n.a	n.a.		22.6	n.a.	n.a.	n.a.		8.6	n.a.	n.a.	n.a.		
Spain	57.4	56.0	1.1	57.1		35.6	37.3	0.0	37.3		30.9	6.7	5.3	12.0		8.7	22.6	1.3	23.8		
Sweden	59.5	66.2	8.4	74.5	40/65[h]	20.1	75.6	0.0	75.6	70	17.0	14.0	14.7	28.7	30[h]	7.9	45.4	0.0	45.4	70	70[h]
UK	51.5	53.0	7.9	60.9		30.3	24.7	0.0	24.7		23.0	8.8	0.0	8.8		13.7	26.1	0.2	26.2		
EU-11 total	61.8	59.0	7.5	66.5		39.9	52.2	0.0	52.2		25.3	15.5	14.2	29.7		11.4	46.0	0.2	46.3		
EU-15 total	60.6					38.8					25.3					11.2					

Cons., consumption; RC, recycling; ER, energy recovery; TR, total recovery; Tg, recycling targets for packaging materials; EU-11, total for 11 member states without Greece, Luxembourg, Ireland and Portugal; n.a., data not available; *recycling and recovery rates include packaging waste quantities exported for recycling/recovery.

[a]Data on energy recovery of paper/cardboard packaging are not available; the figures given in the table are calculated as the difference between total recovery and total recycling.

[b]Data on energy recovery of plastic packaging are not available; the figures given in the table are calculated as the difference between total recovery and total recycling.

[c]Target for plastics applies to recovery.

[d]Material-specific recycling targets apply to sales packaging.

[e]Recycling rate includes feedstock processes.

[f]National Waste Data Report; data refer to 1998.

[g]Voluntary target defined in the Covenant II to be achieved by 2001.

[h]Recycling target for: corrugated cardboard, 65%; paper/cardboard, 40%; aluminum drink containers, 90%; PET drink bottles, 90%.

of 1991; all these can be found in the EUR-Lex web site. The Biowaste Directive, Sewage Sludge Directive, new revised European legislation on batteries are well advanced and available as working documents (drafts), along with the reports on relevant events and studies in the continuously updated EC-Environment and EUR-Lex web sites.

Recently adopted EU legislation on waste tightens up environmental requirements for waste management options and defines more stringent standards for the design and operation of existing and new installations for waste management. Besides the waste streams discussed above, other studies initiated and supported by the European Commission have been carried out in order to develop new or review existing waste directives in compliance with the urgent need of tackling the rapidly growing waste generation and relevant environmental problems. The studied waste streams include PVC issues, as well as the management of bulk waste such as construction and demolition waste as well as the waste resulting from prospecting, extraction, treatment and storage of mineral resources.

To date, European action in the waste field has mainly taken the form of legislation, supported also by initiating and funding technical research, recycling industries, training, awareness-raising actions and exchange of good practice.

According to the statement of the European Commission (EC DG ENV, 1999; EC-Environment), the situation within the EU regarding waste management is still unsatisfactory due to the lack of complete coverage of the full EU territory with comprehensive waste management plans. To enforce drawing up such plans, the EC has initiated infringement procedures against 14 member states. Waste management planning that includes technical, organizational, economic and policy level aspects is considered by the European Commission to be a key part of the European legislation in the field of waste management and the basis of waste management strategies at local, regional and national levels. These plans are also to be an important instrument for awareness raising and citizens' participation in the field of waste management.

The growing waste problem requires solutions at local level, linked to larger management plans and in line with community waste strategy that has to assure sustainable environmental protection without distorting the European internal market. To improve the situation, EC formulated the need for shared actions that include consumers, business and local authorities. In general, these actions are to be based predominantly on awareness, partnership and providing means and provisions for separate collection of different waste.

Not negating or depreciating the role of public awareness and partnership in the consumer–producer–authority relation in the field of waste problem solution, it should be mentioned that this basis proposed by the EC for shared actions might considerably elongate achievement of the target if economic/financial instruments that have been pointed out as "new and better waste management tools" are not adequately considered in these relations.

Another aspect that has not been stressed enough in the EU approach to waste management, though also specified among "new and better tools" (EC DG ENV, 1999; EC-Environment, 2003), is a need of reliable and current waste management statistics. Without this tool, development of the consistent waste management plan that covers the full territory of the EU would be difficult to accomplish, if at all feasible. Enactment of Regulation (EC) No 2150/2002 on waste statistics and establishing a harmonized list of

wastes (Commission Decision 2000/532/EC, 2000) creates a good basis for obtaining comparable statistical data in the following years.

Public awareness plays an important role as an element of the EU waste management strategy and good practice, in particular, in showing preference for "green" products with little packaging, separate collection of waste or taking special care for disposing hazardous household waste and inducing/supporting local authorities in improvement of the local waste situation.

In the public opinion, in 1995, a general increase of perception of waste as a threat for the local environment was observed compared to 1988 (EUROSTAT, 1997). In the scale from 1 to 4, the threat from waste received 2.2 points as an average for the EU (1.8 in 1988), equal to the landscape damage, and higher than the decrease of drinking water quality (2.0), lack of green areas (2.0) and noise (2.1). Among the six factors, only the threat from air pollution was evaluated higher (2.3). This shows a sensitivity of the public opinion to waste management issues. In the different member states, the evaluation scale ranged from 1.3 points (Denmark) to 2.7 points (Italy). The lowest values were received from countries having low waste generation and good waste management practice (Denmark, Finland, The Netherlands), while the highest values were attributed to countries with problematic waste management (Italy 2.7, Greece and Spain 2.4). It is remarkable that in none of the EU member states the decrease of perception of waste as a threat to the environment was observed. This demonstrates a high level of public awareness as a whole and still unsatisfactory waste management practice in the eyes of the public opinion.

According to the same source of the statistical data (EUROSTAT, 2001a), the expenditure of the EU member states on waste management in 1997/1998 ranged from 3.2 (Greece) to 28% (UK) of the total budget for the environmental protection in industry and held mostly the third position after sewage management and air protection (Fig. II.1.2). The highest annual capital expenditure in the last decade of the 20th century on the integrated technologies of industrial waste management in eight EU member states ranged from 25.2 (UK) to 64.2% (Finland), while the latest available data for 1997–1998 accounted for 7.9 (Finland) to 33.7% (Portugal) of the total waste management expenditure that reflects the past and current status of waste disposal facilities modernization (Fig. II.1.3).

The total share of the environmental protection expenditure in GDP of the 11 EU member states (without Denmark, Spain, Italy and Luxembourg) and Switzerland in 1997–1999 ranged from 0.25 (Greece) to 2.12% (Austria), mean 1.20%. Of this, the mean expenditure in public sector accounted for 0.73% (from 0.16 to 1.55%) and in industry, 0.47% (from 0.09 to 0.77%). The relevant share of the environmental protection expenditures in four candidate countries (Czech Republic, Estonia, Hungary and Poland) in their GDP was higher, mean 1.68% (from 1.18% in Estonia to 2.39% in Poland), and showed prevalence in industrial sector (mean 1.00%, from 0.46% in Estonia to 1.49% in Poland) that reflects the efforts of these countries directed to improving the state of their environment, heavily impacted quite recently by the industry, mainly by primary production branches (EUROSTAT, 2001a).

II.1.2.2.2. Enforcement and supporting instruments in waste recycling and reuse

The level of paper and glass waste recycling in the OECD member states makes all the discussion about the distinction between "waste" and "non-waste" (see Chapter I.1)

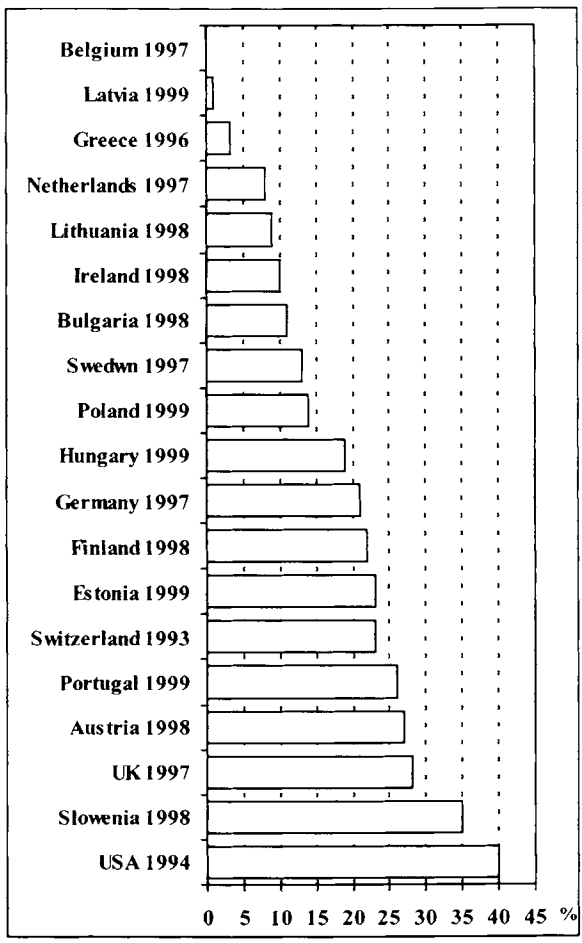


Figure II.1.2. Percentile of waste management in the total environmental protection expenditure (capital and operating costs) in industry in Europe and the USA (after EUROSTAT (2001a)). Data for Belgium comprise the capital costs only.

groundless. These materials, which are potentially thoroughly recyclable, are generally used by proponents of defining recyclable materials as "secondary raw material" or major arguments. The statistical data show that no OECD member state may boast of a thorough recycling of these materials. The rates of paper and glass recycling in 1996 ranged from 2 (Mexico) to 77% (The Netherlands) (mean 43%) and from 4 (Mexico) to 89% (Switzerland) (mean 55%), respectively (OECD, 1998). Data reported for 1996 by EUROSTAT (2000a,b) for paper recycling appear to differ significantly from those by OECD (1998), mostly in plus, though lower percentile also occurs. According to these data, the highest paper recycling rate achieved in the Netherlands, Austria and Germany did not exceed 69–71%, while the lowest one was 17% (Ireland) (Table II.1.3, Fig. II.1.1).

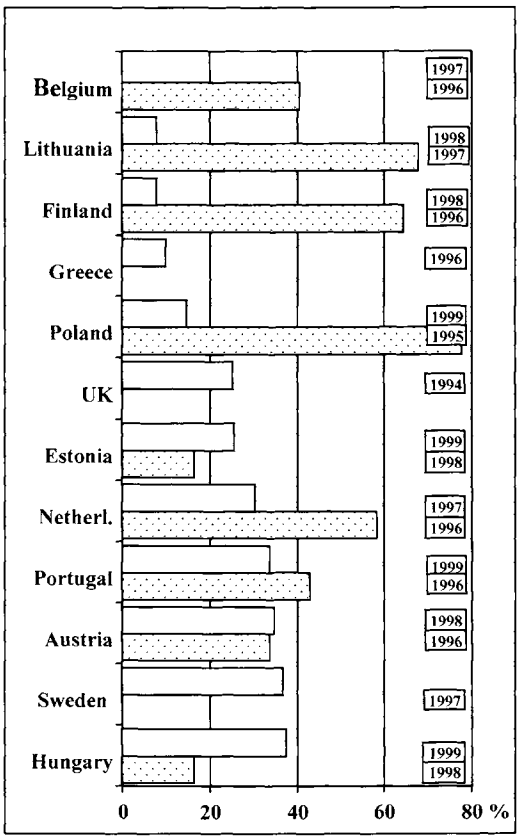


Figure II.1.3. The latest available and maximum rates of integrated technologies' capital costs in the total expenditure on the environmentally safe waste management in industry in the European Union and candidate countries in the last decade of the 20th century (after EUROSTAT, 2001a).

Therefore, there is no rational basis for excluding these materials from the waste stream. It cannot be denied that many OECD countries have made significant progress in paper and glass recycling in the last two decades, though the range of recycling rates in various countries is still extremely wide. In 1997, recycling rates for paper in Germany reached 85.5% and in Austria 83.4%, while mean value for the EU-11 (without Greece, Luxembourg, Ireland and Portugal) accounted for 59.0%. The total maximum paper/cardboard recovery including energy recovery in the EU member states reached as high a level as 95% in Denmark due to a very high rate of the energy recovery, 85.5% in Germany and 84.4% in Austria, while mean value for the EU-11 was 66.5%. Maximum glass packaging recovery in 1997, entirely through recycling, reached 83.9% in Germany and 76.5% in Austria, at a mean value for the EU-11 that was as low as 52.2% (Table II.1.4, data after EC DGXI.E3, 2001). OECD (1998) reported the variable increase of paper recycling from 1980 to 1996 that ranged from 4 to 5% (Japan, UK, Spain) to 32–35% (Switzerland, The Netherlands, Austria). The increase of the rate of glass recycling in this period ranged from 5 (Canada, Greece) to 58–64% (Denmark, The Netherlands). Simultaneously, though,

four countries displayed in 1996 a decrease in the paper recycling rate, from − 1 (Portugal) to − 20% (Poland). Collapse of paper recycling in Poland was mainly due to the failure of a previous collecting system based on the paid individual delivery practice. A well-functioning free selective collection of wastepaper in the neighboring EU countries has made its import to Poland more cost-effective than the national collecting system. An attempt to save it by reducing the price for delivery resulted in a loss of interest by suppliers due to a negative balance of delivery costs and prices. The newly enacted regulations that impose highly restrictive disposal and annual charges for the landfilling of recoverable waste in parallel with financial encouraging of recovery through the product and disposal fees entailed on entrepreneurs, strongly back up this activity and result in fast improvement of this waste recovery in Poland, with the target level of 48% paper and 40% glass recycling (Polish Acts: on packaging and packaging waste, 2001; on the obligations of entrepreneurs on the selected waste management and on the product and deposit fees, 2003; on annual rates of packaging waste recycling and recovery, 2001; consecutive Directives of the Cabinet: of 22 December, 1998, on charges for waste disposal with amendments, last in 2000; of 9 October 2001 (*both repealed*); and on fees for use of the environment, 2003, currently in force).

This case is a good illustration of the fact that waste management is governed by the same economic rules as any other market. This fact should be strongly taken into consideration when selecting enforcement instruments if we want them to work well. The efficiency of these instruments can be easily proven by statistical data, provided no toying with the terminology masks the real status.

In the field of environment protection, a significant part of which is the waste management strategy, public attitude and level of awareness plays an important supporting role. Everyday life shows that appropriate waste management can be easily achieved by an adequate education within a general educational system coupled with organizational and investment efforts that can effectively utilize and enhance public enthusiasm. A well-working free separate collection system requires placing easily accessible well-marked aesthetic containers, precisely functioning container collection/emptying and transportation to the place of reuse, effective and environmentally friendly utilization of collected waste and finally thoroughly informing the public of their role in the waste management system. Any spoiling of public enthusiasm by the wrong functioning of further stages of waste processing results in a deep adverse psychological reaction and a fixed negative perception of the further collaboration with unreliable partners in the waste management chain.

The relatively low level of waste paper and glass recycling in the USA and Canada, which have all the conditions to ensure its implementation, shows that this process is not a self-acting one and needs establishment of adequate enforcement procedures. They should comprise well-balanced incentive and charge/penalty instruments applicable to any other potentially recyclable waste. This contradicts the ideas of proponents of reuse enhancement by expressly excluding certain categories of materials from the definition of waste. The optimum enforcement of waste reuse should thus be based on the "polluter pays" principle and a thorough legal and financial responsibility of a waste generator.

Waste disposal has to have direct economic consequences to make the legal definitions and regulations work properly in the implementation arena. Spectacular success of fly ash

utilization in Poland (see Chapter I.1) is a good example of a properly working enforcement mechanism, worthy of popularization. Waste management in Poland has been regulated by the Act (2001) on waste, which replaced the previous one of 1997 in compliance with the EU Framework Directive 75/442/EEC on waste amended by Council Directive 91/156/EEC (1991). Current enforcement instrument to this law is the Directive of the Cabinet (2003) on fees for economic use of the environment, which replaced the previous ones on charges for waste disposal (2000, 2001), which in turn replaced the earlier Directive (1993) on fees for economic use of the environment, in the part concerning waste, with amendments of 1994, 1995, 1996 and 1997 that consisted mainly in actualization of the payment rates per mass unit of disposed waste. In the currently valid directive, wastes are listed and coded according to the Regulation as regards the single waste list (2001) adopting European list of wastes (Commission Decision 2001/118/EC, 2001). The fees are divided in several categories according to the charge rates per mass unit for disposal of waste, the highest is over 19 times higher than the lowest one. The fee for placing waste at the disposal site comprises also charge for three years' waste storage at this site. These fees and charges are to encourage waste generators or holders to advance seeking opportunities for waste utilization, minimization of the waste stream generated during the production or rendering it harmless in a form other than disposal. The fees and charges for disposal are the highest with respect to HW, waste for which recovery/recycling is technically and technologically sound, commercially effective and environmentally safe, as well as for a thoroughly reusable non-hazardous waste. For ultimate waste, for which at least partial disposal is unavoidable, the charges are lower. The system of charges is directed to advancing waste utilization and stimulating technologies, which assure waste minimization. A well-substantiated regional enforcement system, which includes incentives, charges and penalties and is based on the term "waste", may thus greatly improve its utilization.

To be successful, the industry sectors involved in waste recycling or usable material/energy recovery from waste must not be thrown upon their own into hard competition with easily available natural resources. Being supported financially and organizationally by waste generators acting on the basis of cost/benefit calculations and encouraged by regulations and legislation executed by administration, they would significantly enhance their competitiveness and strengthen the position in the market and public perception. This finally gives desirable results in the minimization of a waste stream and conservation of valuable natural material and energy resources.

II.1.2.2.3. Implementation of waste management options

It is obvious that waste management strategies should consider storage and safe disposal of non-recoverable waste residues. In accordance with the general legal approach in the OECD countries, with the USA legislation articulated in the RCRA (1976, 1984) and Superfund (CERCLA, 1980) as well as with the EU law (Council Directive 75/442/EEC, 1975, amended by Council Directive 91/156/EEC, 1991), and national laws and regulations, waste must be disposed of without endangering human health and without the use of processes and methods likely to harm the environment. In practice, this implies the following major tasks:

- reduce landfilling waste onto land, ensure all required technical means for environmentally safe surface dumping or impoundment, provide permanent early-warning controls over environmental contamination in a dumping site, expedite instant corrective action in case of failure to meet criteria of environmental law;
- minimize or prohibit land disposal of HW, also in specially engineered landfills as the least favored method of managing HW;
- promote improved solid waste disposal techniques (e.g. incineration with energy recovery);
- provide waste treatment in order to reduce its volume or hazardous nature prior to disposal;
- select and expedite remedial actions in the contaminated sites that ensure meeting legal environmental standards.

With the goal of implementing these strategic tasks, a number of guidelines have been developed for waste characterization, short-term and long-term risk and environment impact assessment, site or facility design, construction, monitoring and remediation. Under RCRA (Subtitle C: Hazardous Waste Management) and Superfund law, US EPA has implemented regulations to provide "cradle to grave" management of HW. The program includes standards applicable to generators and transporters of HW and performance standards for permitting HW treatment, storage and disposal facilities. The standards establish the principal groundwater protection policies of the RCRA HW program. EPA has also established criteria for non-hazardous solid waste disposal under Subtitle D (State and Regional Solid Waste Plans), which are to be adopted and enforced by the states. In the EU, besides the Council Directive 1999/31/EU (1999) on the landfill of waste, national legislation and enforcement regulations, the CEN Standards on Waste Characterization are now in an advanced stage of development, partially already approved or to be approved by final votes in 2004 or later (CEN/TC 292, 2003). The basic presupposition at the disposal technique and site selection, designing and construction is that the effectiveness of the environmental protection and controls on it is a first priority. The least-cost analysis is to follow the level of effectiveness determined to be appropriate.

There are not many statistical data available to evaluate the efficiency of the disposal methods. Some idea about the general state of the art in the OECD and EU countries give the data on the municipal waste management (Table II.1.5, Fig. II.1.4) (EUROSTAT, 2001c; OECD, 2002). Waste generation per capita ranged in the OECD member states from 300–310 (Greece, Mexico) to 760 kg (USA) and in the EU from 300 (Greece) to 640–670 kg (Luxembourg, Denmark, Switzerland, Spain). It showed a regularly increasing trend reflecting generally the level of economic welfare (estimated average for OECD accounted for 560 kg and for the EU 520 kg per capita), and in two decades since 1980 increased to 33% in OECD and 40% in the EU. Waste management practice in different countries shows considerably higher diversity, with one general feature. In the majority of countries, landfilling remains the principal option for disposal of waste. A strong positive trend in the last decade is a high and still growing interest in reducing disposed municipal waste volume through recovery of useful materials (recycling) or energy (incineration) and composting (Table II.1.5). In several highly developed European countries, municipal waste reuse was $\geq 65\%$, up to almost 90%. EUROSTAT (2001c) reports significant increase of this form of municipal waste management in the EU

Table II.1.5. Municipal waste generation and management in the OECD, EU member and candidate countries (after OECD, 2002 and EUROSTAT, 2000b,c, 2001c).

Countries	Generation (kg/capita)			Waste management (% of total)						
	1980	1990	2000	Mid-1990s*			Year	1998–1999**		
				R/C	I	L		R/C	I	L
Canada[a]	510	640	–	19	6	75				
Mexico[b]	–	250	310	1		99				
USA[c]	600	740	760	27	16	57				
Japan[c]	380	410	410	4	69	27				
Korea[d]	510	710	360	24	4	72				
Australia[e]	700	690	–	–	–	–				
New Zealand[f]	660	–	–	–	–	–				
Austria[c]	–	420	560	38	14	48	1996	47	16	37
Belgium[g]	360	410	550	14	31	55	1998	50	24	26
Czech Republic[h]	250	310	330	–	–	99	1998	13	5	82
Denmark[i]	400	570	660	23	54	22	1998	36	53	11
Finland[j]	–	410	460	33	2	65	1997	0	5	95
France[k]	–	450	510	9	32	59	1998	14	27	59
Germany[l]	–	540	540	29	17	51	1993	9	21	70
Greece[m]		260	300	7	0	93	1997	8	0	92
Hungary	–	530	450	0	7	93	1999	0	8	92
Iceland	–	620	710	14	17	69	1999	9	8	83
Ireland[n]	190	510	560	8	0	92	1998	9	0	91
Italy	250	350	500	–	6	94	1999	16	6	77
Luxembourg[o]	350	580	640	28	43	28	1998	0	66	64
The Netherlands[p]	490	500	610	38	27	35	1999	80	0	20
Norway[r]	550	530	620	15	16	69	1998	26	12	62
Poland[s]	280	290	320	2	0	98	1999	2	0	98
Portugal[t]	200	300	450	12	0	88	1999	10	8	82
Spain	–	–	670	12	4	83	1999	27	10	63
Sweden[u]	300	370	450	19	42	39	1998	32	35	33
Switzerland	440	610	650	40	46	14	1999	38	41	21
Turkey[w]	270	360	390	2	2	81		–	–	–
United Kingdom[c]	–	470	560	7	9	83	1996	8	0	92
Slovakia[x]	370	300	320	(*13*)	(*10*)	(*77*)	1995	2	0	98
Russian Federation[g]	160	190	340	–	–	–		–	–	–
Bulgaria	–	(*536*)	(*436*)	–	–	(*85*)	1998	0	0	100
Estonia[c]	–	(*354*)	(*394*)	(*0*)	(*0*)	(*100*)	1999	0	0	100
Lithuania[u]	–	(*416*)	(*426*)	–	–	–	–	–	–	–
Latvia	–	(*262*)	(*252*)	–	–	(*100*)	1999	0	0	100
Romania	–	(*302*)	(*326*)	–	–	(*100*)	1999	0	0	100
Slovenia[y]	–	(*514*)	(*515*)	(*5*)	(*0*)	(*95*)	1998	17	8	75

(*continued*)

Countries	Generation (kg/capita)			Waste management (% of total)						
	1980	1990	2000	Mid-1990s*			Year	1998–1999**		
				R/C	I	L		R/C	I	L
North America	500	620	660	*16*	*7*	*77*				
OECD[f]	420	500	560	*17*	*18*	*65*				
EU	370	420	520	*20*	*19*	*61*				
EU Assessing Countries[aa]	–	*(362)*	*(375)*			*(94)*				

Waste generation: Source: OECD (2002); (a) data for 1990 and 2000 are related to 1992 and 1998; (b) data for 1990 are related to 1991; (c) data for 2000 are related to 1999; (d) data for 1980 are related to 1985; (e) data for 1980 and 1990 are related to 1978 and 1992; (f) data for1980, 1990 and 2000 are related to 1982, average of 1986–1991 and 1999, respectively; (g) estimate; (h) data for 1990 and 2000 are related to 1987 and 1996; (i) data for 1990 are related to 1995, data on household waste for 1980 are related to 1985; (j) data for 1990 are related to 1994, estimates on household waste; (k) data for 1990 and 2000 are related to 1989 and 1999; (l) data for 1998; (m) data for 2000 are related to 2001; (n) data for 1990 are related to 1995, data for 2000 are related to 1998; (o) data for 1990 are related to 1992, data for 2000 are related to 1999; (p) data for 1980 are related to 1981; (r) data for 1990 are related to 1992; (s) data are related to collected waste, data for 1985 comprise liquid waste from containers and other tanks; (t) data are related also to Azores and Madera Islands; (x) data for 1980 and 1990 are related to 1987 and 1992, respectively; (u) data for 2000 are related to 1998; (w) data for 1990 and 2000 are related to 1989 and 1998; (y) data for 2000 are related to 1995; (w) estimates based on studies of different towns; (z) data do not comprise former GDR, Czech Republic, Slovakia, Hungary, Poland and Korea; data after EUROSTAT (2000b,c) are bold italic in parenthesis. *Waste management*: R/C, recycling + composting; I, incineration; L, landfilling; (*) Source: OECD (1998); (**) Source: EUROSTAT (2001c). *Mean values*: [aa]estimates (italic) based on the available data given in the respective columns (calculated by the authors).

member states. According to this source, the leading position in 1998–1999 was held by Denmark, the Netherlands and Switzerland (80–90%), Sweden, Belgium and Austria (over 75%), France, Luxembourg and Spain ($\geq 35\%$). Municipal waste composting continues to develop successfully in the EU member states (more information on composting and separate collection issues in view of the EU waste management strategy can be found in the Chapter VI.2 of this book).

This proves a substantial potential for municipal waste reuse, provided the selective collection of waste is adequately organized. A relatively high level of waste recycling and composting in North America (19% in Canada, 27% in the USA in mid-1990s) shows a good progress in this field. In a number of countries with weaker economies, the level of this attractive method of waste management is still low (from 0 to $< 10\%$), and greater progress is needed.

Another option for municipal waste management, which shows significant progress as a result of the implementation of waste management strategy in the developed countries, is incineration (see also Chapter VI.3 of this book). The preferences in the choice of this method of disposal are highly varied. In the most developed countries with a limited availability of land, it is used either as a predominant option (Japan, Luxembourg), or to a differing extent supported by a developed recycling/composting practice (Denmark, Switzerland, Sweden). In the EU, 24 (Belgium) to 66% (Luxembourg) of municipal waste was incinerated in 1998–1999, resulting in a significant reduction of landfilling. In the

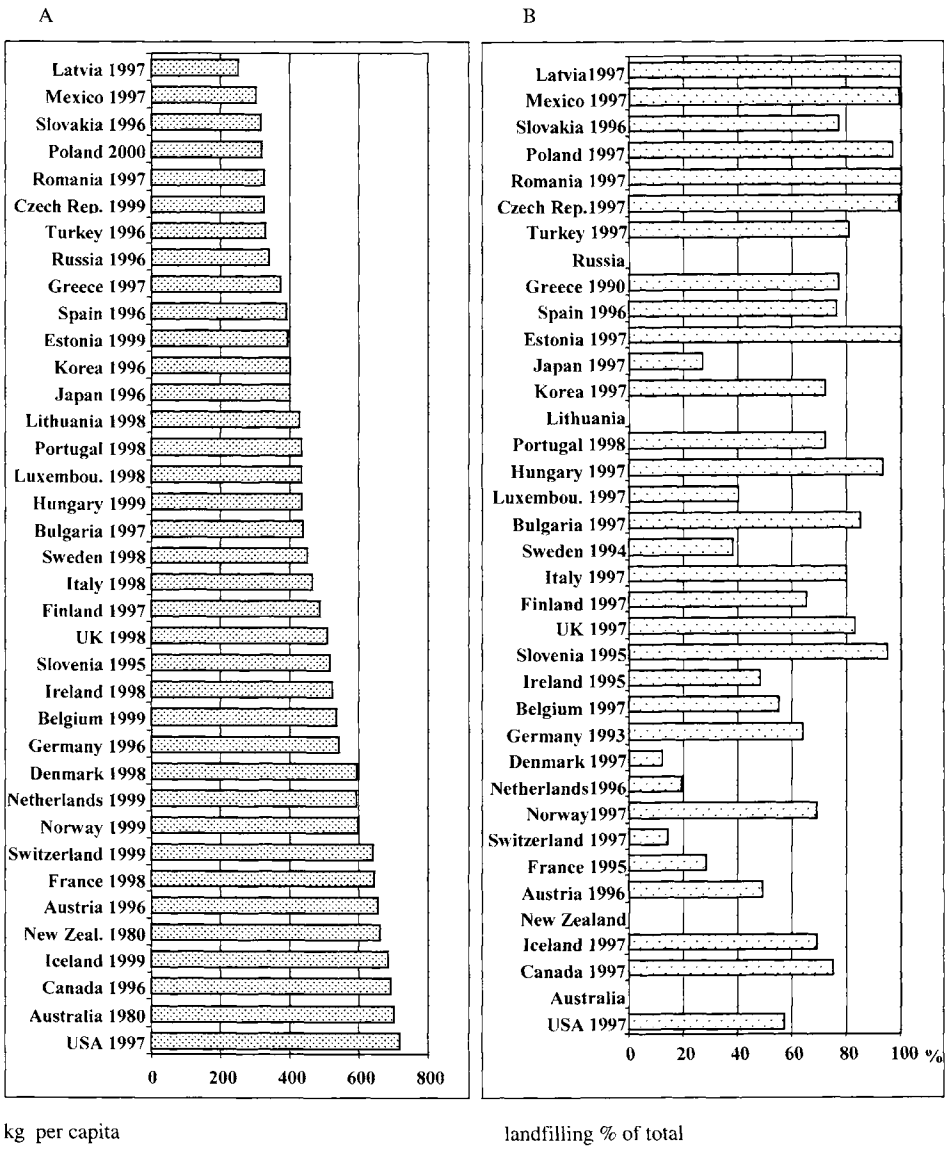


Figure II.1.4. Municipal waste generation and disposal in the OECD member states (after OECD, 1998, 1999 and EUROSTAT (2000a,b,c, 2001b)). Total amount exported for recycling: 3,959,974 t. Total amount imported for recycling: 4,481,983 t.

Netherlands, Belgium and Austria, recycling/composting was the major waste management practice (80, 50 and 47%, respectively).

The data from the beginning of the last decade of the 20th century report that over 70% of municipal wastes in North America and Western Europe were landfilled with little or no treatment (UNEP, 1992). Compared to these data, the present fast, though unequal progress is encouraging, considering the dramatic increase of the amount of municipal

waste per capita (Table II.1.5, Fig. II.1.4) (EUROSTAT, 2000b,c, 2001c; OECD, 2002). The latest available data show that the most frequent landfilling rates in the EU member states range roughly from 60 to 80% (e.g. Germany, Portugal) but can also be as high as 95–98% (Finland, Greece, UK). In the mid-1990s, the mean value for North America was 77%; of this in the USA it was 57%. According to the data derived from EUROSTAT (2001a), the mean value for landfilling municipal waste in the EU and associated countries in 1998–1999 accounted for 61% and ranged from 11 (Denmark) to 72–80% (Portugal, Spain, Greece, Italy). The countries where only a minor part of waste is landfilled (below 50%) have reached this level of reduction due to a concerted use of recycling, composting and incineration. These countries include Denmark (11%), Switzerland (21%), The Netherlands (20%), Sweden (33 %), Belgium (26%) and Austria (37%) and in non-EU countries, also Japan (27%), all have problems with land available for landfill siting. Of these countries, only Japan reached this low level of disposal onto land almost entirely due to incineration.

It should be underlined that non-hazardous waste disposal in adequately constructed and protected sites following the environmental regulations is also one of the options for municipal waste and remains the preferred method in a number of highly developed countries. It is accepted by the national policies and often influenced by a long-term expertise of environmental lobby groups, e.g. firms involved in safe landfilling coupled with production of usable energy (UK, Italy, Ireland). Also in economically weaker countries (Mexico, Czech Republic, Poland, Hungary and other Central and South European countries, Turkey, Greece, Portugal, Spain), landfilling predominates, being regarded as a cost-effective and environmentally safe method of disposal provided all the required protection measures are undertaken.

It has been recognized long ago (RCRA, 1976, 1984) that certain classes of land disposal facilities, in particular open dumps (landfills) and surface impoundments, are not capable of assuring long-term containment of certain waste, in particular large volume and HWs. Remedial actions in emergency cases are likely to be expensive, complex and time-consuming. In the USA, cleanup costs of the past mistakes are estimated at 10–100 times higher than the adequate controls on HW management (UNEP, 1992).

To solve waste management problems and develop a waste management strategy, besides paying particular attention to the proper management of HW, which constitute only 1.3% and municipal waste, which account for 9.0% of the total waste stream in the EU (see Chapter I.2, Tables I.2.1 and I.2.5), it is essential to manage properly the bulk of high-volume so-called "non-hazardous" waste, only a small part of them being inert waste. Long-term behavior of anthropogenic waste material exposed to atmospheric conditions, including material that is considered non-hazardous, is often difficult to predict precisely using general geochemical computer models (e.g. WATEQ 4F, MINTEQ, PHREEQC), so that in case of a false-negative prognosis, a substantial risk to human health and environment from the disposed wastes may occur in the long run. In the US and EU regulatory framework and regulations on waste, as well as in the respective guidelines, the general procedure, comprising environmental impact assessment (EIA), site design and construction in an environmentally safe way in the operational and post-closure stage, and local monitoring networks for detection and subsequent interception or remediation of contaminants before they degrade the ambient environment is to be followed.

II.1.2.3. Remediation and restoration of contaminated sites

In addition to designing and constructing new facilities receiving solid waste, already existing old and more recent facilities that are improperly performing so that they may pose risks to humans and the ambient environment are of concern. The historical development of industrialization in Europe and North America based on mining and metallurgy, followed by chemical industry, resulted in the creation of HW dumping sites in thickly populated areas. In the Central European countries, the problem of improperly constructed and managed dumping sites of solid waste from different industries existed until the end of the Soviet influence. Since the beginning of transformations of political and economical systems towards democracy and free market economy, most of these countries in their legislation on waste adopted the EU regulatory framework and developed adequate control and enforcement mechanisms. The unprotected dumping sites, both abandoned and partially still under operation, created a severe problem in the recent past, which is to be solved in the future. Effective implementation and enforcement of controls is greatly supported by well-trained enforcement administration and a high level of public awareness. The major difficulty in implementation of large-scale remediation and restoration programs is a weaker economical condition of a number of large industries and state budgets. Due to these limitations, the waste management strategies are focused on the proper operation of waste sites or optimum performance of current waste management practice, while the remediation and restoration of the old contaminated sites, where the polluter is frequently not available, is limited to the worst cases.

In the area of the former USSR (Russian Federation, Ukraine, Byelorussia and other new states) and in many developing countries the problem of improperly designed and constructed and badly managed hazardous and other solid waste sites is still a current practice, intensified by a poor economic status.

Risks to humans from toxic materials in contaminated sites derive from contaminated groundwater and airborne particulates and from direct or indirect exposure to contaminated soils. For many sites, radioactivity, explosion and fire are also major risks. Most of these sites also release toxic substances to various ecosystems through direct contact, leaching or runoff. Groundwater contamination at these sites has been the most difficult technical issue and represents a large part of cleanup costs. Groundwater contamination is perceived by the public as a major health issue and may present high risks at specific sites. It is also of concern because it degrades a natural resource and reduces its future uses. A recent NAS study estimated groundwater cleanup costs in the USA of up to US $1 trillion over the next 30 years, and concluded that existing technologies are generally not capable of effectively addressing the problem. Enactment of RCRA in 1976, the Superfund cleanup law in 1980, with the follow-up amendments, RCRA in 1984 and SARA in 1986 in the USA created a legislative basis for HW management practices, but at the same time revealed shortcomings of these programs. Extremely high costs of cleanup to a pristine condition and the low level of implementation of the current Superfund law results in the fact that of over 1200 Superfund sites, less than 1/6 had been cleaned up in the USA by 1994 (Reagan et al., 1994), and not much more progress has been achieved up to now. Besides the facilities receiving HW, other old facilities for solid waste disposal appeared to create a substantial contamination problem for groundwater, which since the 1980s, has loomed as a major environmental issue. In the mid-1970s, US EPA and the state

administrations became increasingly concerned that all waste disposal landfills, including those receiving non-hazardous waste under RCRA, may pose a threat to groundwater quality. There were 93,000 such landfills estimated in the USA. Of these, 75,000 were classified as industrial, and another 18,500 were municipal landfills. These sites invariably had anthropogenic surface impoundments that were problematic with respect to groundwater contamination. Most of them were unlined. About 40% of these facilities were located over unprotected aquifers currently or potentially used as a source of drinking water. Due to the lack of general knowledge, groundwater protection was not taken into consideration when these facilities were sited and constructed (EPA, 1984).

The European approach concerning sanitation requirements of old contaminated sites considers the realistic need of a quality-safe evaluation of such areas in order to take into account both interests of the environment and nature on one side and economy and industry on the other. In practice, this means that the site investigation, risk assessment and selection of remedial concepts is to be use- and site-specific, in accordance with criteria dictated by the defined protection objectives, which are determined by further use of the decontaminated area and corresponding human sensitivities. This approach applies to the presupposition that in the designing of the remedial concept, the required level of environment protection effectiveness is to be established first, and then the least-cost method of achieving it has to be determined (Twardowska et al., 1999). Evaluating the required method to achieve the desired level of effectiveness already involves the least-cost analysis, considering the cleanup to the not a pristine, but to the site- and use-specific level dictated by the sustainable development premises. This makes the cleanup program much more realistic and harmonized with the actual industrial and economic development of the region. Nevertheless, the costs of remedial actions are still very high, which results in the gradual evolving and implementing of cleanup programs.

II.1.2.4. Monitoring

Characterization and monitoring of toxic materials and pollutants released from waste and their pathways in all compartments of the environment are essential parts of the implementation and enforcement side of all waste disposal strategies. Without efficient and cost-effective monitoring technologies it is not possible to either initiate the most appropriate waste management/disposal and remediation activity or determine whether an actual decrease of risk can be achieved by either control or pollution prevention approaches. Effective monitoring used as a benchmark for residual risk reduction is essential in the waste management strategy. As an instrument of an actual short-term and long-term risk assessment from the solid waste disposal facility in an operational and post-closure stage, monitoring networks are utilized both in North America and in the EU countries in non-hazardous and HW sites screening and characterization. The comprehensive life cycle monitoring of landfills (both of solid and HW) is also included in the site characterization and evaluation of lining and cover (capping) performance, as well as in post-closure and remediation strategies. Monitoring thus plays an essential role in the implementation and enforcement procedures of the legislative framework. In the last decade, great advances have been made in the science and

technology associated with early warning monitoring of recoverable groundwater resources. Advanced cost-effective equipment and technologies, standardized techniques and expert systems to assist environment protection regulations of RCRA and Superfund in the USA and to support respective national and the EU legislation on waste have been developed (some of these issues are addressed in Chapter IV of this book). Further, fast advances in this field will create new opportunities for data collection and analysis related to waste management.

II.1.3. Waste management legislation and its implementation in the developing countries and new post-communist states

II.1.3.1. Major issues of solid waste disposal

II.1.3.1.1. Waste management issues in the developing countries

Developing countries face special problems in implementing waste management programs. They include generally poor control of pollution, lack of financial resources, shortage of trained resource personnel with technical and managerial skills and a low level of public awareness. Particularly severe problems and challenges have been created by rapid growth of urbanization and industrialization, not balanced by adequate environmental protection strategies, including the field of waste management. At the beginning of the last decade, UNEP pointed out instances of exporting extremely HW from developed countries to developing ones, which had neither the facilities nor the technical expertise to deal with (UNEP, 1992). These practices have been caused by the increased stringency of requirements for siting, constructing and managing waste disposal areas, stricter controls over waste disposal, in particular HW, and adequately increased costs of waste management that decrease the profits and competitiveness of the manufacturers in the internal and international markets. These practices are banned by international regulations (OECD Council Decisions (88)90 and C(92)39 Final; Basel Convention, 1989, in force since 1992) and are therefore considered illegal. These regulations have been supported by a number of EU regulations enacted since 1988 concerning transfrontier movements of HW to third countries, among them Council Resolution of 21.12.1988 (1989); Council Decision 97/640/EC (1997); Council Regulation (EEC) No 259/93 (1993) on shipments of waste within, into and out of the European Community, as well as Council Regulation (EC) No 1420/1999 (1999) establishing common rules and procedures to apply to shipments to certain non-OECD countries of certain types of waste. All these legal documents, along with decisions concerning the reporting obligations of the member states (1999/412/EC), and determining the control procedures under this Regulation (EC No 1547/1999) can be downloaded from the EU web site EUR-Lex (2003a). In face of the controls set out on the transfrontier movement of HWs, another trend, which successfully avoids these bans, appears to be much more dangerous. This trend is the massive shifting of production plants by manufacturers, in particular by international companies, from the native countries, where high labor costs along with stringent safety and environmental

regulations profoundly increase costs, to the developing countries. There they fully and legally use all the opportunities created by cheap labor, low safety requirements and either lack of legislative frameworks or weak and poorly executed legislation concerning waste management. In most cases, the fast industrialization of developing countries is due to the growing activity of such producers, who unrestrictedly use cheap solutions for dangerous waste materials disposal in these countries, usually landfilling them without any control. The rapid imported technological developments, proliferation of new materials and particularly HW do not meet the adequate level of development in the legislative, economical and educational arena. This may bring about unpredictably dramatic irreversible and long-term consequences to human health and the environment in these countries, which are usually rich in rare and extremely valuable species. Only occasionally is international public opinion shocked by emergency cases with great loss of life (e.g. the Bhopal case in India). Long-term environmental impact, in particular deterioration of groundwater resources and risk for human health from waste disposal sites, remains hidden from view. In these countries, governments, local administration and the common public concern themselves only rarely with HW being disposed off in unlined open dumps. Few know or really understand how seriously their health and resources have been compromised. The otherwise proper conclusion derived by UNEP (1992) that developing countries should move quickly to implement controls over waste disposal to avoid high cleanup costs in the future has no realistic basis to be actualized, though the increasing role of the Basel Convention in controlling illegal traffic of HWs, its activity focused on achievement of environmentally sound management of HWs (ESM) in developing countries through establishing the regional and sub-regional centers for training and technology transfer regarding the management of HWs and other wastes and the minimization of their generation, assistance in implementation of a model national legislation on the management of HWs, development and harmonization of national legislation, as well as improvement in national reporting and transmission of information, results in a visibly increasing awareness of parties to the Basel Convention towards the introduction and implementation of ESM. Nevertheless, in many cases national legislative frameworks of developing countries, if they are already enacted and exist, are not able to solve the problems posed by waste disposal, due to inadequate enforcement mechanisms. At this stage, the developing countries cannot be left on their own, and urgently need the harmonized support and assistance of the international legislative bodies to solve the environmental aspects of importing industrial investments into their countries, including waste management and in particular HW disposal. The international enactment of the environmental laws concerning export of industrial/ technological investments would also prevent international companies from using the disparity in standards set for waste disposal across the world and looking for countries where the environmental laws are the least stringent and enforced. Usually, the developing countries with the weakest economies, legislation and a low general educational level appear to be the most attractive targets for the import of technologies with savings on the costs of environmental protection. These countries are not prepared to solve the problems now, as imported new technologies are not harmonized with their natural development course and they will not also be able to bear the highly increased costs of remediation in future, considering that the USA and EU countries fail in attempts to implement their cleanup programs.

II.1.3.1.2. Waste management issues in the new states of the former USSR

The waste management problems in the new states that emerged from the former USSR are of different nature than those of the developing countries. The new states of the former USSR represent a rather high industrial and educational level and poor economic status (UNDP et al., 2000). They already have profound and often still not thoroughly understood environmental problems with the gigantic uncontrolled, unlined open dumps and impoundments, which resulted from their own unbalanced industrial development (Aksenov et al., 1999; Kitchilin and Ginzburg, 1999; Logatchev, 1999; Streltzov et al., 1999; Zoteev et al, 1999). These countries may also suffer further environmental damage due to their present bad economic situations, poor status of environmental legislation and actual lack of implementation and enforcement mechanisms. The attempts to mask the environmental problems in the Russian Federation are coupled with the lowest capital expenditure per capita for pollution abatement and control, which in 1996 accounted for US $11, 14 times lower than in Germany and over 5 times lower than in Poland. The optimistic situation is a systematically increasing trend, 10-fold compared to only US $1 in 1992 (OECD, 1998), as well as an enactment on 26 June 1998 of a Federal Law "On Wastes of Production and Consumption" in Russian Federation and recently also of the similar laws in several other new states that emerged from the former USSR (SBC, 2001a,b, 2002).

II.1.3.1.3. Common needs

It seems clear that developing countries and new states urgently need national control strategies, which provide legislation on waste, and a regulatory framework within which realistic enforcement procedures can be implemented. Some developing countries try to adopt legislative acts from the developed countries, producing in this way the most dangerous type of legislation, which is the "paper law" with a set of wishful thinking that cannot be implemented. Controls cannot be enforced if a choice of adequate facilities for treatment, disposal and recycling is not available, where there is no mechanism of collection and handling waste from small producers and households, where there are no properly trained enforcement officers, plant operators and managers, and where a legal enforcement procedure is not armed with an adequate incentive/penalty mechanism which exerts desirable effect on waste generators and holders. Waste control strategies in the developing countries should thus be carefully adjusted to the current conditions in each country and consider entirely and solely the realistic options which would work properly, without any gap between legislation and implementation.

In the case of import of industrial investments by foreign or international companies, also as joint venture with a local industry, in the waste management area, foreign/ international investors should follow the harmonized regulations to be evolved by the international legislative bodies similar to those for transboundary movement of waste by the OECD Council Decision C(92)39 Final and Basel Convention (1989, 1992). Now is the last moment when we can prevent severe and irreversible damage of the environment in the great part of the world resulting from the import of technologies while using the

least-cost choices in waste management because of the inadequate laws of developing countries. Experience shows that waste management practice follows the path of least regulatory control and least cost. It should be kept strongly in mind that "we could not expect firms to invest in technologies and to compete against unrestricted land disposal practices where cost alone is allowed to dictate the choice of management method and where a lack of proper regulation indirectly subsidizes the status quo" (Fortuna, 1989). These words written by a principal architect of the 1984 RCRA Amendments almost two decades ago are still fresh and applicable. We also should not expect developing countries to cope alone with the problem that overwhelms their abilities and to harmonize their regulations worldwide. The enactment of unequivocal international regulations on waste management related to the import of investments would greatly support developing countries in their efforts to establish national systems of waste disposal controls.

II.1.3.2. Waste disposal control options, pollution prevention, and information sources for industries in developing nations

According to the recommendations of UNEP (1992), "governments should establish a national system of waste disposal controls including legislation and regulatory framework, implementation and enforcement procedures, meaningful information on waste sources, and adequate facilities." It also seems clear that the legislative bodies must not create paper laws that cannot be implemented under the specific conditions of a given country. The major prerequisite is that the law must work, and therefore the analysis of different realistic applicable options, which can give the best environmental and public health effect, should be performed. Below, various alternative administrative waste control options, advantages and disadvantages are presented for consideration. These options include (1) no controls, (2) mandatory controls, (3) administrative control by industry, (4) individual control by industry, (5) collective control by industry, (6) joint administrative control by government and industry and (7) administrative control by government. Three alternative levels of control are addressed: (1) specified standard, voluntary compliance; (2) low standards, mandatory compliance; and (3) high standards, staged mandatory compliance. Options include ambient standards, discharge standards, prohibitions, disposal charges, licenses/permits, warrants, zoning and subsidies. This section briefly covers the advantages and disadvantages of four industrial waste control strategies: (l) cleaner fuels and raw materials, (2) improved production processes, (3) waste reclamation, recycling/reuse and (4) "end-of-pipe" treatment for suspensions.

The presented options include both the simplest like "no controls" and the most sophisticated ones, which have high capital and operating costs, need well-trained operators, managers and enforcement officers, and require well-equipped pollution control and monitoring systems and a high common life standard, level of education and public awareness. In general, the choice of option should be strictly adequate for the implementation/enforcement ability of the country. The "paper law" that is ignored due to the lack of means to execute it is more depraving than no law at all. Also all "voluntary compliance" options have a destructive effect and thus cannot be recommended.

Advantages and disadvantages of alternative industrial waste administrative control options.

Option	Advantages	Disadvantages
No controls	Popular with industry Short-term industrial growth No capital expenditures No regulatory agencies	Encourages uncontrolled use No incentive to reduce pollution Probable degradation of resources and public health. High capital costs are subsequently encountered
Mandatory controls	Prevents resources' waste Reduced contamination Prevents adverse effects Allows planning of resource use Increased employment due to construction and management of control devices and programs	Diverts capital Increases prices. Forced closing of inefficient plants
Administrative control by industry	Experts in control	Unrealistic to expect industry to police itself Industrial welfare takes precedence over public health
Individual control by industry	Compliance adjusted to achieve minimum loss	Unfair to small industries No control over dispersed industries
Collective control by industry	Considerable cost savings Group of experts control situation Avoids duplication	Needs legal incentives
Joint administrative control by government and industry	Best potential of technical and administrative personnel Equitable internal plant and external land control Mandatory compliance with some industrial control Total environmental, industrial and resource control	New administration required, tends to create dissension Results in debates and compromises caused by conflicting interests
Administrative control by government	Represents society Administrative apparatus already exists Enforceable incentives and penalties insure compliance Enables total resource control Better ultimate quality of life Traditional separation of government and industry	Unpopular with industry Potentially higher short-term cost Political infighting with possible increases in bureaucracy

Advantages and disadvantages of alternative levels of waste control.

Option	Advantages	Disadvantages
Specified standards, voluntary compliance	Simple No red tape or constraints No public effort required Minimum opposition from industry	Almost completely ineffective Politically damaging if public realizes its failure Politically damaging if public realizes its failure Allows virtually unchecked natural resource exploitation and waste disposal
Low standards, mandatory compliance	Achieves some degree of pollution control Least objectionable to industry	Cost of implementation and administration Slows some waste of resources Environmental deterioration remains unchecked
High standards, staged mandatory compliance	Environmental deterioration checked or prevented Maximum long-term resource economic conservation	Industrial opposition Capital costs may be large Costs for administration, requires technical personnel

Advantages and disadvantages of selected regulatory strategies.

Option	Advantages	Disadvantages
Ambient standards	Allows range of alternatives A basis for a comprehensive control program Monitoring indicates when levels are dangerous	Requires monitoring of the environment Encourages increased pollution in clean areas
Discharge standards (uniform)	Relates directly to environmental quality Simple program which can be the basis for other programs Definite pollution limits Direct, effective guideline for safe discharges	Requires administration and enforcement Industries may not be able to meet the standards Variable standards may be more equitable Ignores cost effectiveness Enforcement requires individual firms to be monitored

(*continued*)

Option	Advantages	Disadvantages
Prohibitions	Stops further pollution Simple administration and monitoring Necessary for toxic wastes	May cause permanent or temporary closings
Disposal charges	Costs are internalized Decision-making is decentralized Least-cost method of control which relies on market stimulation	Industrial opposition Some delay inequities inevitable Relating the charge to pollution is difficult Low disposal charges may become an accepted cost
Licenses	Prevents operation of polluting plants Enforces compliance before pollution occurs Encourages periodic review	Requires monitoring to ensure compliance
Warrants	Controls ambient quality by limiting number and quality	Awards favor financially strong firms Other firms may be forced to close Restricts industrial development rather than encouraging better waste management
Zoning	Forces industry to locate in suitable areas Protects sensitive areas Allows separation of industrial and municipal waste Economical, effective treatment and control Simple enforcement	Can supplement need for treatment or pollution controls Permitted area may be uneconomical Development of zoning difficult
Subsidies	Cost of cleanup not a burden to any one society Bases problem for smaller industries Easy to administer	Difficult to determine optimum payment Contrary to the "polluter pays" principle Increased taxes possible Does not encourage cost efficiency Imposes burden on government No incentive to use most cost-effective treatment, equipment or method Encourages end-of-line treatment rather than process change and recovery methods

Advantages and disadvantages of industrial strategies to control pollution.

Option	Advantages	Disadvantages
Cleaner fuel/raw materials	Reduces pollution through prevention Reduces need for waste treatment Less costly and more effective than treatment methods	Substitutes may be in short supply, more costly and/or less suitable
Improved production processes	Conserves limited resources Reduces pollution through prevention Reduces need for waste treatment More effective manufacturing methods also can reduce polluting waste	Processes which reduce pollution may increase costs or reduce efficiency Additional costs may be higher than those of waste treatment
Waste reclamation (recovery, recycling, reuse, by-product use)	Conserves limited resources Increases public relations May reduce costs, pay for itself or return a profit Eliminates need for permits Eliminates need for monitoring Eliminates need for reporting	May be more expensive than waste treatment Not technically or economically feasible for all pollutants
End-of-pipe liquid waste treatment	Conventional treatment methods readily available for most pollutants Effluent waste collectively treated in municipal or industrial waste treatment systems Technology well developed	Residues remaining after treatment need disposal Pollution only reduced, not eliminated Can be expensive if retrofitting is necessary Waste resources

Advantages and disadvantages of solid waste disposal methods.

Option	Advantages	Disadvantages
Ocean and lake dumping	Usually cheap and easy	Contaminates fish and aquatic plant life Introduces toxic pollutants into the food chain Unsightly and damaging to tourist trade Lake dumping may endanger drinking water supply

(*continued*)

Option	Advantages	Disadvantages
Open land dumping	Usually cheap and easy	May contaminate air and water (surface and groundwater) Harbors disease-carrying rodents, insects and micro-organisms Unsightly and odorous Source of toxic leachates
Open burning	Usually cheap and easy	Causes air contamination Odorous and unsightly
Sanitary landfilling	Accepts most types of waste Produces little air pollution and odor Less groundwater pollution than open burning and dumping Can be used for land reclamation Minimizes hazards caused by organic wastes Economical and easy to operate	Nearby residents may object Requires careful maintenance Completed landfills continue to settle and can produce methane gas and toxic leachates for many years Soil cover material may be difficult or costly to acquire
Incinerating	Requires little land Process is rapid Does not require long hauling	Causes air pollution, some possibly toxic if the most advanced technology is not used Unsuitable for many wastes, needs selection or selective collecting Residues require disposal Pollution control and heat recovery systems are very costly Nearby residents usually object Usually located close to solid waste sources and therefore tends to affect larger populations than other disposal methods

Experience shows that regulatory strategies based on prohibitions are also not effective and do not encourage industries to seek optimum solutions for waste management, if the only enforcement instrument is the threat of closure. Usually, as this measure adversely affects the employees not responsible for posing pollution or health hazards, closing is applied in emergency cases, when severe damage to the environment or human health has already occurred. It does not have any preventive or discouraging effect, as such cases are relatively rare. Thus, this regulatory instrument may be considered as "close to none".

For the developing countries, the method of small but firm steps forward in setting and enforcement of staged national waste management law based on the thorough ability of execution at the current stage of development seems to be the best option, e.g. lower standards and mandatory compliance may be a legally accepted level of control if high standards cannot be achieved or controlled.

The principle of financial responsibility of waste generators or holders for its disposal has proven to be the most effective enforcement instrument. It assures the best and instant response through seeking ways to minimize waste production by improvement of technology, waste recycling and reuse, or render them less hazardous. The charges for waste disposal can be used for providing the necessary equipment, training of enforcement officers and environmental education, as well as improving the environment in the communities (e.g. construction of environmentally safe sanitary landfills or organizing proper waste collection systems). The application of this instrument should be given high priority because of its link to sustainable development, i.e. to a mutual support of a clean environment and economic growth. The system of charges must be well thought over, to relate adequately the charge to the level of hazard posed by waste and its reuse or recycling properties. The charges have to encourage better waste management and cannot be either too high to sustain nor too low to become an accepted cost.

An important part of a sound waste management strategy in developing countries, similar to that in the developed states, is a two-way communication with the public and a direct community involvement in all aspects of the environmental decision making process supported by free access to reliable information about sources and levels of environmental pollution and hazards from the waste disposed off in the community.

Foreign companies siting industrial plants in developing countries and called here "import of industries", with respect to waste management, in particular HW disposal, are to follow stringent regulations of developed countries, e.g. based on the EEC Council Directive 91/689/EEC (1991) or the RCRA and adequate guidelines, to be imposed on them by the competent international bodies (OECD Council, Basel Convention). These companies are to bear all the capital and running costs of the waste disposal facilities, which have to meet the stringent international regulatory requirements, as well as financial and legal responsibility for their proper management. They have to establish monitoring to provide information about the effectiveness of environment protection measures at the disposal sites and to eventually track the concentration and impact of toxic substance releases to the environment. If required, they have to undertake corrective remedial actions to intercept pollution and eliminate hazard to the environment and human health. The compliance with international regulations is to be supervised by the bodies that enacted the regulation in cooperation with the national governmental administrative apparatus in the host country where the plant is sited. This way, the environmentally controlled import of industries to the developing countries due to high expertise and technical/technological abilities of the international companies can become an effective instrument of sustainable development, instead of posing threat to the environment of the host nations.

Through collaboration of international and governmental sectors, this optimized waste management strategy should assure the achievement of the required level of sustainable development that is required for both the environmental protection and economic growth of the developing countries.

II.1.4. Effect of international regulations on the control of the transboundary movement of hazardous waste

As has been shown above, in some areas national legislation is not able to solve the broader problems posed by waste disposal. In these cases, their effort is or should be supported by the international conventions. An international mechanism to control transfrontier movement of waste destined for recovery operations within the OECD area has been implemented on the basis of the OECD Council Decision OECD C(92)39/Final. According to the available recent data (OECD, 1998), export/import of HW within this area was almost totally balanced and accounted for 1170.5 thousand tons (export) and 1174.1 thousand tons (import) that comprised 0.4% of the total generated amount. Import exceeded export for 8.5 thousand tons, which is a negligible part of the total HW stream. Within the EU area, import exceeded export by 231.7 thousand tons and accounted for 1021.3 thousand tons (see Table I.2.4, Chapter I.2). The amount exported comprised 2.7% and imported 3.4% of the total amount of HW generated. The biggest waste importers are France, Belgium and Mexico; the biggest exporters are Germany, Luxembourg and the USA. The export accounts for 100% of waste generated in Luxembourg, 5.7% of the total waste stream in Germany and only 0.07% of HW generated in the USA (the USA appears to produce 79.2% of the total OECD HW stream and over 7 times more than the European Union, which illustrates the scale and importance of the HW management in this country). Within the OECD countries, information concerning HW generation and transboundary movement has been greatly improved. The directions of major waste import to the most developed EU countries, which are well prepared regulatory, technically and technologically for environmentally safe waste reuse and disposal, indicates that in the OECD area transboundary movement of HW is effectively controlled by the OECD regulations.

The Basel Convention (1989/1992) is aimed at limiting the international shipment of HW, in particular from OECD countries to non-OECD countries. In 1989, it was ratified by over 100 countries and the European Economic Community (EEC), and in 1992 entered into force. By June 2002, the Basel Convention was ratified by 151 parties. The Basel Convention provides the major international regulations that protect against the unrestricted import of HW to the developing nations, which have neither facilities nor expertise in dealing with it (more information about the Basel Convention and its implementation is given in Chapter II.2). The analysis of generation, export and import of HWs and other wastes by Y-codes carried out by the Secretariat of the Basel Convention for the years 1993–1999 on the basis of data provided by 18 of 101 parties of the Convention for 1993 and by 36 of 151 parties for 1999 that gave some rough idea about the structure, use and disposal of the imported/exported HWs and other wastes, has been presented in Chapter I.2. Of these HWs, only seven are ultimate solids, the rest represents solvents, solutions, emulsions and mixtures, which reflects the difference in definitions of HW: according to the RCRA, HW must be solids (though the interpretation of this term shows that in many cases a waste often is not an ultimate solid – see Appendix A to Chapter I.2), while there is no such criterion in the Basel Convention or the EU list of waste (Commission Decision 2001/118/EC, 2001, amending Decision 2000/532/EC, 2000; Basel Convention, 1989/1992 as of July 1999). The major part of the transboundary movement of HW among all reporting parties in 1999 was reported to be used for

recycling operations (49% of total amount exported and 71% of total amount imported) (Fig. II.1.5). Most of the exported and imported HW shipped for recycling operations was going for recycling/reclamation of metals and metal compounds R4, other inorganic materials R5 and catalysts R8. The next highest amounts of exported HW were directed for solvents reclamation/regeneration R2, recycling/reclamation of organic substances R3 and regeneration of acids or bases R6, and in lesser amounts for generating energy R1. The remaining minor amounts were distributed among seven different operations. A high percentage of imported wastes was recycled by unspecified operations (Fig. II.1.6).

Disposal operations comprised 11% of the total amount exported and 27% of the total amount of wastes imported. Predominant disposal operation for exported wastes was declared to be incineration, while most of imported waste was reported to be directed to landfilling, in lesser amounts to incineration and landfilling in the specially engineered landfills; other disposal operations comprised minor amounts of waste (Fig. II.1.7)

The statistical data obtained by SBC from the reporting parties display substantial inconsistencies: (i) there is 1766 thousand tons (22% of total) discrepancy between export and import; (ii) of the total amount exported, 3251 thousand tons, i.e. 40% of total, was directed to unspecified operations; (iii) there are striking differences between the amounts of exported and imported wastes directed for different recycling/disposal operations as declared by the reporting parties.

The incompleteness of information and difficulties in obtaining accurate data require that the charts, which have been presented above, have to be considered with a great deal of caution. This shows that the level of protection that has been reached in the control of shipment of HWs between the OECD member states is still far from being achieved by the parties of the Basel Convention. The diversity of the general development, lack of a reliable or any information on waste generation and on trends in the quantity and

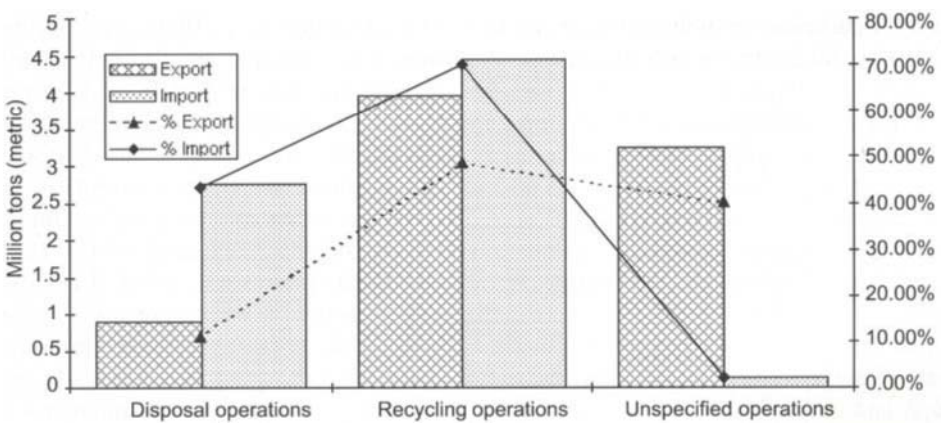


Figure II.1.5. Transboundary movement of hazardous wastes and other wastes by operations among all reporting parties in 1999 (after SBC, 2001b). Explanation of R-codes (Annex IVB of the Basel Convention – see Chapter II.2, Appendix A): R1 – generating energy; R2, R3, R6 – solvents, organic substances, acids or bases; R4, R5, R8 – metals, other inorganics, catalysts; R7, R10, R11, R13 – residual materials; R9 – re-refining/other reuse of used oil; R – mixed R operations. Total amount exported: 8,104,960 t. Total amount imported: 6,338,474 t.

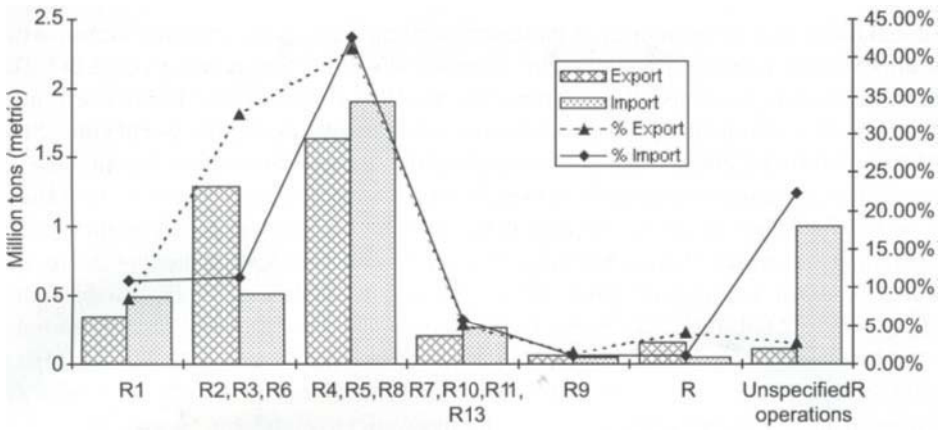


Figure II.1.6. Transboundary movement of hazardous wastes and other wastes for recycling among all reporting parties in 1999 (after SBC. 2001b). Explanation of D-codes (Annex IVA of the Basel Convention – see Chapter II.2, Appendix A): D1, D2, D4 – landfill, land treatment, surface impoundment; D3, D12 – deep injection, underground storage; D5 – specially engineered landfill; D8 – biological treatment; D9 – physico-chemical treatment; D10 – incineration on land; D13, D14, D15 – blending, repackaging, interim storage, the amounts for mixed D wastes are not included because of their negligible value. Exports for mixed D operations: 2200 t; imports for mixed D operations is not included because of its negligible value: 6.2 t. There was no import for unspecified D operations. Total amount exported for disposal: 893,649 t. Total amount imported for disposal: 1,727,591 t.

composition of waste streams, disparity in terminology, legislative framework and the regulatory/enforcement mechanisms create significant difficulties in controls of transboundary waste movement between the OECD and the developing countries. Nevertheless, the considerable progress in the control of transboundary HW shipment to developing countries is unquestionable, to a great extent due to activities of the Basel Convention in the field of statistics, reporting and transmission of information.

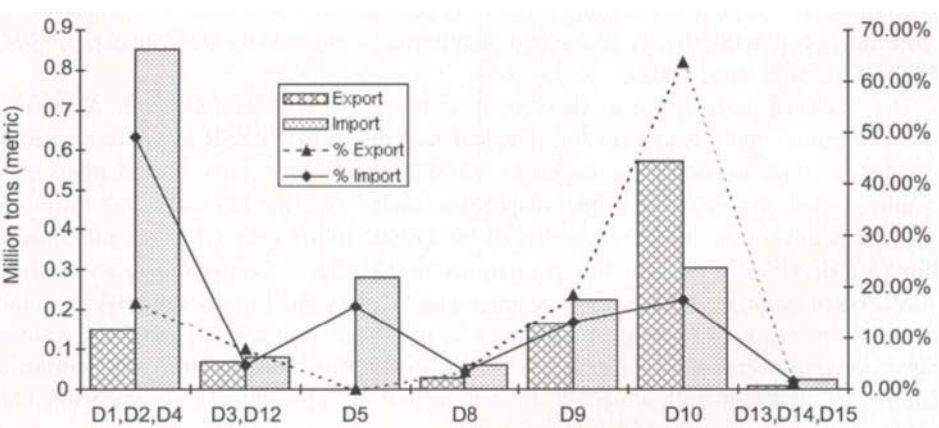


Figure II.1.7. Transboundary movement of hazardous wastes and other wastes for disposal among all reporting parties in 1999 (after SBC, 2001b).

Continuously increasing number of parties responding to the questionnaire "Transmission of Information" reflects a trend in improved national reporting by parties to the SBC. This information that is compiled and issued by the Secretariat of the Basel Convention significantly contributes to the development of statistics on wastes worldwide (SBC, 2000a,b, 2001a,b, 2002). Many activities of the Basel Convention are focused on optimizing mechanisms to achieve the major aim of control of transboundary movements of HWs and their disposal. Among these activities, the progress in unification of terminology on waste, characterization of hazard from waste, development of the revised Model National Legislation (SBC, 1995) and the developments in the establishment of Regional and Sub-regional Centers for Training and Technology Transfer, transmission of information on transboundary waste movement under the Convention and exchange of information between parties of the Convention on national legislation, statistics and waste management practice can be considered the most effective and spectacular ones (SBC, 1996; Basel Convention Statistics, 2002; Basel Convention Publications, 2002).

The revised version of the Model National Legislation developed by the Convention (SBC, 1995) provides assistance to states to take appropriate legal, administrative and other measures to implement and enforce the provisions of the Basel Convention. It comprises the elements for inclusion in legislation for the management of HWs and a draft model national law on the control of transboundary movements of HWs and other wastes and their disposal (SBC Legal Working Group, 2002 update).

The elements for inclusion in legislation on the management of HWs and other wastes specify the aim, the authority responsible for implementation of a law in this regard and its obligation, as well as the control of the management and monitoring of the generation of HWs and other wastes. The model national law on the control of the transboundary movements of HWs and other wastes and their disposal sets out the aim of the national legislation, defines relevant terms, provides for the establishment of a regulatory authority and addresses export, import, transit and illegal traffic issues in HWs and other wastes. The aforementioned activity of the Basel Convention tends thus to harmonize national laws and definitions related to waste management and the transboundary movement of HW and other waste. It is aimed at assisting developing countries in elaborating a national law on waste and in following strictly all the tight requirements imposed by the Convention (SBC, 2000b; SBC web sites, 2002).

The lack of access of a significant number of African, Central American, Asian/Oceania countries and several new states of the former USSR to the international convention aimed to control the shipment of HW to developing countries endangers them by unrestricted import and improper disposal of such waste (the USA also has not joined the Basel Convention, but as a member of the OECD follows the OECD regulations on shipment of HW). Although the regulations of the Basel Convention also consider protection of non-party countries by a statement, "a party shall not permit HWs or other wastes to be exported to a non-party or to be imported from a non-party," the granted transfrontier movement of wastes between its signatories and the non-party countries requires a stringent follow-up of an administrative procedure and a documented justification of the exporting country of the necessity of export and a proper management of waste by the importing country (for more information about the Basel Convention, see Chapter II.2 of this book).

II.1.5. Conclusions

Despite the substantial, though uneven progress in waste management in the last decade, in particular in the EU and the OECD member states, the harmonization of waste terminology, completeness and reliability of statistics, the level of minimization of a waste stream through reuse/recycling and reduction of a waste disposal in landfills on land still cannot be considered satisfactory. A relatively low mean level of reuse of such thoroughly recyclable waste materials as paper and glass in the OECD area makes groundless the suggestions to exclude recyclable waste materials from the definition of waste.

The unrealistic legislation on waste along with weak enforcement mechanisms and the "import of industries" by international companies, which use a lack of proper regulations for choosing the cheapest waste management solutions, results in open uncontrolled dumping of hazardous and other wastes and gives rise to current and future pollution problems in the developing countries. The staged waste management strategies, which provide for a legislative and regulatory/enforcement framework, carefully adjusted to execution ability along with setting international regulations over waste management in "imported industries" by a Convention similar to the Basel Convention, would create effective instruments for the sustainable development of these countries.

While OECD regulations seem to significantly improve the control over the transfrontier movement of HW within the OECD, the Basel Convention faces bigger problems with providing the same protection to developing countries. Besides generally poor control of pollution, weak economies and shortage of trained technical, managerial and enforcement personnel, the disparity in national definitions and the difficulties in obtaining accurate data from the developing countries – signatories of the Convention – have a generally lower efficiency of controls over transboundary movement of waste and a scarcity of reliable information about the quantity and composition of waste streams between the parties and non-parties of the Convention. The activities of the Basel Convention in providing tools for evaluating the hazard posed by wastes, developing and spreading the revised model national legislation on waste management and establishing regional centers for training and technology transfer are aimed to achieve harmonized legal basis in the signatory countries for adequate progress in the environmentally safe waste management at the national and global level. Still existing substantial discrepancies between national and international waste management regulations and directives bring about an urgent need for a better integration and harmonization of policies as a prerequisite of an integrated regional and global strategy focused on the environment protection and conservation of the natural resources and energy. This should be considered as a first priority task in the field of waste management.

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Chapter II.2
The Basel Convention and its implementation

Iwona Rummel-Bulska

II.2.1. Introduction

In the late 1980s, a dramatic increase in the costs of hazardous waste disposal due to a tightening of environmental regulations in industrialized countries led to searching for cheaper solutions through shipping hazardous waste to developing countries and to Eastern Europe that had no adequate legal protection against these practices. When "toxic trade" was revealed, international will to prevent this activity resulted in the drafting and adoption of the Basel Convention.

The Basel Convention is first and foremost a global environmental treaty that strictly regulates the transboundary movements of hazardous wastes and provides an obligation for Parties to ensure their environmentally sound management (ESM) and their disposal.

The Basel Convention was adopted unanimously in 1989 by the 116 States participating in the Conference of Plenipotentiaries, which was convened by the United Nations Environment Programme (UNEP). The final act of the Basel Conference was signed by 105 States and the European Economic Community (EEC).

The Basel Convention, which entered into force on 5 May 1992, has proven to be an effective international Convention. The increasing number of Parties – 151 States and the member states of the European Union as of 19 June 2002 – is recognition from the international community of the importance of the Convention (Basel Convention – UNEP, 2002).

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (1998 update) represents new norms, rules and procedures in laws governing the movements and disposal of hazardous wastes at international as well as at national levels. This instrument represents the intention of the international community to solve this global environmental problem in a collective manner. The governing body of the Basel Convention is *the Conference of the Parties (COP)* that is composed of all governments that have ratified the Convention or acceded to it. Currently there are five subsidiary bodies of the COP that have different mandates covering relevant fields of activities, namely:

- *The Working Group for the Implementation* – to review the main activities and documents under the Basel Convention before they are adopted by the COP.
- *The Technical Working Group (TWG)* – to prepare technical guidelines for the ESM of hazardous wastes and for disposal options.

- *The Legal Working Group (LWG)* – to study the issues related to the establishment of a mechanism for monitoring the implementation of and compliance with the Convention.
- *The Joint Meeting of the Technical and Legal Working Groups* – to debate issues, which have relevance to both the technical and legal aspects of a number of issues.
- *The Bureau* composed of actual and previous Bureau members of the COP – to provide general policy and general operational directions to the Secretariat between meetings of the COP.

Institutionalization of the national activities and international cooperation was needed to address the growing generation of hazardous wastes and their transboundary movements. Precise estimates of hazardous waste generation in the world have not yet been established. In accordance with estimates of the Secretariat of the Basel Convention (SBC), there are over 400 million tons of hazardous wastes generated each year. A large amount of hazardous wastes crosses national frontiers. A large volume of these movements used to come and go and is still going on from industrialized countries to developing countries as well as to countries in Eastern and Central Europe. The Basel Convention represents a first step in defining the global means to reduce and strictly control the movements of hazardous wastes and to ensure that these wastes are disposed of in an environmentally sound manner. It provides realistic measures to strengthen the protection of the global environment from the possible harmful effects of the transboundary movements of hazardous wastes and their disposal. It focuses on the protection of health and the environment. It includes the obligation to reduce the generation of hazardous wastes to a minimum and to ensure that each country has the sovereign right to ban the import of hazardous wastes into its territory. It also prohibits the export and import from and to non-Parties to the Convention unless such movement of hazardous wastes is subject to bilateral, multilateral or regional agreements or arrangements whose provisions are not less stringent than those of the Basel Convention. It requests that hazardous wastes should be disposed of as close as possible to their source of generation and that transboundary movement of hazardous wastes could only be allowed if it is carried out in accordance with the strict control system provided by the Convention, which includes prior informed consent by the importing country as well as by the transit country.

Transboundary movements of hazardous wastes carried out in contravention are to be considered illegal traffic and a criminal act.

The Basel Convention calls for international cooperation between Parties in the ESM of hazardous wastes and the improvement of national capabilities to manage hazardous waste in an environmentally sound manner as well as for the development of a technical and legal infrastructure including legislation and regulations needed, which should be undertaken by countries, in particular developing countries. Training, education and public awareness are considered to be important elements in the development of the countries' capability. Where a lack of resources is observed, technical assistance should be provided through the SBC.

The arena of international environmental law is dynamic. The Basel Convention has already developed after the first, second, third, fourth and fifth, tenth anniversary meetings of the COP held in Uruguay in December 1992, in March 1994 and September 1995 in Geneva, in February 1998 in Kuching, Malaysia, and in December 1999 in Basel, Switzerland, where a number of Decisions and Amendments were adopted by the Parties

for the implementation of the Convention. Official documents for meetings of the COP and its subsidiary bodies and other publications and documentation are available in the Official Web site of the SBC.

One could see from an analysis of these Decisions that the Basel Convention is already developing into the legal international act dealing not only with the control of transboundary movements of hazardous wastes but also involving on a larger scale the problem of their environmentally sound disposal as well as technical assistance, mainly through the establishment of a training system and technology transfer centers and through the building of public awareness. The Convention is to be developed further by the ratification of the Basel Protocol on Liability and Compensation for Damage resulting from the Transboundary Movements of Hazardous Wastes and Other Wastes and their Disposal adopted at the fifth meeting of the COP in December 1999. The Protocol was opened for signature until 10 December 2000 and was signed by 13 Parties to the Convention. In order for the Protocol to enter into force, 20 Parties to the Basel Convention must ratify, accede, approve, accept or formally confirm it.

II.2.2. Basel Convention 1989/1992

II.2.2.1. Main principles and provisions

The Convention recognizes that the most effective way of protecting human health and the environment from the danger posed by such wastes is the reduction of their generation to a minimum in terms of quantity and/or hazard potential. This is the underlying philosophy behind the objectives set in the Convention together with the ESM of the hazardous wastes nonetheless generated. In this respect, the Basel Convention stipulates that three main interdependent and mutually supportive goals have to be fulfilled:

- Transboundary movements of hazardous wastes should be reduced to a minimum consistent with their ESM.
- Hazardous wastes should be treated and disposed of as close as possible to their source of generation.
- Hazardous waste generation should be reduced and minimized at the source.

In conjunction with these goals:

- Every State has the sovereign right to ban the import of hazardous wastes. The Parties to the Convention shall not allow any transboundary movement of hazardous wastes to a State that has prohibited their import. Transboundary movements shall also be prohibited if the exporting State has reason to believe that the wastes in question shall not be managed in an environmentally sound manner.
- A Party shall not permit hazardous wastes to be exported to a non-Party or to be imported from a non-Party, unless it is in accordance with a bilateral, multilateral or regional agreement, the provisions of which are no less environmentally sound than those of the Basel Convention.
- The State of export shall not allow a transboundary movement of hazardous wastes to commence until it has received the written consent, based on prior detailed information of the State of import, as well as of any State of transit.

- When a transboundary movement of hazardous wastes that is carried out in accordance with the Convention cannot be completed in an environmentally sound manner, the State of export has the duty to ensure the re-importation of the wastes.
- Transboundary movements of hazardous wastes that do not conform to the provisions of the Convention are deemed to be illegal traffic. The Convention states that "illegal traffic in hazardous wastes is criminal". The State responsible for an illegal movement of hazardous wastes has the obligation to ensure their environmentally sound disposal, by re-importing the wastes or otherwise. Every Party shall introduce national legislation to prevent and punish illegal traffic in hazardous wastes. Several sets of technical guidelines to assist developing countries in the implementation of the Convention and in ESM of hazardous wastes were adopted. Others were prepared by the TWG and adopted at the meetings of the Contracting Parties.

II.2.2.2. Definitions and obligations

- The Basel Convention defines "wastes" as *substances or objects that are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law*. Hazardous wastes that are subject to transboundary movement will fall under the scope of the Convention if they *belong to any category contained in Annex I to the Convention provided that the wastes in question exhibit one or more of the hazardous characteristics listed in Annex III to the Convention and are disposed of by any operation specified in Annex IV to this Convention or if they are defined as such in the national and domestic legislation of the Party of export, import and transit* (see Appendix A). Every Party has the sovereign right to include in its national or domestic legislation other wastes that it considers hazardous in addition to those referred to in the Annexes to the Convention and to make any subsequent changes. The Secretariat shall inform all Parties of this information.
- Wastes that belong to any category contained in Annex II, namely: wastes collected from households and residues arising from the incineration of household wastes are covered by the Convention as "other wastes".
- Wastes, which, as result of being radioactive, are subject to international control systems, including international instruments, applying specifically to radioactive materials, are excluded from the scope of this Convention. Referring especially to this part in definition of the Conference of the Contracting Parties at its meeting in 1994 welcomed the preparation by the IAEA Diplomatic Conference (1997) of a draft Convention on Safety of Management of Radioactive Wastes and requested the SBC to continue its cooperation with the IAEA in particular in the preparation of a draft Convention on Safety of Management of Radioactive Wastes particularly in relation to the question of the inclusion of low-level radioactive wastes in its scope.
- Excluded from the scope of the Convention are wastes that derive from the normal operations of a ship.

The scope and provisions of the Basel Convention as well as the Decisions adopted by the COP do not make a distinction between hazardous wastes generated by military establishments and the same wastes generated from non-military sources.

The Basel Convention clearly specifies that it is the specific characteristics and composition of the wastes that will make them hazardous or non-hazardous, irrespective of the qualification of the source of generation. The principal purpose of the strict control system operated under the Basel Convention is to ensure the ESM of hazardous wastes whatever the place of generation, treatment, storage, recovery, and final disposal.

Each Party may totally or partially prohibit the import of hazardous wastes for disposal within its national jurisdiction and shall inform each other through the Secretariat of such decisions. Parties shall prohibit or not permit the export of hazardous wastes to the Parties, which have prohibited their import. In the case where that State of import has not prohibited the import of the particular waste, Parties shall prohibit or not permit the export of hazardous wastes if the State of import does not consent in writing to each specific import (see procedures below).

Parties shall not allow the export of hazardous wastes to a Party or shall prevent the importation of a hazardous waste if it has reason to believe that the waste will not be disposed of in an environmentally sound manner. Exports of hazardous wastes to a non-Party or imports from a non-Party are prohibited. Exports of hazardous wastes for disposal shall not be allowed within the area south of 60 South latitude, whether or not such wastes are subject to transboundary movement.

Parties shall also require that information about a proposed transboundary movement of hazardous wastes be provided to the States concerned according to the procedures provided in the Convention in order to state clearly the effects of the proposed movement on human health and the environment. They shall also require that hazardous wastes that are to be subject to transboundary movement be packaged, labeled, and transported in conformity with generally accepted and recognized international rules and standards in the field of packaging, labeling and transport, and that due account is taken of relevant internationally recognized practices. Transboundary movements shall also be accompanied by a movement document from the point of commencement to the point of disposal. Parties shall designate or establish one or more competent authorities and one focal point. These and any changes there of shall be informed to the Secretariat.

The state of export shall notify, or shall require the generator or exporter to notify, in writing, through the channel of the competent authority of the State of export, the competent authority of the State of import and transit of any proposed transboundary movement of hazardous wastes. The notification shall contain the declarations and information specified in the Convention, written in a language acceptable to the State of import.

The State of export shall not allow the generator or exporter to begin the transboundary movement until it has received written confirmation that the notifier has received the written consent of the State of import, and the notifier has received from the State of import confirmation of the existence of a contract between the exporter and the disposer specifying ESM of the wastes. Each State of transit, which is a Party, shall promptly acknowledge to the notifier receipt of the notification and may then respond in writing, within 60 days, consenting to the movement with or without conditions, denying permission for the movement, or requesting additional information.

The State of export may, subject to the written consent of the States concerned allow the generator or the exporter to use a general notification where hazardous wastes having

the same physical and chemical characteristics are shipped regularly to the same disposer via the same customs office of exit of the State of export, via the same office of entry of the State of import, and, in the case of transit, via the same customs office of entry and exit of the State or States of transit. The general notification and written consent may cover multiply shipments during a maximum period of 12 months.

The State of import shall respond to the notifier in writing, consenting to the movement with or without conditions, denying permission for the movement, or requesting additional information. A copy of the final response of the State of import shall be sent to the competent authorities of the Parties concerned. If the import is allowed, the importer must inform both the exporter and the authority of the State of export of its receipt of the wastes, and of the completion of disposal as specified in the notification.

The Parties shall require that each person who takes charge of a transboundary movement sign the movement document either upon delivery or receipt of the wastes in question. They shall also require that the disposer inform both the exporter and the competent authority of the State of export of receipt by the disposer of the wastes in question and, in due course, of the completion of disposal as specified in the notification. If no such information is received within the State of export, the competent authority of the State of export or the exporter shall so notify the State of import.

The notification and response required in the Convention shall be transmitted to the competent authority of the Parties concerned or to such governmental authority as may be appropriate in the case of non-Parties.

Parties shall, in addition, inform each other through the Secretariat of any decisions taken by them to limit or ban the export of hazardous wastes or other wastes. They shall transmit, consistent with national laws and regulations, through the Secretariat to the COP established under the Convention, before the end of each calendar year, a report on the previous calendar year, containing information on the designated competent authorities and focal points; transboundary movements of hazardous wastes in which they have been involved, including the amount of hazardous wastes exported, their category, characteristics, destination, any transit country and disposal method as stated on the notifications; the amount of hazardous wastes imported, their category, characteristics, origin, and disposal methods; disposal which did not proceed as intended; and efforts to achieve a reduction of the amount of hazardous wastes subject to transboundary movement; the measures adopted by them to implement the Convention; available qualified statistics compiled by them on the effects on human health and the environment of the generation, transportation and disposal of hazardous wastes; bilateral, multilateral and regional agreements entered into pursuant to the Convention; accidents occurring during the transboundary movement and disposal of hazardous wastes, and the measures undertaken to deal with them; disposal options operated within their national jurisdiction; measures undertaken for development of technologies for the reduction and/or elimination of production of hazardous wastes and other matters as the COP shall deem relevant.

The Parties shall ensure that copies of each notification concerning any given transboundary movement of hazardous wastes, and the response to it, are sent to the Secretariat when a Party which considers that its environment may be affected by that transboundary movement has requested that this should be done.

II.2.3. Protocol on Liability and Compensation (1999)

The LWG, which was working on the development of a Protocol on Liability and Compensation for Damages Caused by Transboundary Movement of Hazardous Wastes and Their Disposal since 1991, completed its task and the Protocol on Liability and Compensation was adopted by the Contracting Parties of the Basel Convention at their Conference in December 1999.

The definition of damage that results from an accident during the transboundary movement of hazardous wastes and their disposal was defined. The main issues agreed upon by the Contracting Parties included the question of who is liable; it was agreed that the generator of wastes or the exporter is strictly liable for damage resulting from import and export.

The persons liable shall establish and maintain during the period of the time limit of liability, insurance, bonds or other financial guarantees covering their liability under the Protocol for amounts not less than the minimum limits specified in it. States may fulfill this obligation by a declaration of self-insurance. Nothing shall prevent the use of deductibles or co-payments as between insurer and the insured, but the failure of the insured to pay a deductible or co-payment shall not be a defense against the person who has suffered the damage.

II.2.4. Environmentally sound management

A central goal of the Basel Convention is ESM, the aim of which is to protect human health and the environment by minimizing hazardous waste production whenever possible. ESM means addressing the issue through an "integrated life-cycle approach", which involves strong controls from the generation of a hazardous waste to its storage, transport, treatment, reuse, recycling, recovery and final disposal (SBC Information).

The COP in Basel, Switzerland (COP-5, 1999) adopted Basel Declaration on Environmentally Sound Management (Ministerial Declaration) (1999), which specified the priority fields of activities that should be undertaken to achieve this goal subject to the Basel Convention:

- prevention, minimization, recycling, recovery and disposal of hazardous and other wastes, taking into account social, technological and economic concerns;
- active promotion and use of cleaner technologies and production;
- further reduction of transboundary movements of hazardous and other wastes, taking into account the need for efficient management, the principles of self-sufficiency and proximity and the priority requirement of recovery and recycling;
- prevention and monitoring of illegal traffic;
- improvement and promotion of institutional and technical capacity-building, as well as the development and transfer of environmentally sound technologies, especially for developing countries and countries with economies in transition;
- further development of regional and subregional centers for training and technology transfer;

- enhancement of information exchange, education and awareness-rising in all sectors of society;
- cooperation and partnership at all levels between countries, public authorities, international organizations and academic institutions;
- development of mechanisms for compliance with and for the monitoring and effective implementation of the Convention and its amendments.

The Declaration specified also proposed priority activities in these fields, their objective, method and outcome, including such activities as: organizing international conference and workshops to further define the concept of, identify opportunities for, and to provide a forum that will facilitate exchange of information and experience on ESM, as well as enhance partnership with all stakeholders; development of methodologies for ESM; evaluation of economic instruments, e.g. fiscal and investment policies or programs; continuation of development and/or enhancement synergies with United Nations and intergovernmental organizations for a more efficient use of resources and to share experiences on ESM and cleaner technologies; development of electronic information systems on ESM; building up institutional and technological capacity; providing training for customs and other enforcement officers; developing inventory of generation and stockpiles of hazardous waste; enhancement of cooperation and partnership arrangements with the private sector, non-governmental organizations (NGOs), academia, and local communities for the promotion of ESM; and strengthening of regional and subregional centers for training and technology transfer for ESM.

II.2.5. Illegal traffic

The COP adopted a strategy to prevent and monitor illegal traffic in hazardous wastes. The Parties are clearly moving towards implementing a strategy to combat illegal traffic. This strategy contains key elements such as the need for countries to promulgate or develop stringent national or domestic legislation pertaining to the control of transboundary movements of hazardous wastes and to incorporate in their legal systems appropriate sanctions or penalties for the illegal traffic. In order to build up the capacity for a comprehensive response to the issue of illegal traffic, the strategy's call for regional or sub-regional cooperation should be encouraged and should be strengthened as required which it exists. The United Nations regional commissions as well as other regional bodies and convention or protocols, NGOs, industry, private sector and World Custom Organization (WCO) should take an effective role in the monitoring and prevention of illegal traffic. The SBC also works closely on this subject with Interpol.

In order to facilitate the initiatives of governments in this respect, the Secretariat could assist Parties in developing national or domestic legislation to deal with such traffic. It could also assist Parties in capacity building including the development of an appropriate infrastructure allowing for the prevention and penalization, as well as the monitoring of illegal traffic. This is an essential and critical part of the global regulatory system of the Basel Convention. Indeed it is important that adequately trained, in cooperation with WCO, International Maritime Organization (IMO), Interpol, etc. customs and port officers, judiciary personnel and police forces be able to exercise full control over

the hazardous wastes being moved across frontiers in order to make sure that the material being inspected corresponds to both the transport manifest and the Movement Document that accompany the wastes or to reveal cases of illegal traffic in such wastes. Confirmed cases of illegal traffic should be reported to the Secretariat using the "Form for Confirmed Cases of Illegal Traffic".

National enforcement is a prerequisite of the effective implementation of the Basel Convention. From an operational point of view, a properly integrated national enforcement program should include: tracking of hazardous waste shipments; visits to company sites (and other sites); transport control/checks/inspections; sampling and testing; information exchange. To make it work properly, there is a need for a proper infrastructure, adequate staffing of trained enforcement personnel, and appropriate logistical support and knowledge of hazardous wastes.

II.2.6. Legal and technical guidelines

To assist policy-makers, experts and technicians with the implementation of the Convention and the ESM of hazardous wastes and their disposal, a number of legal, technical and scientific guidelines have been developed by the Working Group for the Implementation, Legal and Technical Working Groups (LWG and TWG), negotiated and adopted by the Contracting Parties.

II.2.6.1. Guidelines for implementation and to the control system

The Manual for Implementation, Technical and Legal Guidelines of the Basel Convention and other guidance documents available in the Official Web site of the SBC aim at assisting Parties as well as non-Parties to understand the obligations set up in the Convention.

The COP-4 (1998) in Kuching, Malaysia, adopted Guide to the Control System that is a detailed instruction manual for the control procedure, and for completing the notification and the movement documents. Forms for movement, notification, as well as for confirmed cases of illegal traffic are also provided on line.

II.2.6.2. Legal guidelines

The COP-2 (Geneva, 1994) accepted Model National Legislation developed by the LWG in order to assist Parties and non-Parties in revising their national legislation in relation to the transboundary movement and management of hazardous wastes; COP-3 (Geneva, 1995) approved the revised model (LWG, 1995) for immediate use.

II.2.6.3. Technical and scientific guidelines

The COP adopted the Framework Guidance Document on the Preparation of Technical Guidelines for the Environmentally Sound Management of Wastes subject to the Basel

Convention. The set of four technical guidelines on priority waste streams was adopted, namely on:

(a) hazardous waste from the production and use of organic solvents (Y6),
(b) hazardous waste: waste oils from petroleum origins and sources (Y8),
(c) wastes comprising or containing PCBs, PCTs and PBBs (Y10), and
(d) wastes collected from households (Y46).

The Conference also adopted the set of three Technical Guidelines on Disposal Operations:

- Technical Guidelines on Specially Engineered Landfill (D5),
- Technical Guidelines on Incineration on Land (D10), and
- Technical Guidelines on Used Oil Re-refining or other Re-uses of Previously Used Oil (R9).

The Parties agreed on the program for the TWG that includes the preparation of new sets of technical guidelines for the ESM of hazardous wastes and the further elaboration of criteria for such wastes destined for recovery operations.

The provisions of the Basel Convention provide a number of obligations to Parties to ensure that if pollution occurs as a result of transboundary movement of hazardous wastes or their management, they shall minimize the consequences thereof for human health and the environment. In addition, the SBC has as one of its functions to cooperate with Parties and with relevant international organizations in the provision of experts and equipment for the purpose of rapid assistance to States in event of an emergency situation.

The TWG of the Basel Convention has developed the technical elements for guiding States in their activities to be carried out within the framework of ESM of hazardous wastes, which include:

- provisions for the establishment of emergency plans specifying the steps to be taken in the event of occurrences such as fire, explosion and spillage, and
- consideration of the problems created by contamination of the environment by hazardous wastes
- taking into account their environmental and health effects in both the short and long term.

II.2.7. Technical assistance and training

The successful implementation of the Basel Convention and of the decisions taken by the COP and the achievement of the ESM of hazardous wastes rely upon developing the adequate capacity at the national or regional levels and upon the active and effective cooperation among Parties, and of Parties with non-Parties and international organizations taking into account, in particular the needs of developing countries and countries embarked in the transition of their economy. Such cooperation is required for the development and implementation of environmentally sound technologies that would create less hazardous wastes or for the improvement of existing technologies with a view to eliminating, as far as practicable, the generation of such wastes. At the same time,

international cooperation represents an essential mechanism by or through which countries would ensure the management of hazardous wastes. They nonetheless produce in an environmentally sound manner.

The SBC has developed training programs, including curricula at the national level in collaboration with national authorities, and organized several national and regional seminars or workshops on the implementation of the Basel Convention and the ESM of hazardous wastes.

Based on the identification of the specific needs of the different regions and subregions for training and technology transfer regarding the management of hazardous wastes and other wastes and the minimization of their generation, the Parties agreed on the selection of sites for the establishment of regional centers for training and technology transfer in Africa, Asia and Pacific; Latin America and Caribbean; and Eastern and Central Europe. The Secretariat assisted Parties in developing of training programs on the implementation of the Convention and the ESM of hazardous wastes. One of the main tasks of the Secretariat is to cooperate with, assist and respond to the needs of the Parties in the implementation of the Convention and of the decisions adopted by the meetings of the COP. In view of the fact that the implementation of the Convention and its supporting decisions have also an impact on countries that are not Party to the Convention, the Secretariat plays also an active role in assisting them upon request or by providing information or guidance on the ESM of hazardous wastes and its related institutional and legal requirements.

II.2.8. Bilateral, multilateral and regional agreements or arrangements

II.2.8.1. Provisions and regulations

In accordance with the provisions of the Convention, the Parties may enter into bilateral, multilateral or regional agreements or arrangements regarding transboundary movement of hazardous wastes or other wastes with Parties or non-Parties provided that such agreements or arrangements do not derogate from the ESM of hazardous wastes arid other wastes as required by this Convention.

The COP decided that when the Parties have entered into bilateral, multilateral or regional agreements arid arrangements they shall report to the Open-ended Ad Hoc Committee responsible for facilitating the implementation of the Convention, through the Secretariat, on the conformity of such agreements or arrangements taking into consideration a list of questions which were developed by the Committee itself. The purpose of using the set of questions is to assist Parties when reporting, in focusing on particular issues.

One of the main principles of the Basel Convention is to impose strict control measures on the transboundary movements of hazardous wastes in order to avoid the negative effects on health and the environment that could result from the movements of such wastes without having the necessary guarantees of their proper handling from their generation to their final disposal. It was clear during the negotiations leading to the Basel Convention that permitting a Party to deal with non-Parties would be a valve through which the Party could derogate from the obligations it has undertaken under the terms and provisions of the

Basel Convention and thus practicing the movement and disposal of hazardous wastes without any kind of guarantee and safety for human health and the environment. As a result of this reasoning and also in order to encourage non-Parties to become Party to the Basel Convention, the provision of paragraph 5 or Article 4 was included in the Basel Convention "A Party shall not permit hazardous wastes or other wastes to be exported to a non-Party or to be imported from a non-Party".

Of direct link to this Article comes the provision of Article 11 in both its paragraphs 1 and 2, permitting Parties to deal with non-Parties under the condition of concluding bilateral and multilateral agreements or arrangements "which stipulate provisions which are not less environmentally sound than those provided for by this Convention" for agreements concluded after the entry into force of the Basel Convention and which "are compatible with the ESM of hazardous wastes and other wastes as required by this Convention" if these agreements are concluded before their entry into force of the Basel Convention.

The above-quoted provisions of Article 11 allow the Parties to the Convention to deal with non-Parties on the basis of parallel rules to the Basel Convention to be included in bilateral or multilateral agreements. The provisions of the Basel Convention, therefore, permit export and import to and from non-Parties only under the conditions that it is based on rules not less environmentally sound than the ones of the Convention.

The reference to this right is in both the preamble as well as in paragraph 1 of Article 4 of the Convention.

Paragraph 6 of the preamble "Fully recognizing that any State has the sovereign right to ban the entry or disposal of foreign hazardous wastes and other wastes in its territory" and paragraph 1(a) of Article 4 stipulates that "Parties exercising their right to prohibit the import of hazardous wastes or other wastes for disposal shall inform the other Parties of their decision pursuant to Article 13".

It is clear from these two provisions that the right to ban is a general one which shall, if used, be applied *vis-à-vis* all other countries equally Parties and non-Parties to the Convention. Exercising such a right is, therefore, in compliance with the principle of non-discrimination. Also doubts cannot be raised that the country which exercises this right is following a protectionism policy because from the definition of waste it is clear that they are not goods which are produced to be commercialized but are generated as a result of the production process of other goods.

As referred to the above, Article 11 of the Basel Convention regulates the relationship with non-Parties on a non-discriminatory base. No problems have been raised in implementing this Article. Should any problem be raised in the future, the Open-ended Ad Hoc Committee, established under the terms of Decision I/9 of the first meeting of the COP to the Basel Convention, will deal with it.

In accordance with Article 4 paragraph 1, Parties have the right to prohibit both imports (para 1(a)) and/or exports of hazardous wastes (para 1(b)). The first meeting of the COP to the Basel Convention adopted Decision I/27 that requested the industrialized countries to prohibit the export of hazardous wastes to developing countries for final disposal, and requested the developing countries to prohibit the import of hazardous wastes from industrialized countries. During the negotiations leading to the signature of the Basel Convention, it was emphasized by several delegates that this article only confirms the sovereign right of every country to ban import and/or export of hazardous wastes.

Recognizing the increasing desire and demand of the international community for the prohibition of transboundary movements of hazardous wastes and their disposal especially in developing countries, the second meeting of the COP, held from 21 to 25 March 1994 in Geneva, less than 2 years after the entry into force of the Convention (May 1992), adopted a decision establishing the immediate prohibition of all transboundary movements of hazardous wastes which are destined for final disposal from OECD to non-OECD countries. The transboundary movement of hazardous wastes from OECD to non-OECD countries destined for recycling or recovery operations was to be phased out by 31 December 1997. This transitional period had been seen as necessary for those concerned with these movements to enable them to take appropriate measures consistent with the ESM of such wastes.

The Parties to the Convention agreed during the Conference that it was imperative to render such prohibition effective and decided on a control system through regular reporting on the implementation of the decision. In addition, those non-OECD States not possessing a national hazardous waste import prohibition and which allowed the import from OECD States of hazardous wastes for recovery operations until 31 December 1997, let the SBC know about their specific or particular situation and were to specify the categories of hazardous wastes that are acceptable for import, the quantities to be imported, to which recovery process the waste will be subject to and the final destination or disposal of the residues derived from such operations. The Parties also recognized the need to cooperate and work actively to ensure the effective implementation of this decision.

The third meeting of the COP to the Basel Convention was held in September 1995 in Geneva. It was attended by more than 100 States, UN bodies and specialized agencies, other IGOs and Secretariats of Conventions, NGOs and the private sector. The COP adopted 28 decisions comprising a comprehensive program of work for the following biennium.

A decision was adopted to amend the Convention with respect to a prohibition by each Party member of OECD, EC, Liechtenstein, of all transboundary movements of hazardous wastes that are destined for final disposal to other States. It also phased out and prohibited by 31 December 1997 all transboundary movements of hazardous wastes for recovery, recycling, reclamation, direct re-use or alternative uses from Party members of the OECD, EC, Liechtenstein, to other States. The wastes subject to such prohibitions are characterized as hazardous under the Convention.

The Amendment was approved by a number of OECD members, and on behalf of the EC by Council Decision 97/640/EC of 22 September 1997 (see Chapter II.1).

The Contracting Parties that have not approved the Amendment by 31 December 1997 were urged to ratify it at the fourth meeting of the Conference of the Contracting Parties, which took place in Kuching, Malaysia in 1998.

II.2.8.2. Lists of wastes: criteria for classification and characterization

In connection to the decision on adoption of the Amendment, the third meeting of the COP to the Basel Convention requested the TWG to continue its work on hazard characterization of wastes subject to the Basel Convention (decision II/12) as well as to continue its work on the development of lists of wastes that are hazardous and wastes that are not subject to the Convention.

In this context, the criteria for classification of hazardous wastes under the Basel Convention, which have been already for some time discussed between Contracting Parties, were developed and adopted and the lists of wastes were agreed upon and accepted by the Contracting Parties. The clearer definition was developed on the hazard classes described in Annex III, in particular for classes H 10–H 13, as well as the lists of hazardous wastes were established together with the applicable procedure for their review.

The TWG explored limit values for use, when appropriate, in applying the "de minimis" approach; this approach was not, however, adopted.

The adopted lists of wastes, which are serving implementation of the Amendment, are as follows:

- *List A*: wastes subject to the Basel Convention and to its Amendment;
- *List B*: wastes, which are not subject to the Amendment (concerns wastes related to article 1.1 of the Convention);
- *List C*: wastes where uncertainties prevailed as to their classification on list A or list B.

The agreed procedure for changing the place of wastes is as follows:

- Any Contracting Party; observer State, national authority; NGO, company or individual person have the right to fill in an initial application form with the proposed placement of wastes under list A or list B and present it to national authorities for the Basel Convention within its country. It is for the government to decide how and through which competent authority and/or focal point of the Basel Convention this application form will be forwarded to the SBC.
- It is understood that the competent authority(ies) and/or focal point is/are to decide if it considers the application form properly filled in and if it agrees to forward this application form for consideration at the next meeting of the TWG.
- The TWG or any special group with competencies to review the application form will consider the application at its next meeting if possible. If the TWG would be of the opinion that the special additional information, explanation or any further advice would be needed, it would have the right to approach appropriate bodies/authorities/NGO including private sector/industry for the necessary expertise.

The TWG is giving priority to the assessment of all wastes temporarily placed on list C for their placement on list A or list B. Wastes on list C are wastes for which uncertainties prevail as to their hazardousness. In order to advance with this work, which is practically of continuing character, States Party to the Convention, States non-Party, industry/business and environmental organizations are to provide explanatory material on a number of wastes placed on list C for their further assessment by the TWG.

Submitting the lists of wastes to COP-4 provided advice on the status of lists – that is, how they are to be interpreted and used by competent authorities within the framework of the control procedure established under the Basel Convention. The following is an explanation:

List A: The waste placed on list A are characterized as hazardous wastes under Article 1 paragraph 1(a) of the Convention. They, therefore, belong to any category contained in Annex I to the Convention and exhibit any of the characteristics of Annex III to the Convention. The wastes placed on list A are subject to the amendment to the Convention.

List B: The wastes placed on list B are not the wastes characterized as hazardous under Article 1, paragraph 1(a) of the Convention, unless they contain Annex I material to an extent causing them to exhibit one or more Annex III hazard characteristics. Wastes placed on list B either do not belong to Annex I to the Convention, or belong to Annex I but, in this latter case, do not exhibit any of the hazard characteristics described in Annex III to the Convention. Wastes on list B could be defined, or considered to be, hazardous wastes by the national or domestic legislation of the Party of export, import or transit by virtue of Article 1, paragraph 1(b) of the Convention, in which case they would be subject to the control procedure established under the Convention.

List C: The wastes placed on list C are wastes for which uncertainties prevail as to their hazardousness and as such are awaiting classification by the TWG. All wastes on list C will be assessed by the TWG for placement on either list A or list B. The entries on list C are, therefore, temporary. Wastes placed on list C for which a category contained in Annex I to the Convention can be identified and are subject to the control procedure established under the Convention. Wastes placed on list C that do not belong to a category in Annex I of the Convention but which exhibit any hazard characteristics contained in Annex III to the Convention will not be assigned to either list A or list B. Finally, there may be wastes placed on list C for which uncertainties exist as to their classification under the categories of wastes of Annex I to the Convention: these wastes shall not be subject to the control procedure established under the Convention until a decision can be taken by the TWG as to their eventual classification under Annex I.

In this regard and concerning the relationship between list A and the use of Annex III, it is important to note that there is a need for a clear, stable list A of wastes which is not open to challenge. On the other hand, it is likely that any practical list of wastes may contain ambiguities and generalizations. This may lead to a situation where an exporter or a generator may discover a descriptor for a specific waste, although consideration non-hazardous, happens to coincide with or correspond to a general description of an entry onto list A.

When an exporter or generator is confronted with a waste that is placed on list A but considered harmless and tradable, he or she would then be able to submit an application form to the TWG (using the procedure established by the TWG), for the classification of this waste. Together with the application, the exporter or generator should provide any information about the hazardousness (or lack of) of the wastes, with reference to Annex III, as is necessary to assist the TWG with the process of assigning wastes to a list. On receipt of the application by SBC, the waste in question would be placed on list C pending classification by the TWG.

The amended Annex I, and lists A (as Annex VIII) and B (as Annex IX) were incorporated in the Basel Convention, which was adopted at the COP-4 – fourth meeting of the COP in 1998 (SBC, 1999).

II.2.9. Trade and environment and the Basel "ban"

II.2.9.1. International legal instruments and provisions

The relationship between Trade and Environment has recently taken a new dimension in view of the promotion of Free Trade internationally by the World Trade Organization

(WTO) and other organizations and of the necessity to protect the environment and the proper management of natural resources implemented mainly by UNEP, UN Department for Policy Coordination and Sustainable Development (DPCSD) and others.

The following international legal instruments: Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES), the Montreal Protocol on Ozone Depleting Substances, the Basel Convention, the Convention on Biological Diversity as well as the non-legally binding London Guidelines for the Exchange of Information on Chemicals in International Trade include specific provisions restricting or governing trade.

CITES (1973) is basically a series of provisions that restrict trade in endangered species of wild plants and animals or parts thereof. The most conspicuous of these are the tusks of elephants and the rhino horn. The Montreal Protocol (1987) prohibits trade in the controlled substances that deplete the ozone layer with non-Parties. It provides for the same control on products that contain the controlled substances and will soon cover products prepared with the controlled substances. The Basel Convention prohibits the transboundary movement (export/import) of hazardous wastes with non-Parties and puts specific requirements for the movement of such wastes between Parties. The Biodiversity Convention (1992) specified the conditions under which Parties can have access to the biological resources present in other Parties, and the London Guidelines for the Exchange of Information on Chemicals in International Trade (1989) puts specific requirements before a chemical is exported to another country.

All these are restrictions on trade in potentially toxic chemicals; in chemicals, which deplete the ozone layer; in movement and disposal of hazardous wastes; on access to dwindling biological resources; and, on trade in endangered species, which are meant to achieve protection of the environment and hence of the life and health of human beings, plants and animals.

All this was developed to a large extent within the context of Article XX of the General Agreement on Trade and Tariffs (GATT) (1947), which stipulates that: "Subject to the requirement that such measures are not applied in a manner which would constitute a means of arbitrary or unjustifiable discrimination between countries where the same conditions prevail, or a disguised restriction on international trade, nothing in this Agreement shall be construed to prevent the adoption or enforcement by any Contracting Parties of measures:

(b) necessary to protect human, animal or plant life or health;
(j) relating to the conservation of exhaustible natural resources if such measures are made effective in conjunction with restrictions on domestic production or consumption."

During the development of the Montreal Protocol, the Basel Convention and the London Guidelines, the representatives of GATT were present. Negotiating countries while agreeing on the above listed trade restrictions continuously referred during the negotiations to Article XX of GATT on exceptions.

II.2.9.2. Trade provisions' effect on non-parties

It is worth adding that Agenda 21 in paragraph 38.26 requested the United Nations Conference on Trade and Development (UNCTAD) to "...play an important role taking into account the importance of the inter-relationships between development, international

trade and the environment and in accordance with its mandate in the area of sustainable development."

The issue of trade provisions affected non-Parties either alone or as it relates to the issue of extraterritoriality, which constitutes two of the core issues that are being discussed by the Group on Environmental Measures and International Trade convened under GATT. Whether the trade restrictions in environmental agreements of the global character were a condition *sine qua non* to protect the environment and human health is still the subject of debate at WTO.

II.2.9.3. The OECD approach to trade and environment issues

At the OECD, Trade and Environment has been the subject of discussion and analysis for the last few years. The work has been carried out by the Joint Session on Trade and Environment Experts under the auspices of the Environment Committee and Trade Committee of the OECD preparing a set of guidelines dealing with this subject. In 1992, this body stated that:

> "It is agreed that the best approach to tackling environmental problems can be through environmental measures, whether of a regulatory or economic nature, directed at the fundamental environmental problem. There are cases where trade measures are an important accompaniment of non-trade measures for the effective implementation of environmental policies."

OECD prepared in 1999 a comprehensive study on the trade related issues of the Basel Convention as a case study on environment and trade issues (OECD, 1999).

It has to be remembered that the issue of the relationship between trade and environment covers areas outside the international environmental agreements namely on commodity prices and intellectual property rights and patents in areas of environmentally sound technologies and genetically engineered biological resources.

II.2.9.4. Obligations and rights of the parties

The Parties to the Basel Convention have to fulfill their obligations in accordance with the Basel Convention and it is clearly the responsibility of the Parties to both WTO and the Basel Convention to implement the international agreements to which they are Parties. It, therefore, has to be clearly understood that not one of these agreements revolves or threatens in any way the provisions of the other agreement, as has sometimes been stated.

As stated above, the Basel Convention contains two provisions referring to the international trade. The first one is related to the obligations of the Parties to the Convention not to allow import or export from or to non-Parties to the Convention (paragraph 5 of Article 4), and the second related provision is the right of the Parties to ban the import of hazardous wastes (paragraph 6 of the preamble and paragraph 1(a) of Article 4).

II.2.9.4.1. The obligation of the Parties to the Convention not to import from or export to non-Parties to the Convention

One of the main principles of the Basel Convention is to impose strict control measures on the transboundary movements of hazardous wastes in order to avoid the negative effects on health and the environment, which could result from the movements of such wastes without having the necessary guarantees of their proper handling from their generation to their final disposal. It was clear during the negotiations leading to the Basel Convention that permitting a Party to deal with non-Parties will be a valve through which the Party could derogate from the obligations it has undertaken under the terms and provisions of the Basel Convention and thus practicing the movement and disposal of hazardous wastes without any kind of guarantee and safety for human health and the environment. As a result of this reasoning and also in order to encourage non-Parties to become Party to the Basel Convention, the provision of paragraph 5 or Article 4 was included in the Basel Convention "A Party shall not permit hazardous wastes or other wastes to be exported to a non-Party or to be imported from a non-Party".

Of direct link to this Article comes the provision of Article 11 in both its paragraphs 1 and 2, permitting Parties to deal with non-Parties under the condition of concluding bilateral and multilateral agreements or arrangements "which stipulate provisions which are not less environmentally sound than those provided for by this Convention" for agreements concluded after the entry into force of the Basel Convention and which "are compatible with the environmentally sound management of hazardous wastes and other wastes as required by this Convention" if these agreements are concluded before their entry into force of the Basel Convention.

The above-quoted provisions of Article 11 allow the Parties to the Convention to deal with non-Parties on the basis of parallel rules to the Basel Convention to be included in bilateral or multilateral agreements. The provisions of the Basel Convention, therefore, permit export and import to and from non-Parties only under the conditions that it is based on rules not less environmentally sound than the ones of the Convention.

II.2.9.4.2. The right of the Parties to ban the import of hazardous wastes

The reference to this right is in both the preamble as well as in paragraph 1 of Article 4 of the Convention.

Paragraph 6 of the preamble "Fully recognizing that any State has the sovereign right to ban the entry or disposal of foreign hazardous wastes and other wastes in its territory" and paragraph 1(a) of Article 4 stipulates that "Parties exercising their right to prohibit the import of hazardous wastes or other wastes for disposal shall inform the other Parties of their decision pursuant to Article 13".

It is clear from these two provisions that the right to ban is a general one which shall, if used be applied *vis-à-vis* all other countries equally Parties and non-Parties to the Convention. Exercising such a right is, therefore, in compliance with the principle of non-discrimination.

Also, doubts cannot be raised that the country that exercises this right is following a protectionism policy because from the definition of waste it is clear that they are not goods which are produced to be commercialized but are generated as a result of the production

process of other goods. The concept of protecting the waste generated locally has, therefore, no place within the logic of the Basel Convention.

II.2.9.5. The Basel ban and its relation to trade clauses

The following important points related to trade clauses under the Basel Convention should be emphasized:

1. Trade between Parties and non-Parties to the Basel Convention is not prohibited. But in order to enhance the principle of non-discrimination and equal treatment, the Basel Convention requests in accordance with Article 11 its Parties when dealing with non-Parties to conclude bilateral agreements or arrangements stipulating provisions, which are not less environmentally sound than those provided for by the Basel Convention. Therefore, in relation to the control of transboundary movements of hazardous wastes Parties and non-Parties will have to respect standards recognized as essential by the international community for the protection of the environment. Trade restrictions against non-Parties do not only aim to induce non-Parties to accede to the agreements but also to achieve the aim of non-discrimination. Article 11 of the Basel Convention on bilateral and multilateral agreements, which complement the provisions of Article 4 prohibits transboundary movements of wastes with non-Parties. Article 11 allows such movements through the conclusions of agreements or arrangements not less stringent than the provisions of the Basel Convention. Therefore, the aim of both Articles 4 and 11 of the Basel Convention is to set international standards in relation to the transboundary movement of hazardous wastes, to be respected by Parties and non-Parties to the Basel Convention. This approach of the Basel Convention enhances the principle of equal treatment and non-discrimination.
2. The ban adopted by COP-3 as an Amendment to the Convention and which constitutes a prohibition of transboundary movements of hazardous wastes from OECD, EC, and Liechtenstein to other States is based on the recognition that the movement of hazardous wastes, especially to developing countries, has a high risk of not constituting ESM of hazardous wastes and not on the basis of any trade consideration including protectionism.

As a general principle regarding the trade clauses, it has to be emphasized that a clear differentiation is to be made between unilateral actions by some governments related to establishment of environmental standards which have direct impact on trade and the global environment agreements, which do establish rules that could affect trade but which are agreed upon by a very large number of governments.

II.2.10. Concluding remarks

The significance and role of a global agreement, which is the Basel Convention, in the protection of the environment and human health against the consequences of uncontrolled movement and dumping of hazardous wastes, is difficult to overestimate. The fundamental aims of the Basel Convention formulated in the Draft Strategic Plan for the Implementation (2000–2010) are "the reduction of transboundary movements of hazardous and other

wastes subject to the Basel Convention, the prevention and minimization of their generation, the ESM of such wastes and the active promotion of the transfer and use of cleaner technologies". That the Convention is ratified by 151 Parties (member countries and the European Union) as of June 2002 proves its global character.

During the first decade since adoption and entering into force (1992–2002), the activity of the Basel Convention was focused on setting up a framework for the transboundary movement of hazardous wastes, on developing criteria for ESM of hazardous wastes and other wastes and on establishing the control system of waste, based on the prior notification.

In this period, significant progress has been achieved in implementation of its decisions directed to global environmental protection through the collective international control of transboundary movements of hazardous wastes and their disposal, as well as in developing and improving regulatory tools, information exchange for harmonization of the national legislation and definitions, and in providing training and technology transfer, as well as legal and technical assistance in the ESM of hazardous wastes and minimization of their generation by the Parties to the Convention. The development of national reporting on the generation and movement of hazardous wastes, based on annual questionnaires, is a significant contribution of the Basel Convention to the global statistics on hazardous waste.

Milestones of the Basel Convention's History that exerted profound effect on the global management of hazardous wastes, since its adoption in 1989 and entry into force in 1992 comprise: Ban Amendment (1995) that calls for prohibiting exports of hazardous wastes (for any purpose) from OECD countries to all other parties to the Convention; Classification and Characterization of Wastes (1998) – the development of lists of specific wastes characterized as hazardous and non-hazardous; Ministerial Declaration (1999) on ESM that set out the agenda for the next decade, with a special emphasis on minimizing hazardous waste, and Protocol on Liability and Compensation (1999) for damages caused by accidental spills of hazardous waste during export, import or disposal.

Taking into consideration a disparity of economical, legislative and enforcement mechanisms in the Parties, inadequate availability and transmission of information related to generation, export and import of hazardous wastes, as well as still a substantial number of countries that for various reasons have not yet ratified the Convention, among them the USA, which is the biggest producer of hazardous waste, the majority of African countries, as well as several states of Asia/Oceania region and of the former USSR, there is still a potential threat of both export and of using some countries as a sink for hazardous waste.

During the next decade, the Convention will build on the achievements of the first decade towards full implementation and enforcement of treaty commitments, emphasizing the minimization of hazardous and other wastes and the strengthening of capacity-building. The Draft Strategic Plan for the Implementation of the Basel Convention (2000–2010) uses the framework of the 1999 Ministerial Basel Declaration. According to its preamble, it identifies and describes those activities considered achievable by the parties in partnership with all concerned and interested stakeholders within the agreed 10-year time frame, and sets out detailed short (2003–2004) and mid-to-long-term activities (2005–2010). The proposed major activities for 2003–2004 supporting the aims of the Basel Declaration include:

(a) assistance in the development and implementation of national legislation and capacity-building and other tools necessary for ESM;
(b) development of waste prevention and minimization programs and tools, and orientation for assistance in their implementation;
(c) assistance in the establishment and strengthening of the operation of the Basel Convention Regional Centres (BCRCs) within their core functions and their priority work program as the main regional delivery mechanism for the concrete implementation of the strategic plan;
(d) promotion of effective sustainable partnership with major stakeholders, in particular the private sector, to identify and implement joint opportunities for ESM activities;
(e) improved coordination and coherence of activities between the Basel Convention and other Multilateral Environmental Agreements (MEAs);
(f) reduction and monitoring of transboundary movements of hazardous and other wastes.

The full work program (10-year period) is expected to take place in a series of phases of regionally based activities.

As states the Draft Strategic Plan, the world-wide ESM of hazardous and other wastes as called for in the 1999 Ministerial Basel Declaration on Environmentally Sound Management requires action at all levels of society: training, information, communication, methodological tools, capacity building with financial support, transfer of know-how, knowledge and sound and proven cleaner technologies and processes are driving factors to assist in the concrete implementation of the Basel Convention.

Collective efforts of the continuously growing international community supported by the Basel Convention harmonized with other international and national regulations should bring further progress in solution of a global environmental problem of hazardous waste management.

Appendix A

Excerpt from:

Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal adopted by the Conference of the Plenipotentiaries on March 1989, entry into force 5 May 1992 (with amended Annex I and two additional Annexes VIII and IX, adopted at the fourth meeting of the Conference of the Parties in 1998).

Official Web site of the SBC: http://www.basel.int/text/con-e.htm

Annex I

Categories of wastes to be controlled

Waste Streams

Y1 Clinical wastes from medical care in hospitals, medical centers and clinics
Y2 Wastes from the production and preparation of pharmaceutical products
Y3 Waste pharmaceuticals, drugs and medicines

Y4 Wastes from the production, formulation and use of biocides and phytopharmaceuticals
Y5 Wastes from the manufacture, formulation and use of wood preserving chemicals
Y6 Wastes from the production, formulation and use of organic solvents
Y7 Wastes from heat treatment and tempering operations containing cyanides
Y8 Waste mineral oils unfit for their originally intended use
Y9 Waste oils/water, hydrocarbons/water mixtures, emulsions
Y10 Waste substances and articles containing or contaminated with polychlorinated biphenyls (PCBs) and/or polychlorinated terphenyls (PCTs) and/or polybrominated biphenyls (PBBs)
Y11 Waste tarry residues arising from refining, distillation and any pyrolytic treatment
Y12 Wastes from production, formulation and use of inks, dyes, pigments, paints, lacquers, varnish
Y13 Wastes from production, formulation and use of resins, latex, plasticizers, glues/adhesives
Y14 Waste chemical substances arising from research and development or teaching activities which are not identified and/or are new and whose effects on man and/or the environment are not known
Y15 Wastes of an explosive nature not subject to other legislation
Y16 Wastes from production, formulation and use of photographic chemicals and processing materials
Y17 Wastes resulting from surface treatment of metals and plastics
Y18 Residues arising from industrial waste disposal operations
Wastes having as constituents:
Y19 Metal carbonyls
Y20 Beryllium; beryllium compounds
Y21 Hexavalent chromium compounds
Y22 Copper compounds
Y23 Zinc compounds
Y24 Arsenic; arsenic compounds
Y25 Selenium; selenium compounds
Y26 Cadmium; cadmium compounds
Y27 Antimony; antimony compounds
Y28 Tellurium; tellurium compounds
Y29 Mercury; mercury compounds
Y30 Thallium; thallium compounds
Y31 Lead; lead compounds
Y32 Inorganic fluorine compounds excluding calcium fluoride
Y33 Inorganic cyanides
Y34 Acidic solutions or acids in solid form
Y35 Basic solutions or bases in solid form
Y36 Asbestos (dust and fibres)
Y37 Organic phosphorus compounds
Y38 Organic cyanides
Y39 Phenols; phenol compounds including chlorophenols

Y40 Ethers
Y41 Halogenated organic solvents
Y42 Organic solvents excluding halogenated solvents
Y43 Any congenor of polychlorinated dibenzo-furan
Y44 Any congenor of polychlorinated dibenzo-p-dioxin
Y45 Organohalogen compounds other than substances referred to in this Annex (e.g. Y39, Y41, Y42, Y43, Y44)

(a) To facilitate the application of this Convention, and subject to paragraphs (b), (c) and (d), wastes listed in Annex VIII are characterized as hazardous pursuant to Article 1, paragraph 1 (a), of this Convention, and wastes listed in Annex IX are not covered by Article 1, paragraph 1 (a), of this Convention.
(b) Designation of a waste on Annex VIII does not preclude, in a particular case, the use of Annex III to demonstrate that a waste is not hazardous pursuant to Article 1, paragraph 1 (a), of this Convention.
(c) Designation of a waste on Annex IX does not preclude, in a particular case, characterization of such a waste as hazardous pursuant to Article 1, paragraph 1 (a), of this Convention if it contains Annex I material to an extent causing it to exhibit an Annex III characteristic.
(d) Annexes VIII and IX do not affect the application of Article 1, paragraph 1 (a), of this Convention for the purpose of characterization of wastes.

Annex II

Categories of wastes requiring special consideration
Y46 – Wastes collected from households
Y47 – Residues arising from the incineration of household wastes

Annex III

List of hazardous characteristics
UN Class Code Characteristics
1 H1 Explosive
An explosive substance or waste is a solid or liquid substance or waste (or mixture of substances or wastes) which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such speed as to cause damage to the surroundings.
3 H3 Flammable liquids
The word "flammable" has the same meaning as "inflammable". Flammable liquids are liquids, or mixtures of liquids, or liquids containing solids in solution or suspension (for example, paints, varnishes, lacquers, etc., but not including substances or wastes otherwise classified on account of their dangerous characteristics) which give off a flammable vapor at temperatures of not more than 60.5°C, closed-cup test, or not more than 65.6°C, open-cup test. (Since the results of open-cup tests and of closed-cup tests are not strictly comparable and even individual results by the same test are often variable, regulations varying from the above figures to make allowance for such differences would be within the spirit of this definition.)

4.1 H4.1 Flammable solids
Solids, or waste solids, other than those classed as explosives, which under conditions encountered in transport are readily combustible, or may cause or contribute to fire through friction.
4.2 H4.2 Substances or wastes liable to spontaneous combustion
Substances or wastes which are liable to spontaneous heating under normal conditions encountered in transport, or to heating up on contact with air, and being then liable to catch fire.
4.3 H4.3 Substances or wastes which, in contact with water emit flammable gases
Substances or wastes which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities.
5.1 H5.1 Oxidizing
Substances or wastes which, while in themselves not necessarily combustible, may, generally by yielding oxygen cause, or contribute to, the combustion of other materials.
5.2 H5.2 Organic peroxides
Organic substances or wastes which contain the bivalent-O–O- structure are thermally unstable substances which may undergo exothermic self-accelerating decomposition.
6.1 H6.1 Poisonous (Acute)
Substances or wastes liable either to cause death or serious injury or to harm health if swallowed or inhaled or by skin contact.
6.2 H6.2 Infectious substances
Substances or wastes containing viable micro organisms or their toxins which are known or suspected to cause disease in animals or humans.
8 H8 Corrosives
Substances or wastes which, by chemical action, will cause severe damage when in contact with living tissue, or, in the case of leakage, will materially damage, or even destroy, other goods or the means of transport; they may also cause other hazards.
9 H10 Liberation of toxic gases in contact with air or water
Substances or wastes which, by interaction with air or water, are liable to give off toxic gases in dangerous quantities.
9 H11 Toxic (Delayed or chronic)
Substances or wastes which, if they are inhaled or ingested or if they penetrate the skin, may involve delayed or chronic effects, including carcinogenicity.
9 H12 Ecotoxic
Substances or wastes which if released present or may present immediate or delayed adverse impacts to the environment by means of bioaccumulation and/or toxic effects upon biotic systems.
9 H13 Capable, by any means, after disposal, of yielding another material, e.g. leachate, which possesses any of the characteristics listed above.
Tests
The potential hazards posed by certain types of wastes are not yet fully documented; tests to define quantitatively these hazards do not exist. Further research is necessary in order to develop means to characterize potential hazards posed to man and/or the environment by these wastes. Standardized tests have been derived with respect to pure substances and materials. Many countries have developed national tests which can be applied to materials

listed in Annex I, in order to decide if these materials exhibit any of the characteristics listed in this Annex.

Annex IV

Disposal operations

A. Operations which do not lead to the possibility of resource recovery, recycling, reclamation, direct re-use or alternative uses

Section A encompasses all such disposal operations which occur in practice.

D1 Deposit into or onto land, (e.g. landfill, etc.)

D2 Land treatment, (e.g. biodegradation of liquid or sludgy discards in soils, etc.)

D3 Deep injection, (e.g. injection of pumpable discards into wells, salt domes of naturally occurring repositories, etc.)

D4 Surface impoundment, (e.g. placement of liquid or sludge discards into pits, ponds or lagoons, etc.)

D5 Specially engineered landfill, (e.g. placement into lined discrete cells which are capped and isolated from one another and the environment, etc.)

D6 Release into a water body except seas/oceans

D7 Release into seas/oceans including sea-bed insertion

D8 Biological treatment not specified elsewhere in this Annex which results in final compounds or mixtures which are discarded by means of any of the operations in Section A

D9 Physico chemical treatment not specified elsewhere in this Annex which results in final compounds or mixtures which are discarded by means of any of the operations in Section A, (e.g. evaporation, drying, calcination, neutralization, precipitation, etc.)

D10 Incineration on land

D11 Incineration at sea

D12 Permanent storage (e.g. emplacement of containers in a mine, etc.)

D13 Blending or mixing prior to submission to any of the operations in Section A

D14 Repackaging prior to submission to any of the operations in Section A

D15 Storage pending any of the operations in Section A

B. Operations which may lead to resource recovery, recycling reclamation, direct re-use or alternative uses

Section B encompasses all such operations with respect to materials legally defined as or considered to be hazardous wastes and which otherwise would have been destined for operations included in Section A

R1 Use as a fuel (other than in direct incineration) or other means to generate energy

R2 Solvent reclamation/regeneration

R3 Recycling/reclamation of organic substances which are not used as solvents

R4 Recycling/reclamation of metals and metal compounds

R5 Recycling/reclamation of other inorganic materials

R6 Regeneration of acids or bases

R7 Recovery of components used for pollution abatement
R8 Recovery of components from catalysts
R9 Used oil re-refining or other reuses of previously used oil
R10 Land treatment resulting in benefit to agriculture or ecological improvement
R11 Uses of residual materials obtained from any of the operations numbered R1–R10
R12 Exchange of wastes for submission to any of the operations numbered R1–R11
R13 Accumulation of material intended for any operation in Section B

Annex VIII

List A
Wastes contained in this Annex are characterized as hazardous under Article 1, paragraph 1 (a), of this Convention, and their designation on this Annex does not preclude the use of Annex III to demonstrate that a waste is not hazardous.
A1 *Metal and metal-bearing wastes*
A1010 Metal wastes and waste consisting of alloys of any of the following:

- Antimony
- Arsenic
- Beryllium
- Cadmium
- Lead
- Mercury
- Selenium
- Tellurium
- Thallium

but excluding such wastes specifically listed on list B.
A1020 Waste having as constituents or contaminants, excluding metal waste in massive form, any of the following:

- Antimony; antimony compounds
- Beryllium; beryllium compounds
- Cadmium; cadmium compounds
- Lead; lead compounds
- Selenium; selenium compounds
- Tellurium; tellurium compounds

A1030 Wastes having as constituents or contaminants any of the following:

- Arsenic; arsenic compounds
- Mercury; mercury compounds.
- Thallium; thallium compounds

A1040 Wastes having as constituents any of the following:

- Metal carbonyls
- Hexavalent chromium compounds

A1050 Galvanic sludges
A1060 Waste liquors from the pickling of metals
A1070 Leaching residues from zinc processing, dust and sludges such as jarosite, hematite, etc.
A1080 Waste zinc residues not included on list B, containing lead and cadmium in concentrations sufficient to exhibit Annex III characteristics
A1090 Ashes from the incineration of insulated copper wire
A1100 Dusts and residues from gas cleaning systems of copper smelters
A1110 Spent electrolytic solutions from copper electrorefining and electrowinning operations
A1120 Waste sludges, excluding anode slimes, from electrolyte purification systems in copper electrorefining and electrowinning operations
A1130 Spent etching solutions containing dissolved copper
A1140 Waste cupric chloride and copper cyanide catalysts
A1150 Precious metal ash from incineration of printed circuit boards not included on list B
A1160 Waste lead-acid batteries, whole or crushed
A1170 Unsorted waste batteries excluding mixtures of only list B batteries. Waste batteries not specified on list B containing Annex I constituents to an extent to render them hazardous.
A1180 Waste electrical and electronic assemblies or scrap containing components such as accumulators and other batteries included on list A, mercury-switches, glass from cathode-ray tubes and other activated glass and PCB-capacitors, or contaminated with Annex I constituents (e.g. cadmium, mercury, lead, polychlorinated biphenyl) to an extent that they possess any of the characteristics contained in Annex III (note the related entry on list B B1110)
A2 *Wastes containing principally inorganic constituents, which may contain metals and organic materials*
A2010 Glass waste from cathode-ray tubes and other activated glasses
A2020 Waste inorganic fluorine compounds in the form of liquids or sludges but excluding such wastes specified on list B
A2030 Waste catalysts but excluding such wastes specified on list B
A2040 Waste gypsum arising from chemical industry processes, when containing Annex I constituents to the extent that it exhibits an Annex III hazardous characteristic (note the related entry on list B B2080)
A2050 Waste asbestos (dusts and fibers)
A2060 Coal-fired power plant fly-ash containing Annex I substances in concentrations sufficient to exhibit Annex III characteristics (note the related entry on list B B2050)
A3 *Wastes containing principally organic constituents, which may contain metals and inorganic materials*
A3010 Waste from the production or processing of petroleum coke and bitumen
A3020 Waste mineral oils unfit for their originally intended use
A3030 Wastes that contain, consist of or are contaminated with leaded anti-knock compound sludges
A3040 Waste thermal (heat transfer) fluids

A3050 Wastes from production, formulation and use of resins, latex, plasticizers, glues/adhesives excluding such wastes specified on list B (note the related entry on list B B4020)
A3060 Waste nitrocellulose
A3070 Waste phenols, phenol compounds including chlorophenol in the form of liquids or sludges
A3080 Waste ethers not including those specified on list B
A3090 Waste leather dust, ash, sludges and flours when containing hexavalent chromium compounds or biocides (note the related entry on list B B3100)
A3100 Waste paring and other waste of leather or of composition leather not suitable for the manufacture of leather articles containing hexavalent chromium compounds or biocides (note the related entry on list B B3090)
A3110 Fellmongery wastes containing hexavalent chromium compounds or biocides or infectious substances (note the related entry on list B B3110)
A3120 Fluff – light fraction from shredding
A3130 Waste organic phosphorous compounds
A3140 Waste non-halogenated organic solvents but excluding such wastes specified on list B
A3150 Waste halogenated organic solvents
A3160 Waste halogenated or unhalogenated non-aqueous distillation residues arising from organic solvent recovery operations
A3170 Wastes arising from the production of aliphatic halogenated hydrocarbons (such as chloromethane, dichloro-ethane, vinyl chloride, vinylidene chloride, allyl chloride and epichlorhydrin)
A3180 Wastes, substances and articles containing, consisting of or contaminated with polychlorinated biphenyl (PCB), polychlorinated terphenyl (PCT), polychlorinated naphthalene (PCN) or polybrominated biphenyl (PBB), or any other polybrominated analogues of these compounds, at a concentration level of 50 mg/kg or more
A3190 Waste tarry residues (excluding asphalt cements) arising from refining, distillation and any pyrolitic treatment of organic materials
A4 *Wastes which may contain either inorganic or organic constituents*
A4010 Wastes from the production, preparation and use of pharmaceutical products but excluding such wastes specified on list B
A4020 Clinical and related wastes; that is wastes arising from medical, nursing, dental, veterinary, or similar practices, and wastes generated in hospitals or other facilities during the investigation or treatment of patients, or research projects
A4030 Wastes from the production, formulation and use of biocides and phytopharmaceuticals, including waste pesticides and herbicides which are off-specification, outdated, or unfit for their originally intended use
A4040 Wastes from the manufacture, formulation and use of wood-preserving chemicals
A4050 Wastes that contain, consist of or are contaminated with any of the following:

- Inorganic cyanides, excepting precious-metal-bearing residues in solid form containing traces of inorganic cyanides
- Organic cyanides

A4060 Waste oils/water, hydrocarbons/water mixtures, emulsions

A4070 Wastes from the production, formulation and use of inks, dyes, pigments, paints, lacquers, varnish excluding any such waste specified on list B (note the related entry on list B B4010)
A4080 Wastes of an explosive nature (but excluding such wastes specified on list B)
A4090 Waste acidic or basic solutions, other than those specified in the corresponding entry on list B (note the related entry on list B B2120)
A4100 Wastes from industrial pollution control devices for cleaning of industrial off-gases but excluding such wastes specified on list B
A4110 Wastes that contain, consist of or are contaminated with any of the following:

- Any congenor of polychlorinated dibenzo-furan
- Any congenor of polychlorinated dibenzo-dioxin

A4120 Wastes that contain, consist of or are contaminated with peroxides
A4130 Waste packages and containers containing Annex I substances in concentrations sufficient to exhibit Annex III hazard characteristics
A4140 Waste consisting of or containing off specification or outdated chemicals corresponding to Annex I categories and exhibiting Annex III hazard characteristics
A4150 Waste chemical substances arising from research and development or teaching activities which are not identified and/or are new and whose effects on human health and/or the environment are not known
A4160 Spent activated carbon not included on list B (note the related entry on list B B2060)

Annex IX

List B
Wastes contained in the Annex will not be wastes covered by Article 1, paragraph 1 (a), of this Convention unless they contain Annex I material to an extent causing them to exhibit an Annex III characteristic.
B1 *Metal and metal-bearing wastes*
B1010 Metal and metal-alloy wastes in metallic, non-dispersible form:

- Precious metals (gold, silver, the platinum group, but not mercury)
- Iron and steel scrap
- Copper scrap
- Nickel scrap
- Aluminum scrap
- Zinc scrap
- Tin scrap
- Tungsten scrap
- Molybdenum scrap
- Tantalum scrap
- Magnesium scrap
- Cobalt scrap
- Bismuth scrap
- Titanium scrap

- Zirconium scrap
- Manganese scrap
- Germanium scrap
- Vanadium scrap
- Scrap of hafnium, indium, niobium, rhenium and gallium
- Thorium scrap
- Rare earths scrap

B1020 Clean, uncontaminated metal scrap, including alloys, in bulk finished form (sheet, plate, beams, rods, etc), of:

- Antimony scrap
- Beryllium scrap
- Cadmium scrap
- Lead scrap (but excluding lead-acid batteries)
- Selenium scrap
- Tellurium scrap

B1030 Refractory metals containing residues
B1040 Scrap assemblies from electrical power generation not contaminated with lubricating oil, PCB or PCT to an extent to render them hazardous
B1050 Mixed non-ferrous metal, heavy fraction scrap, not containing Annex I materials in concentrations sufficient to exhibit Annex III characteristics
B1060 Waste selenium and tellurium in metallic elemental form including powder
B1070 Waste of copper and copper alloys in dispersible form, unless they contain Annex I constituents to an extent that they exhibit Annex III characteristics
B1080 Zinc ash and residues including zinc alloys residues in dispersible form unless containing Annex I constituents in concentration such as to exhibit Annex III characteristics or exhibiting hazard characteristic H4.3
B1100 Metal-bearing wastes arising from melting, smelting and refining of metals:

- Hard zinc spelter
- Zinc-containing drosses:

– Galvanizing slab zinc top dross (>90% Zn)
– Galvanizing slab zinc bottom dross (>92% Zn)
– Zinc die casting dross (>85% Zn)
– Hot dip galvanizers slab zinc dross (batch)(>92% Zn)
– Zinc skimmings

- Aluminum skimmings (or skims) excluding salt slag
- Slags from copper processing for further processing or refining not containing arsenic, lead or cadmium to an extend that they exhibit Annex III hazard characteristics
- Wastes of refractory linings, including crucibles, originating from copper smelting
- Slags from precious metals processing for further refining
- Tantalum-bearing tin slags with less than 0.5% tin

B1110 Electrical and electronic assemblies:

- Electronic assemblies consisting only of metals or alloys
- Waste electrical and electronic assemblies or scrap (including printed circuit boards) not containing components such as accumulators and other batteries included on list A, mercury-switches, glass from cathode-ray tubes and other activated glass and PCB-capacitors, or not contaminated with Annex I constituents (e.g. cadmium, mercury, lead, polychlorinated biphenyl) or from which these have been removed, to an extent that they do not possess any of the characteristics contained in Annex III (note the related entry on list A A1180)
- Electrical and electronic assemblies (including printed circuit boards, electronic components and wires) destined for direct reuse, and not for recycling or final disposal.

B1120 Spent catalysts excluding liquids used as catalysts, containing any of:

Transition metals, excluding waste catalysts (spent catalysts, liquid used catalysts or other catalysts) on list A:	Scandium	Titanium
	Vanadium	Chromium
	Manganese	Iron
	Cobalt	Nickel
	Copper	Zinc
	Yttrium	Zirconium
	Niobium	Molybdenum
	Hafnium	Tantalum
	Tungsten	Rhenium
Lanthanides (rare earth metals):	Lanthanum	Cerium
	Praseodymium	Neody
	Samarium	Europium
	Gadolinium	Terbium
	Dysprosium	Holmium
	Erbium	Thulium
	Ytterbium	Lutetium

B1130 Cleaned spent precious-metal-bearing catalysts

B1140 Precious-metal-bearing residues in solid form which contain traces of inorganic cyanides

B1150 Precious metals and alloy wastes (gold, silver, the platinum group, but not mercury) in a dispersible, non-liquid form with appropriate packaging and labeling

B1160 Precious-metal ash from the incineration of printed circuit boards (note the related entry on list A A1150)

B1170 Precious-metal ash from the incineration of photographic film

B1180 Waste photographic film containing silver halides and metallic silver

B1190 Waste photographic paper containing silver halides and metallic silver

B1200 Granulated slag arising from the manufacture of iron and steel

B1210 Slag arising from the manufacture of iron and steel including slags as a source of TiO_2 and vanadium

B1220 Slag from zinc production, chemically stabilized, having a high iron content (above 20%) and processed according to industrial specifications (e.g. DIN 4301) mainly for construction

B1230 Mill scaling arising from the manufacture of iron and steel

B1240 Copper oxide mill-scale

B2 *Wastes containing principally inorganic constituents, which may contain metals and organic materials*

B2010 Wastes from mining operations in non-dispersible form:

- Natural graphite waste
- Slate waste, whether or not roughly trimmed or merely cut, by sawing or otherwise
- Mica waste
- Leucite, nepheline and nepheline syenite waste
- Feldspar waste
- Fluorspar waste
- Silica wastes in solid form excluding those used in foundry operations

B2020 Glass waste in non-dispersible form:

- Cullet and other waste and scrap of glass except for glass from cathode-ray tubes and other activated glasses

B2030 Ceramic wastes in non-dispersible form:

- Cermet wastes and scrap (metal ceramic composites)
- Ceramic based fibers not elsewhere specified or included

B2040 Other wastes containing principally inorganic constituents:

- Partially refined calcium sulfate produced from flue-gas desulfurization (FGD)
- Waste gypsum wallboard or plasterboard arising from the demolition of buildings
- Slag from copper production, chemically stabilized, having a high iron content (above 20%) and processed according to industrial specifications (e.g. DIN 4301 and DIN 8201) mainly for construction and abrasive applications
- Sulfur in solid form
- Limestone from the production of calcium cyanamide (having a pH less than 9)
- Sodium, potassium, calcium chlorides
- Carborundum (silicon carbide)
- Broken concrete
- Lithium–tantalum and lithium–niobium containing glass scraps

B2050 Coal-fired power plant fly-ash, not included on list A (note the related entry on list A A2060)

B2060 Spent activated carbon resulting from the treatment of potable water and processes of the food industry and vitamin production (note the related entry on list A A4160)

B2070 Calcium fluoride sludge

B2080 Waste gypsum arising from chemical industry processes not included on list A (note the related entry on list A A2040)

B2090 Waste anode butts from steel or aluminum production made of petroleum coke or bitumen and cleaned to normal industry specifications (excluding anode butts from chlor alkali electrolyses and from metallurgical industry)

B2100 Waste hydrates of aluminum and waste alumina and residues from alumina production excluding such materials used for gas cleaning, flocculation or filtration processes

B2110 Bauxite residue ("red mud") (pH moderated to less than 11.5)

B2120 Waste acidic or basic solutions with a pH greater than 2 and less than 11.5, which are not corrosive or otherwise hazardous (note the related entry on list A A4090)

B3 *Wastes containing principally organic constituents, which may contain metals and inorganic materials*

B3010 Solid plastic waste:

The following plastic or mixed plastic materials, provided they are not mixed with other wastes and are prepared to a specification:

- Scrap plastic of non-halogenated polymers and co-polymers, including but not limited to the following:
  - ethylene
  - styrene
  - polypropylene
  - polyethylene terephthalate
  - acrylonitrile
  - butadiene
  - polyacetals
  - polyamides
  - polybutylene terephthalate
  - polycarbonates
  - polyethers
  - polyphenylene sulfides
  - acrylic polymers
  - alkanes C10–C13 (plasticiser)
  - polyurethane (not containing CFCs)
  - polysiloxanes
  - polymethyl methacrylate
  - polyvinyl alcohol
  - polyvinyl butyral
  - polyvinyl acetate
- Cured waste resins or condensation products including the following:
  - urea formaldehyde resins
  - phenol formaldehyde resins
  - melamine formaldehyde resins
  - epoxy resins
  - alkyd resins
  - polyamides
- The following fluorinated polymer wastes
  - perfluoroethylene/propylene (FEP)
  - perfluoroalkoxy alkane (PFA)
  - perfluoroalkoxy alkane (MFA)
  - polyvinylfluoride (PVF)
  - polyvinylidenefluoride (PVDF)

B3020 Paper, paperboard and paper product wastes
The following materials, provided they are not mixed with hazardous wastes:
Waste and scrap of paper or paperboard of:

- unbleached paper or paperboard or of corrugated paper or paperboard
- other paper or paperboard, made mainly of bleached chemical pulp, not colored in the mass
- paper or paperboard made mainly of mechanical pulp (for example, newspapers, journals and similar printed matter)
- other, including but not limited to 1) laminated paperboard 2) unsorted scrap.

B3030 Textile wastes
The following materials, provided they are not mixed with other wastes and are prepared to a specification:

- Silk waste (including cocoons unsuitable for reeling, yarn waste and garnetted stock)
  - not carded or combed
  - other
- Waste of wool or of fine or coarse animal hair, including yarn waste but excluding garnetted stock
  - noils of wool or of fine animal hair
  - other waste of wool or of fine animal hair
  - waste of coarse animal hair
- Cotton waste (including yarn waste and garnetted stock)
  - yarn waste (including thread waste)
  - garnetted stock
  - other
- Flax tow and waste
- Tow and waste (including yarn waste and garnetted stock) of true hemp (*Cannabis sativa* L.)
- Tow and waste (including yarn waste and garnetted stock) of jute and other textile bast fibers (excluding flax, true hemp and ramie)
- Tow and waste (including yarn waste and garnetted stock) of sisal and other textile fibers of the genus Agave
- Tow, noils and waste (including yarn waste and garnetted stock) of coconut
- Tow, noils and waste (including yarn waste and garnetted stock) of abaca (Manila hemp or *Musa textilis* Nee)
- Tow, noils and waste (including yarn waste and garnetted stock) of ramie and other vegetable textile fibres, not elsewhere specified or included
- Waste (including noils, yarn waste and garnetted stock) of man-made fibers

- of synthetic fibers
- of artificial fibers

- Worn clothing and other worn textile articles
- Used rags, scrap twine, cordage, rope and cables and worn out articles of twine, cordage, rope or cables of textile materials

- sorted
- other

B3040 Rubber wastes
The following materials, provided they are not mixed with other wastes:

- Waste and scrap of hard rubber (e.g. ebonite)
- Other rubber wastes (excluding such wastes specified elsewhere)

B3050 Untreated cork and wood waste:

- Wood waste and scrap, whether or not agglomerated in logs, briquettes, pellets or similar forms
- Cork waste: crushed, granulated or ground cork

B3060 Wastes arising from agro-food industries provided it is not infectious:

- Wine lees
- Dried and sterilized vegetable waste, residues and byproducts, whether or not in the form of pellets, of a kind used in animal feeding, not elsewhere specified or included
- Degras: residues resulting from the treatment of fatty substances or animal or vegetable waxes
- Waste of bones and horn-cores, unworked, defatted, simply prepared (but not cut to shape), treated with acid or degelatinised
- Fish waste
- Cocoa shells, husks, skins and other cocoa waste
- Other wastes from the agro-food industry excluding by-products which meet national and international requirements and standards for human or animal consumption

B3070 The following wastes:

- Waste of human hair
- Waste straw
- Deactivated fungus mycelium from penicillin production to be used as animal feed

B3080 Waste parings and scrap of rubber
B3090 Paring and other wastes of leather or of composition leather not suitable for the manufacture of leather articles, excluding leather sludges, not containing hexavalent chromium compounds and biocides (note the related entry on list A A3100)
B3100 Leather dust, ash, sludges or flours not containing hexavalent chromium compounds or biocides (note the related entry on list A A3090)
B3110 Fellmongery wastes not containing hexavalent chromium compounds or biocides or infectious substances (note the related entry on list A A3110)
B3120 Wastes consisting of food dyes

B3130 Waste polymer ethers and waste non-hazardous monomer ethers incapable of forming peroxides
B3140 Waste pneumatic tyres, excluding those destined for Annex IVA operations
B4 *Wastes which may contain either inorganic or organic constituents*
B4010 Wastes consisting mainly of water-based/latex paints, inks and hardened varnishes not containing organic solvents, heavy metals or biocides to an extent to render them hazardous (note the related entry on list A A4070)
B4020 Wastes from production, formulation and use of resins, latex, plasticizers, glues/adhesives, not listed on list A, free of solvents and other contaminants to an extent that they do not exhibit Annex III characteristics, e.g. water-based, or glues based on casein starch, dextrin, cellulose ethers, polyvinyl alcohols (note the related entry on list A A3050)
B4030 Used single-use cameras, with batteries not included on list A
Footnotes

1. Characterization of wastes: ...
2. Corresponds to the hazard classification system included in the United Nations Recommendations on the Transport of Dangerous Goods (ST/SG/AC.10/1Rev.5, United Nations, New York, 1988)
3. Decision III/1 (Amendment to the Basel Convention)

The Conference,
Decides to adopt the following amendment to the Convention:
"Insert new preambular paragraph 7 bis:
Recognizing that transboundary movements of hazardous wastes, especially to developing countries, have a high risk of not constituting an environmentally sound management of hazardous wastes as required by this Convention;
Insert new Article 4A:

1. Each Party listed in Annex VII shall prohibit all transboundary movements of hazardous wastes which are destined for operations according to Annex IV A, to States not listed in Annex VII.
2. Each Party listed in Annex VII shall phase out by 31 December 1997, and prohibit as of that date, all transboundary movements of hazardous wastes under Article 1(I)(a) of the Convention which are destined for operations according to Annex IV B to States not listed in Annex VII. Such transboundary movement shall not be prohibited unless the wastes in question are characterized as hazardous under the Convention.

References

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For further information

The Secretariat of the Basel Convention (SBC), Official Web site of the SBC: http://www.basel.int/.

The Secretariat of the Basel Convention (SBC), Publications and Other Documentation. Official Web site of the SBC: http://www.basel.int/pub/pub.html.

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PART III

Chemical pollution potential from solid waste: short- and long-term effects

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Solid Waste: Assessment, Monitoring and Remediation
Twardowska, Allen, Kettrup and Lacy (Editors)
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III.1
Assessment of pollution potential from solid waste

Irena Twardowska

III.1.1. Introduction

The majority of disposed wastes, including recyclable waste, is not environmentally safe. Waste as a freshly generated anthropogenic material usually is not geochemically stable. Hence, contaminant release at different stages of waste exposure to environmental conditions, either at the disposal site, or in case of its bulk use for construction purposes, e.g. as a common fill, can be anticipated. The leaching of soluble constituents upon contact with water is regarded as a main mechanism of release, which results in a potential risk to the environment.

The need for reliable assessment and prediction of waste material behavior under specific conditions of exposure resulted in the development of a multitude of leaching/extraction tests and testing schemes by different groups of analysts and national regulatory bodies. In the USA, the basic set of guidelines for solid waste analysis for environmental risk assessment includes a multi-volume continuously updated assemblage, USEPA SW-846 (1996–2003). There, different techniques for waste sampling, preservation, storage and analysis dependent upon the physical state of a material, test aim, frequency of sampling and type of contaminants are presented. The testing program comprises waste material, disposal site and all the compartments of the environment in the vicinity of the site in the area of waste processing and utilization (i.e. waste, landfill air, groundwater, soil, run-off water, soils and pore solution of the vadose zone and plants). These guidelines are widely available and are in common use in the USA and several other countries.

In Europe, the variety of data and schemes developed in many countries evoked a need of integration and unification of approaches towards evaluating the leaching behavior of waste materials that are either disposed or used in construction. The main goal behind these efforts is the development and harmonization of reliable testing procedures for short- and long-term risk assessments, which would consider specificity, but also similarities in the leaching behavior of different waste and other materials. The stronger links between different research groups involved in this issue in Europe were developed through the Measurements and Testing Program of the EC, Working Group B of ISCOWA – The International Society for the Environmental and Technical Implications of Construction with Alternative Materials (Laboratory Testing and Environmental Impact Assessment), WASCON conferences on environmental implications of construction with waste

materials and technology developments held in 1991, 1994, 1997, 2000 and 2003, the Workshop on the Harmonization of Leaching/Extraction Tests for Environmental Risk Assessment held in 1996 and follow-up development of the European Network for Harmonization of Leaching/Extraction Tests (2000).

One of the most important results from these studies is the leaching similarity of different waste materials having corresponding geochemical properties. These similarities allow for a common approach in the characterization of leaching by focusing on the relevant key contaminants and a limited number of controlling parameters in relation to quality control and regulatory testing (van der Sloot et al., 1993, 1994a,b, 1996, 1997; Eighmy and van der Sloot, 1994; van der Sloot, 1996, 2000a) affords unification of data reporting and comparison in different fields, and therefore facilitates evaluation and regulatory control of waste and non-waste materials with respect to long-term environmental impact and its mitigation, in particular when usable materials are transformed into waste and vice versa.

The above works and studies set a foundation for the development of a protocol for assessing environmental risk from solid wastes and generically relevant materials based on their leaching behavior. This protocol has already started to materialize in the outcome of standardization activity of CEN/TC 292 – European Committee for Standardization/ Technical Committee Characterization of Waste, and in a linkage with eight other core Environmental and related Technical Committees (TCs), e.g. TC 308 on sludges, and five other liaisons outside CEN: International Organization for Standardization ISO/TC 190 on Soil Quality, UNEP, EFTA, EC/DGXI and EC/DGXII. These European Standards are being developed primarily to support the needs of the EU and EFTA countries, in particular to provide methods for testing of waste in a standardized form for the EU member states to fulfill the requirements of the EU Directives related to waste management.

The EC Landfill Directive (EC, 1999) imposed a large number of requirements with respect to the quality of the waste that may be accepted for landfill; a list of waste characterization methods to be standardized had to be prepared by July 2001. To fulfill this requirement, TAC Subcommittee on the EC Landfill Directive developed a so-called "toolbox" of methods for testing of waste, which the EC member states should have available as CEN or ISO Standards (TAC Landfill, 2001). This toolbox comprises a list of methods and procedures for sampling, pre-treatment, evaluation of general waste properties, methods of digestion of raw waste, waste analysis, and leaching tests, as well as specifies the needs for research for development of further methods and procedures.

Recently, the initiative has also been undertaken with the aim of development within the CEN Environmental and related TCs, and external liaison bodies of horizontal standards for upcoming EU directives on sludge, soil and biowaste and thus to produce, where possible, one standard as opposed to several elaborated in a vertical manner (CEN BT, 2001; CEN/TC 292, 2002c, 2003; Project HORIZONTAL, 2003).

The three basic fields of waste characterization are being covered by the European standardization activity: (1) waste sampling; (2) leaching behavior; and (3) analysis of waste and eluates. A complementary activity for all these fields is (4) terminology – related terms and definitions that assure univocal data comparison and interpretation. This activity is aimed to developing reliable testing procedure for short- and long-term environmental risk assessment from waste disposed of or utilized for different purposes.

Below, the current stage of studies and European standards development, along with problems and pitfalls of prognoses based on standard tests will be discussed.

III.1.2. Testing procedures for risk assessment

III.1.2.1. General approach to characterization and testing of waste

Simplified arbitrary test procedures related to regulatory limits, and thus having direct economic consequences, very often bear no relation to the actual situation to be controlled and hence should not be considered as a sound decision-making tool. The comparison of different regulatory test methods designed for different purposes, mainly to assess the potential for long-term environmental impact and used in the USA (EP-tox, TCLP, availability test), Germany (leach test DIN 38414 S4), France (leach test X 31-210), Switzerland (leach test TVA) and the Netherlands (availability test NVN 2508, column test NVN 2508, serial batch extraction NVN 2508, and monolith tank leaching NVN 5432) showed a low efficiency in achieving that goal (van der Sloot et al., 1991b). The reason for the failure was explained by the attempt of evaluating all materials for all disposal/use options by one decision test. It was further concluded that the best approach toward the testing procedure to be applied as a basis for decision making on different aspects of waste handling (e.g. treatment, recycling, utilization, disposal) requires application of scenarios based on actual environmental data, matrix composition and origin of the materials, specific for the purpose and exposure conditions. Due to a number of research projects undertaken in the last decades in various research centers, the understanding of leaching behavior of waste has grown substantially and resulted in a better identification of release mechanisms and controlling factors. One of the fundamental conclusions derived from these studies has been the need of a strong consideration of the time-dependent release for prediction of the long-term leaching behavior of waste on a time scale far beyond that of any realistic laboratory-leaching test. The major premise for the short- and long-term assessment is the systematic behavior of inorganic constituents controlled by several basic variables – of these liquid to solid ratio (*L/S*) (reflecting the time factor), pH, redox Eh and complexation have been considered the most important ones.

III.1.2.2. Generic leach pattern of waste

A crucial observation for the long-term prediction of leaching behavior of constituents is the III-stage generic leach pattern that comprise wash-out (I), solubility-controlled dissolution (II) and delayed release (III) stages shown in Figure III.1.1 (van der Sloot et al., 1993). This pattern reflects a situation when after decline of a solubility controlling phase, e.g. availability of adequate buffering agents, the massive release of constituents at a high rate may occur at some point delayed in time. In general, the correct prediction of the occurrence and intensity of the delayed release (III) stage appears to be a particularly problematic task. In the most frequent case, the development of this phase is determined by two kinetically defined processes of acid generation and buffering of constituents release, either due to the direct attack of generated acid loads (instant neutralization), or independent dissolution of buffering constituents, when dynamics of acid generation may

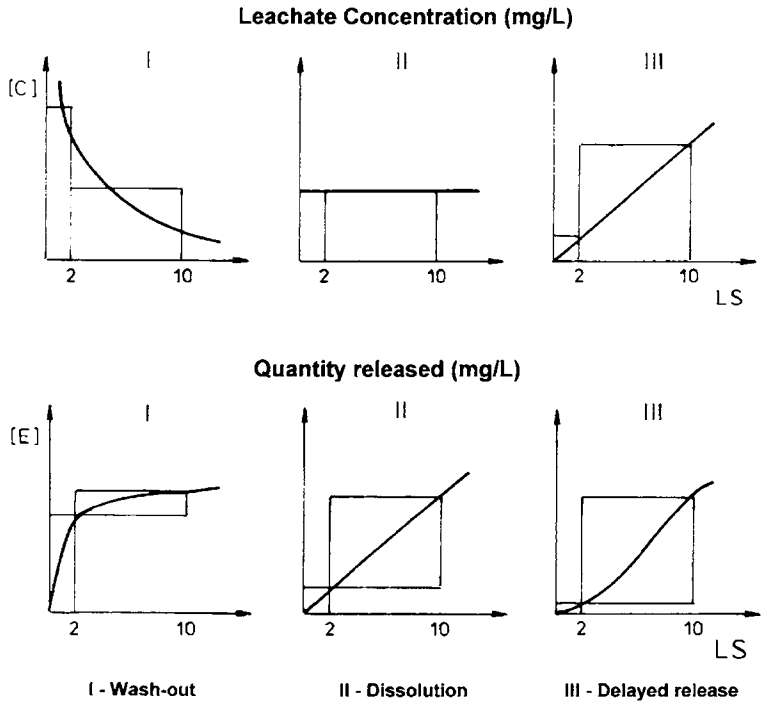


Figure III.1.1. Patterns of concentrations in leachate and cumulative loads in the three-stage mechanisms of constituent release from waste matrix (after van der Sloot et al., 1993).

prevail over the buffering agents availability in pore solution in spite of their still abundant total content in the system (e.g. carbonate dissolution in microenvironments of heterogeneous waste material). The complexity of real systems makes the correct prediction of the delayed release (III) stage development extremely difficult and requires complete and detailed information not just on the chemical composition, but also on the phase composition of a waste material, including the forms, dispersion and specific surface of the phases in the matrix, which influence their reactivity and availability (Twardowska et al., 1988; Twardowska and Szczepańska, 2002).

III.1.2.3. Long-term leaching behavior issues

The kinetically defined processes of constituent release makes simulation of long-term leaching behavior in a laboratory particularly complicated. It is generally agreed that a single batch test will never allow for long-term prediction. The compression of a time scale during accelerated testing may cause a deep distortion of the actual pattern, as adequate acceleration of process kinetics is generally not possible. Therefore, a reasonable level of compromise should ensure proper information and a good confidence in the tests for long-term risk assessment from waste relating to mass transfer, environmental physico-chemical parameters and the time scale (Quevauviller, 1996).

The comparison of agreement of different regulatory leaching test procedures for waste materials and construction materials with field data showed numerous examples of discrepancy, e.g. poor agreement of USEPA tests such as EP-tox, TCLP extracts, synthetic acid rainwater (SAR) extracts, CO_2 saturation test and deionized (DI) water extracts with the field leachate due to the difference between low Eh potential in the field leachate compared to high Eh in the laboratory tests (van der Sloot et al., 1991b). Also studies on leaching characteristics of coal combustion fly ash (FA) deposits in the natural conditions showed significant differences in comparison with the data obtained in laboratory leaching tests (Fällman and Hartlén, 1994; Janssen-Jurkovičová et al., 1994; Meij and Schaftenaar, 1994; Meij and te Winkel, 2000; Twardowska and Szczepanska, 2002). Due to the much more complicated nature of the environmental interactions, the distortion of the time scale may cause serious qualitative and quantitative errors in prediction of the leaching behavior of a material. In particular, kinetically determined processes and reactions such as weathering, dissolution of amorphous phases and formation of secondary minerals, as well as the effect of flow conditions upon the actual composition and ionic strength of pore solutions are not adequately considered in these tests. Correct prediction of the leaching behavior of trace elements from the material requires the precise modeling of processes occurring within the macro-components of a material, which are responsible for the formation of factors controlling trace metal release (pH, Eh, exposure). The complexity of real systems makes this task extremely difficult. Nevertheless, significant progress in the development of reliable testing procedures for prediction of the leaching behavior of waste within the wash-out (I) and dissolution (II) stages has already been achieved.

III.1.2.4. Waste environmental evaluation scheme

As a result of complex studies and analysis on constituent release from granular material carried out in numerous European laboratories, a substantial part of them being conducted since the late eighties within the research program of the Netherlands Energy Research Foundation ECN, a more flexible material- and site-specific approach to waste environmental evaluation than one unified decision test has been proposed in order to improve the basis for decisions concerning waste management options (van der Sloot et al., 1991a,b, 1994b, 1996, 1997; Eighmy and van der Sloot, 1994; van der Sloot, 2000a). Material characteristics, site-specific information and long-term aspects of major element chemistry as input data, as well as the modeling of constituent release and the sensitivity of the system to environmental factors are essential elements in this approach (Fig. III.1.2). Besides material specificity, the interactions between waste and soil were found to be of great importance in controlling the net release of contaminants from waste disposal and reuse activities (van der Sloot et al., 1991a; Hockley et al., 1992; Hjelmar et al., 2000; Odegard et al., 2000). The current regulatory waste testing methods neglect the waste–soil interface effects and are focused on evaluating entirely the waste properties. This results in inconsistency with field data, most often giving false-positive evaluation of the environmental hazard from waste. The novel approach suggests site-specific evaluation of the environmental hazard, which considers inclusion of waste–soil interaction into the waste testing procedure. A classification system for waste–soil interactions, with diffusion-dominated interfaces and equilibrium reactions has been used as a basis for an approach to the subject that aims to incorporating this model into the macroscopic soil

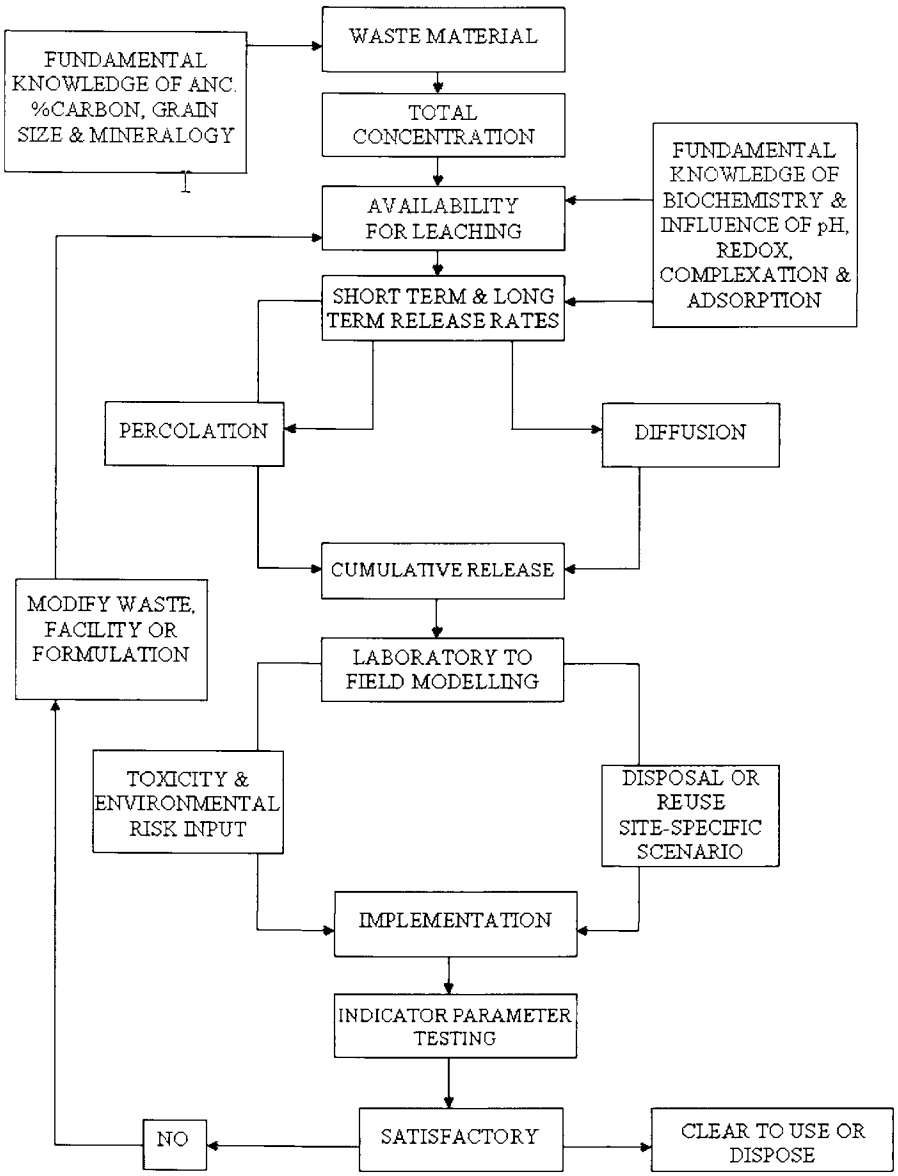


Figure III.1.2. Solid waste testing and evaluation flow chart (after van der Sloot et al., 1991b).

models and creating a link between macroscopic soil and groundwater contamination models for long-term environmental impact assessment and public policy (van der Sloot et al., 1991a; Hockley et al., 1992; Odegard et al., 2000). This approach, though rational, still presents considerable practical difficulties in developing reliable predictive models and thus has not yet been implemented in standardization and regulatory test procedures.

A flow chart summarizing the above approach to evaluation of waste materials based on leaching data and environmental factors, which distinguish inorganic, organic and volatile organic compounds, is presented in Figure III.1.3 (van der Sloot et al., 1991b). Each of these kinds of compounds is to be treated differently in the subsequent steps. The specific features of this scheme are as follows:

- The leaching is addressed in terms of constituent release as a function of time.
- The evaluation procedure includes different tests for waste material and stabilized waste material.
- The procedure comprises sampling, waste analysis and leaching.
- The properties required for long-term environmental impact assessment are indicated and addressed in relevant levels of testing.
- The aspects to be considered at the different levels of testing are also indicated.
- The waste–soil interfaces and a field validation is the last step preceding potential environmental impact assessment.

It has been assumed that the integration of leaching data, controlling factors and environmental conditions ultimately leads to an assessment of potential environmental impact and to the decision concerning the environmental sustainability of a waste site with or without the controlling measures.

The scheme gives the outline of the testing procedure required for an environmental impact assessment, but not yet necessarily developed in detail for diverse kinds of contaminants, waste materials and tests. To date, the particular tests and levels of testing in this scheme display different extent of development. In the research and standardization activity at the European level, the advances in these areas reflect the place of a standard in the business plan and target dates.

The comprehensive framework of the unified systematic approach to evaluation of leaching behavior of granular inorganic waste based on the general geochemical principles (pH and redox-dependent precipitation/dissolution, liquid phase complexation and sorption), applied to a wide range of waste materials by a number of authors was outlined by Eighmy and van der Sloot (1994). The subsequent stages of integrating information on leaching behavior of waste comprise:

I "Basic Characterization": physical properties (structure of matrix, particle size, specific surface), solid phases at the particle surface, mineralogical and chemical composition.

II Evaluation of "Systematic Leaching Behavior" with use of the fundamental information derived from step I. The framework of the evaluation procedure includes: (i) serial batch, column, or lysimeter tests to assess cumulative release rate (mg/kg) vs. cumulative *L/S* ratio/or time, or pH, in relation to the total content (mg/kg) or environmentally available fraction of element (mg/kg) over geologic time (i.e. 1000–10,000 years. Here though, entirely soluble compounds available at the moment of testing can be assessed. No generation of new loads of soluble compounds is considered in this test); (ii) determination whether the leaching process is kinetic- or equilibrium-based to estimate the duration of required observation of a leaching process; (iii) additional leaching tests for elucidating the controlling effect of Eh, complexation and sorption processes; (iv) geochemical thermodynamic modeling to

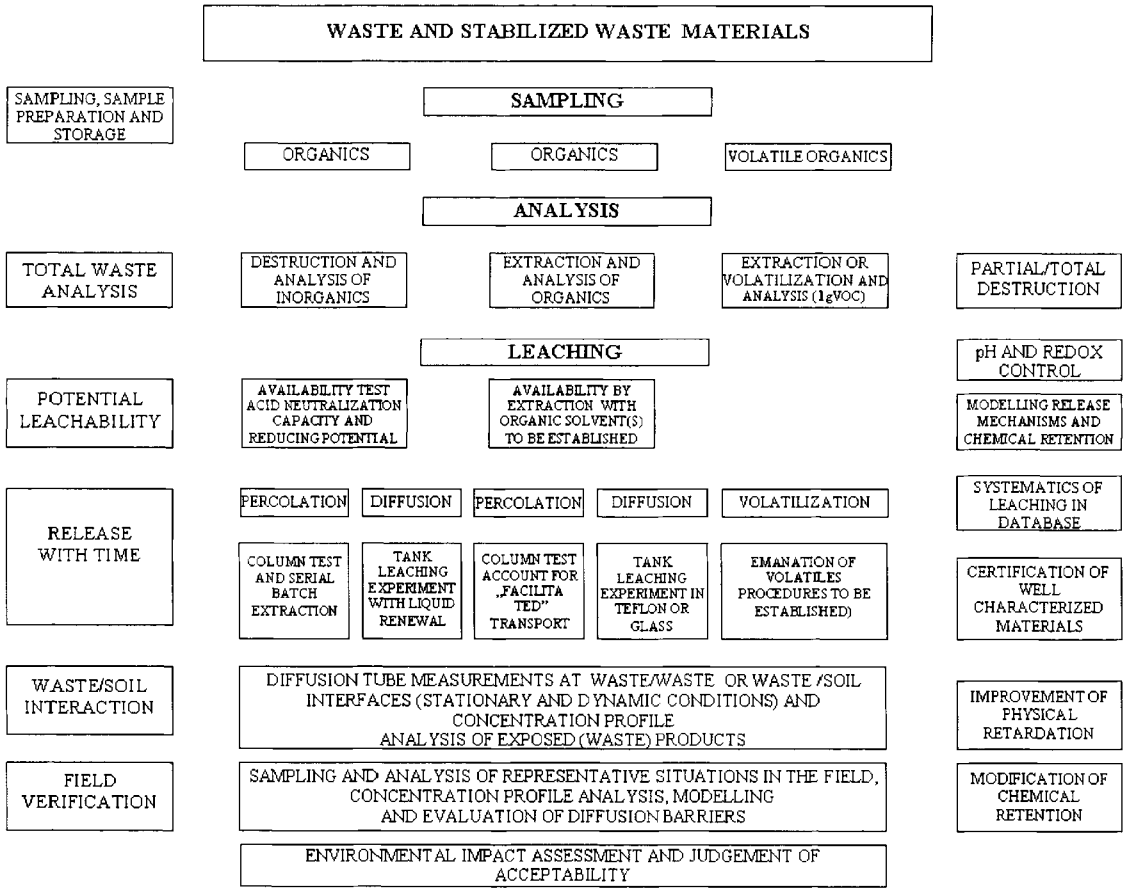


Figure III.1.3. Scheme for the evaluation of long-term release from waste and stabilized waste material (after van der Sloot et al., 1991a).

verify equilibrium-based leaching behavior; and (v) kinetic modeling to verify kinetic-based leaching behavior (to be developed).

III "Field Verification" (comparative evaluation) of laboratory test- and predictive data identified in step II by means of: (i) full-scale data from applied projects; (ii) large-scale pilot or demo data; and (iii) lysimetric studies.

IV "Accelerated Testing": simplified leaching procedures, and long-term prediction of leaching behavior, in particular for assisting industry with QC, upstream and downstream modifications in waste stream, and cost reduction. The framework for these procedures includes: (i) rapid, concise, reliable tests for characterization, compliance and verification of data derived from the step II; (ii) accelerated aging, weathering, destruction tests; and (iii) simulated long-term leaching or extraction tests.

III.1.3. European standardization activity

III.1.3.1. Testing levels and categories

The above frameworks set a foundation for the development of a protocol and a set of European Standards for assessing environmental risk from solid wastes and generically relevant materials based on their leaching behavior.

Standardization activity comprising basic fields of waste characterization, i.e. waste sampling, evaluation of leaching behavior and analysis of waste and eluates in different stages of development (CEN/TC 292, 2002b). The status of standardization of terminology on waste (material and management related terms and definitions) that assures univocal data comparison and interpretation has been addressed in Chapter I.

The test standards in force, which are intended to identify the leaching properties of granular waste and sludges, are generally divided into three categories (EN 12457-1/2/3/4, 2002):

1. Basic characterization tests are used to obtain information on the short- and long-term leaching behavior and characteristics properties of waste materials. *L/S* ratios, leachant composition, factors controlling leachability such as pH, redox potential, complexing capacity and physical parameters are addressed in these tests.
2. "Compliance" tests are used to determine whether the waste complies with specific reference values. The tests focus on key variables and leaching behavior identified by basic characterization tests.
3. "On-site verification" tests are used as a rapid check to confirm that the waste is the same as that, which has been subjected to the compliance test(s).

These categories are adequate to the three-tier procedure of characterization and testing of waste provided in Annex II of the EC Landfill Directive (1999) referring to Levels 1, 2 and 3 of testing (Fig. III.1.4).

The Level 1 of testing is considered to be the key to the waste acceptance system. Its purpose is to determine the intrinsic properties of the waste in order to decide on the appropriate methods and site for the treatment, disposal or reuse of the waste. According to the Landfill Directive, the waste producer, before removal from the producer's premises,

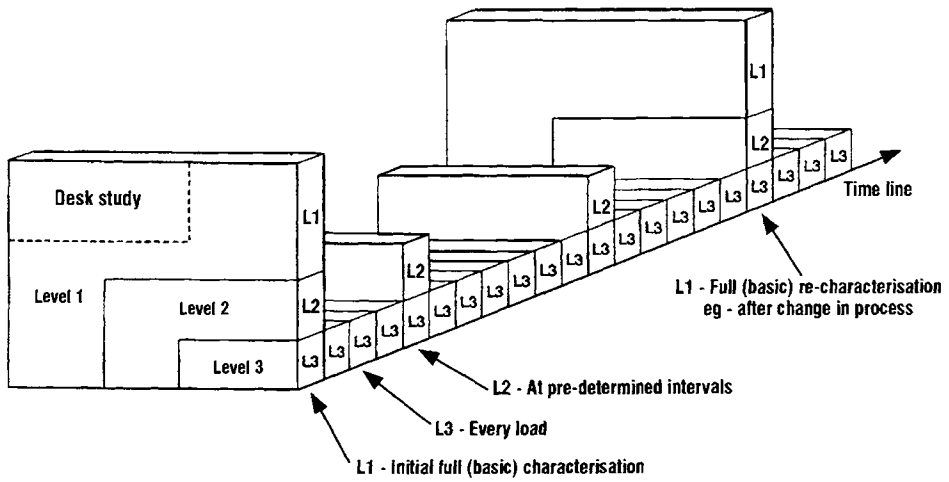


Figure III.1.4. Scheme of a three-tier hierarchy for characterization, sampling and testing of waste (according to Annex II of the Landfill Directive, 1999).

should use it for assessment of waste characteristics. Once the comprehensive characterization of the waste material is documented, provided the waste is of a consistent nature, only infrequent confirmation of this characterization by the waste producer is necessary. Therefore, the periodic monitoring in Levels 2 and 3 is based on the bank of characterization data provided by Level 1.

III.1.3.2. Waste sampling

Sampling is the first step and an essential part of the reliable environmental risk assessment from waste material related to its treatment/disposal/reuse options. It should follow the three-tier procedure of waste characterization and give representative material for testing. The hydrogeochemical monitoring practice shows that this step is critical for quality requirements: about 30% of errors are being committed during collecting and transport of samples, 60% of errors falls to sample treatment and preparation for analysis and just 10% are the analytical errors (Ramsey et al., 1992; Ramsey, 1993). In waste characterization testing the errors are probably more evenly distributed between sampling and the testing scenario and its interpretation, while analytical errors also play a marginal role. Due to the variety of waste material and other related issues such as different sampling goals, strategies, techniques, and the risk posed by this waste to the environment, the sampling scenario should be designed accordingly on an individual basis.

As a result, for European Standards for Waste Sampling the concept of the "shop shelf" approach was developed, which allows the appropriate parts of the standard to be selected according to a sampling program. This idea is being materialized in the development of the series of coordinated basic Draft European Normative Standards dealing with sampling techniques and procedures (CEN/TC 292.WG1, 2000). The standards in this series, which already underwent the CEN-enquiry are: characterization of waste – sampling of liquid and granular waste materials including paste-like materials and sludges – a framework

for sampling plan preparation (WI 29001, 2003); Part 1: selection and application of criteria for sampling under various conditions (WI 292002, 2001); Part 2: sampling techniques (WI 292017, 2001); Part 3: sample pre-treatment in the field (WI 292018, 2001); Part 4: procedures for sample packaging, storage, preservation, transport and delivery (WI 292019, 2001). Terms and definitions related to sampling constitute an integral part of these standards.

This approach tends to acknowledge waste material, process and objective variability, allowing the standard to be adaptable to technical environment and objectives for sampling. The sampling objectives, along with the sequence of operations required to fulfill them are detailed in an overall *sampling program* that is defined as "total sampling operation, from the first step in which the objectives of sampling are defined to the last step in which data is analyzed against these objectives." The details of the program must be discussed and agreed with all involved parties.

The links between the essential elements of a sampling program, *sampling plan* being one of these elements, are illustrated in a process map (Fig. III.1.5). The Draft European Standard (WI 292001) sets out the general principles to be applied in the preparation of a sampling plan for the characterization of waste materials to previously set objectives. Key elements of a sampling plan are defined in Figure III.1.6. Waste sampling plan with reference to the program objectives should be in conformity with a relevant level of testing according to the three-tier general procedure for waste characterization and testing (Fig. III.1.4) and ensures a representative nature of the sampling. In this pre-standard, probabilistic sampling is seen as the preferred option. The appropriate sampling techniques are considered to be selected from PrEN, WI 292017 (Part 2) using statistical guidance from prEN, WI 292002 (Part 1).

The Draft European Standard PrEN, WI 292002 (Part 1): "selection and application of criteria for sampling under various conditions" presents statistical principles and purpose of sampling, types and pattern of sampling (probabilistic and methodology-agreed), as well as methodology of determining the size and number of samples, defining the sampling scheme and statistical principles (objectives, types of variability, population parameters and sample statistics, the scale of sampling and reliability).

The Draft European Standard PrEN, WI 2920017 (Part 2): "sampling techniques" describes techniques used in the recovery of the sample and defined as "the physical procedure employed by the sampler to collect part or parts of a discarded or secondary material for subsequent investigations." The standard details two types of sampling procedures:

- Primary sampling that is representative of the whole mass being sampled (e.g. a core taken through a well-mixed stream).
- Spot sampling that removes a portion of a total mass. It is generally used when sampling large masses, where access across or coring through the material is impractical or dangerous.

The sampling technique adopted depends on a combination of different characteristics of the material and circumstances encountered in the sampling location. This part of the (draft) European Standard describes techniques for sampling liquid and granular waste material, including paste-like materials and sludges, found in a variety of locations. The standard also gives guidance on the selection and preparation of equipment, apparatus

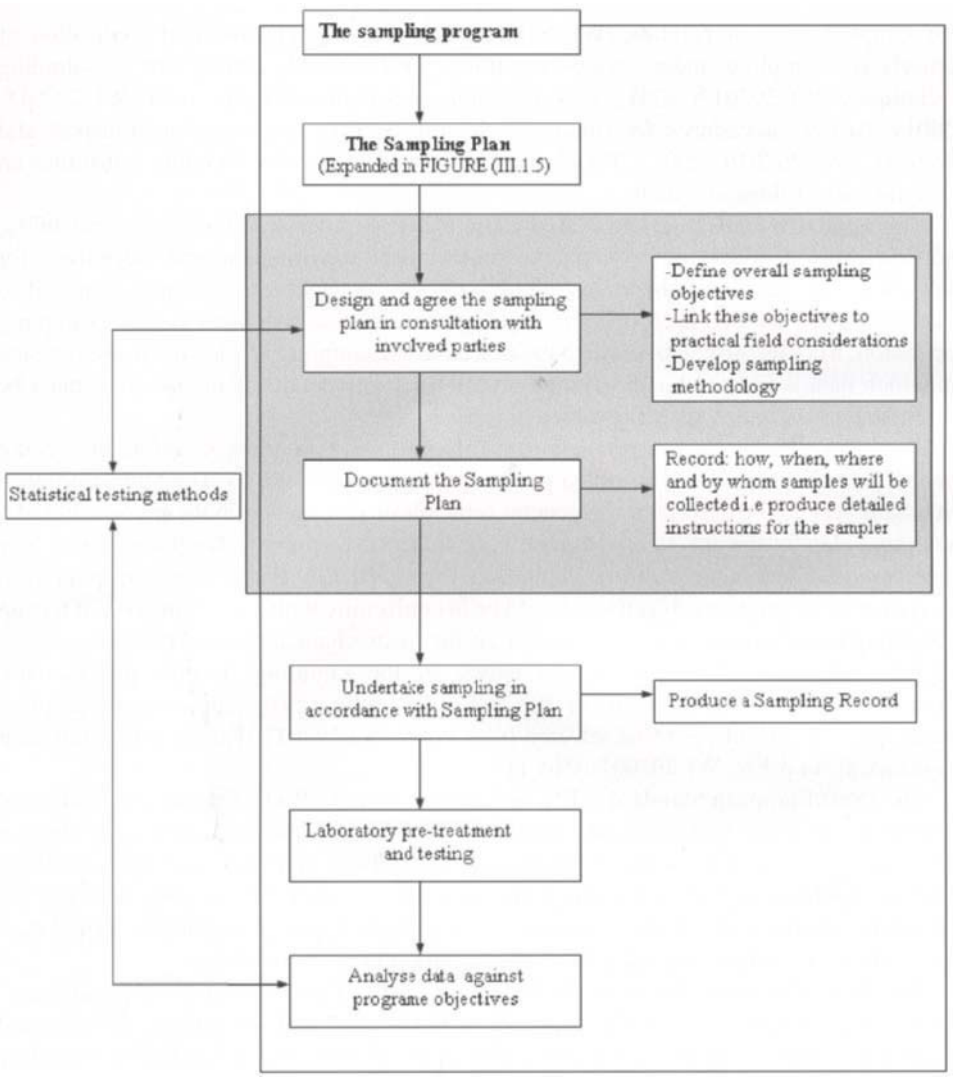


Figure III.1.5. Links between the essential elements of a sampling program (after WI 292001, CEN/TC 292/WG 1, 2001).

used in the waste sampling program and recommendations on sample handling, along with the relevant terms and definitions.

The Draft European Standard PrEN, WI 292018 (Part 3): "sample pre-treatment in the field" specifies procedures for field sample size reduction for the above kinds of waste, among them for generic sub-sampling of solid waste to provide sub-sample in the field that is representative of the overall sample and suitable for submission to the laboratory. It does not deal with sub-sampling in the laboratory or the preparation of samples for analysis.

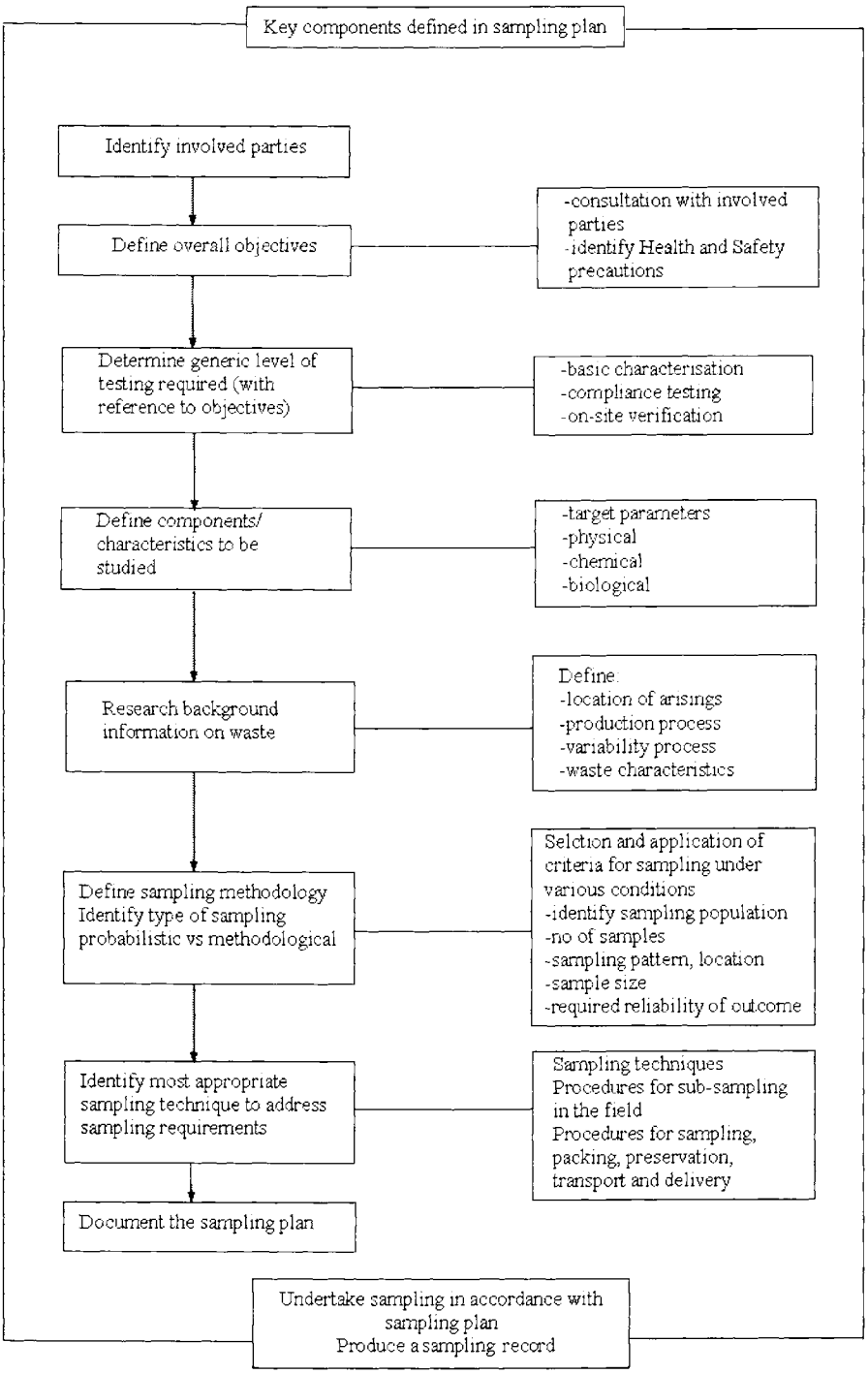


Figure III.1.6. Key elements of a sampling plan (after WI 292001, CEN/TC 292/WG 1, 2001).

The Draft European Standard PrEN. WI 292019 (Part 4): "procedures for sample packaging, storage, preservation transport and delivery" describes recommendations or methods for the packaging, preservation, short-term storage and transport of samples of both solid and liquid waste, including paste-like substances and sludges, or for samples of similar materials. It is applicable for all wastes or secondary materials, excluding domestic wastes.

In order to facilitate the enforcement of the Landfill Directive (EC, 1999), EC requested CEN/TC 292 (2002a) to prepare the Draft European Standard on Sampling – Part 5 (WI 292041, 2003) that should incorporate the examples of several sampling scenarios of the typical sampling situations relevant for the Landfill Directive: piles, moving belts, falling streams, truckloads and tanks. They may be generic sampling plans for typical situations or sampling plans developed especially for specific situations and include sampling of granular, monolithic, paste-like waste and sludge, as well as sampling of inert, non-hazardous and hazardous waste (the target date for Formal Vote for this Standard is 2005).

The role of sampling, sub-sampling, storage and pre-treatment at different levels in the characterization of waste is presented in Figure III.1.7.

III.1.3.3. Determination of the leaching behavior of waste

III.1.3.3.1. Basic characterization tests

The release of soluble constituents upon contact with water is regarded as a main mechanism of release, which results in a potential risk to the environment during the reuse or disposal of waste materials. The basic assumption for testing is that leaching behavior of waste is influenced by several parameters and external factors, of which the chemical nature of waste in terms of pH, reducing properties and degradable organic matter content, the nature of the leachant, the contact time of the leachant with the waste and release mechanism (solubility or diffusion), as well as the chemical, physical and geotechnical natures of the environment, to which the waste is exposed, are considered of particular importance. For examination of the influence and importance of these factors, the basic characterization tests have been developed.

For basic characterization, a methodology for the determination of the leaching behavior of waste under specified conditions has been formulated in the European Standard EN 12920: (2003), where the steps required to achieve such a characterization are specified. This generally requires several tests to be performed, to use or establish a behavioral model and the validation of the model.

The standardization procedures that will allow supplying reliable data for the significant part of waste stream and for its site-specific long-term leaching behavior are currently in progress. Up-flow percolation test (under specified conditions) (prCEN/TS 14405, 2002) belongs to the category basic characterization tests and specifies a test to determine the leaching behavior of inorganic constituents from granular waste without or with size reduction. The waste body is subjected to percolation with water as a function of *L/S* ratio under hydraulically dynamic conditions. The method is a once-through column leaching test and the test results establish the distinction between different release patterns, for instance washout and

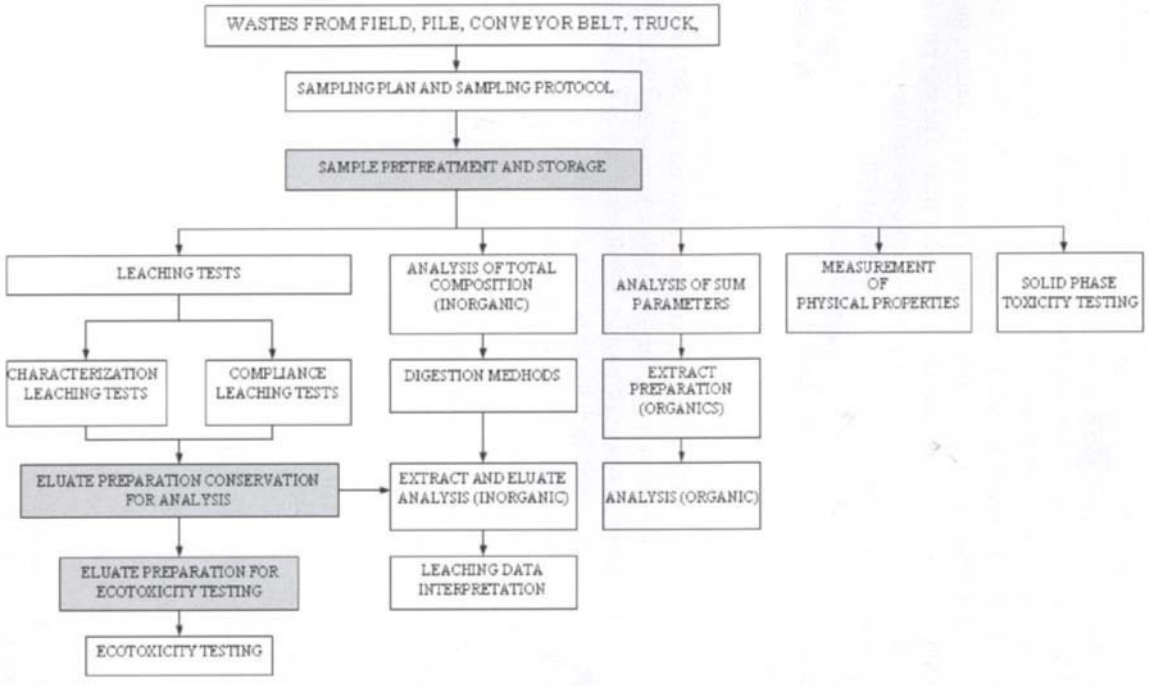


Figure III.1.7. Role of sampling, sub-sampling, storage and pretreatment of waste at different levels in the characterization of waste (after van der Sloot, 2002).

release under the influence of interaction with the matrix, when approaching local equilibrium between waste and leachant. The release of soluble constituents upon contact with water is regarded as a main mechanism of release, which results in a potential risk to the environment during the reuse or disposal of waste materials.

Other leaching behavior tests under development (expected Formal Vote in 2004 and 2005, respectively) that belong to the category of basic characterization tests consider determining the influence of pH on the release of inorganic constituents from a waste into the aqueous solution. These tests are intended to provide knowledge of the potential and anticipated leachability of pH-controlled specified, potentially harmful or hazardous components from waste. In the first one (pH "static test" WI 292033, 2003) pH is controlled at pre-selected values over the entire testing period by continuous measurement and automatic addition of acid or base to reach desired pH values. The test provides insight in the sensitivity of leaching of components from a specific material to pH (Figure III.1.8 exemplifies the influence of pH on the leaching behavior of Cd).

In the second one (acid (ANC) and base neutralization capacity (BNC) test WI 292046, 2003) equilibrium conditions are established at different pH values as a result of the reaction between pre-selected amounts of acid or base and test portions of the waste material. This test is applicable to determine the ANC and BNC of a waste material. Preceding research works demonstrate the data difference between both pH-controlled leaching tests (van der Sloot and Hoede, 1997), and provide data on ANC and BNC for a wide range of materials (van der Sloot, 1996; van der Sloot and Hoede, 1997; van der Sloot et al., 1997,2000a; EU/European Network project, 2000) that are exemplified in Figure III.1.9. Size reduction is performed in both tests to accelerate reaching of equilibrium condition. Influence of pH on leaching with initial acid/base addition is to be evaluated with use of prCEN/TS 14429 (2003).

A further development of pH-controlled tests is WI 292XXX (2002). In the test, equilibrium condition is established at near neutral pH as a result of the reaction between pre-selected amounts of acid or base and test portion of the waste material. Also, in this test, size reduction is performed to accelerate reaching of equilibrium condition. Dissolved organic carbon (DOC) analyzed in the eluate provides a measure for biodegradability (e.g. see Figure III.1.10). Analytical data from the test on the influence of pH on the leaching behavior may be used for modeling metal–DOC interaction (Fig. III.1.11) that has been found to be an important factor affecting heavy metal release (Meima et al., 1999; EU/European Network project, 2000).

III.1.3.3.2. Compliance tests

The four procedures described in the four European Standards EN 12457–1/2/3/4 (2002) are one- or two-stage batch tests based on different *L/S* ratios. They deal with the specifications of a compliance test for leaching of granular waste materials and sludges under specific conditions. In these compliance tests, the final conditions of the test are imposed by the waste itself. The key factors influencing leaching, which are considered in these tests are contact time, *L/S* ratio, pH, reducing properties and the leaching of organic contaminants.

The compliance tests comprised by EN 12457–1/2/3/4:2002 are based on the assumption that equilibrium or pseudo-equilibrium is reached under the test conditions;

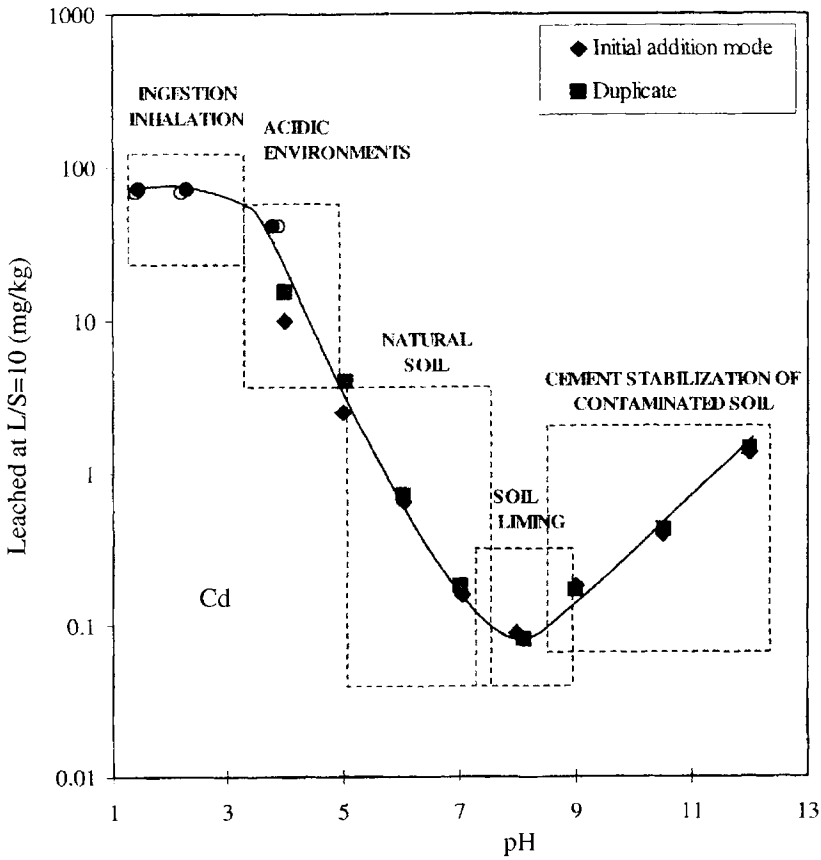


Figure III.1.8. Illustration of the influence of pH on the leaching behavior of Cd in a heavily sewage sludge amended soil in relation to different scenarios (test performed with initial acid/base addition) (after EU project SMT4-CT96-2066).

24 h are considered to be sufficient to reach this condition. Influence of *L/S* ratio is the major factor addressed in this standard. In its four parts, different *L/S* are specified (10, 8 and 2), leading generally to different test results. As in this standard the waste itself imposes the final conditions of the test, sample handling and storage, as well as laboratory preparation such as size reduction, performance of the leaching test and analysis tend to limit the changes of these factors induced by the external exposure or fine grinding. Considering that the leaching of organic contaminants is governed by processes, which differ substantially from that of inorganic contaminants and still are not well addressed, the standard specifies a scope that excludes organics.

The informative part of the standard (Annex A) underlines, that "the test results obtained with the compliance test specified in this standard only allow a direct comparison with regulatory limits on a pass/fail basis". A comprehensive evaluation of the leaching behavior requires a basis or framework of reference such as that

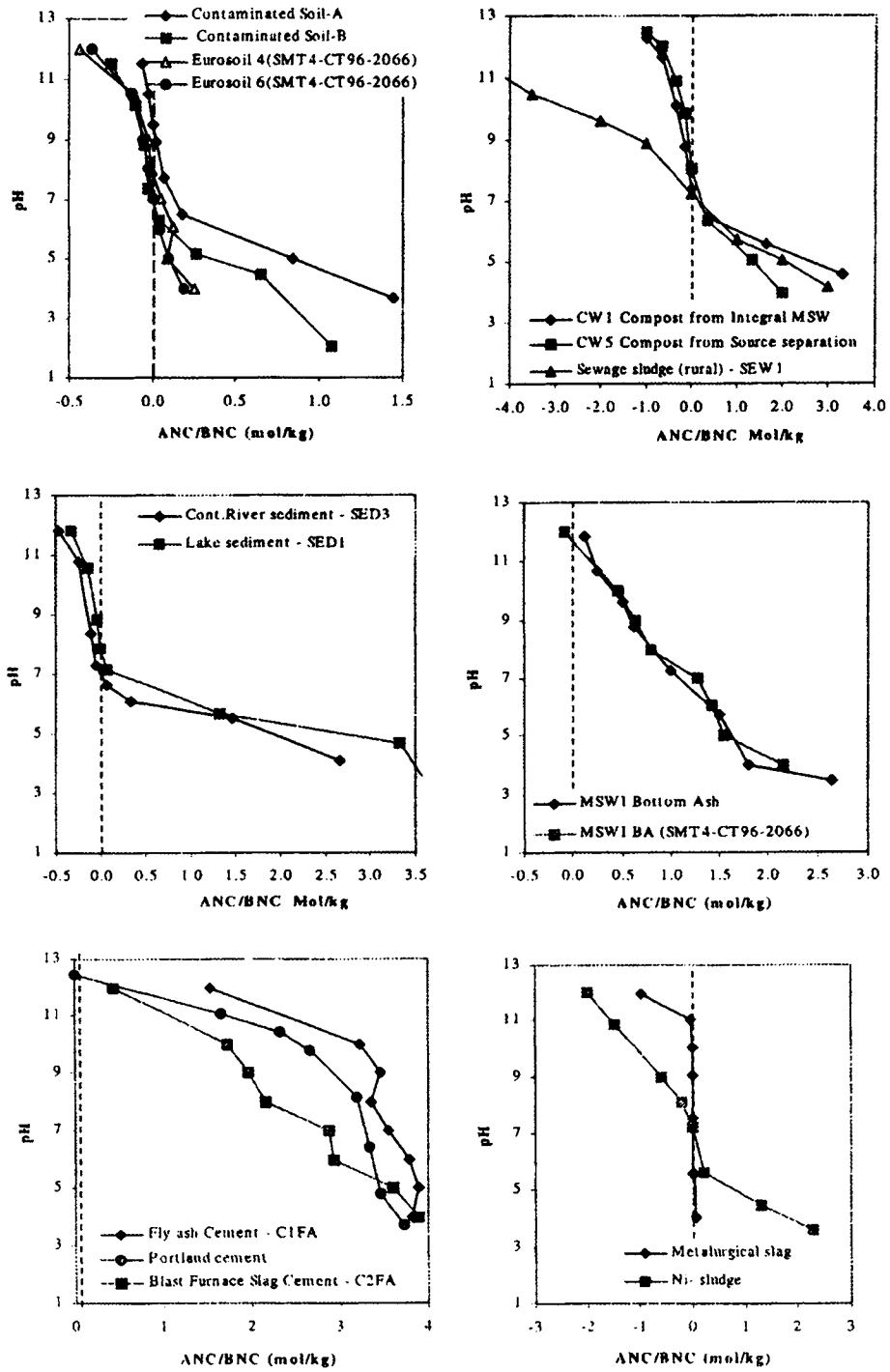


Figure III.1.9. Acid/base neutralization curves for different materials (after Meima et al., 1999; EU project SMT4-CT96-2066; van der Sloot et al., 2000). The base addition is given as negative values.

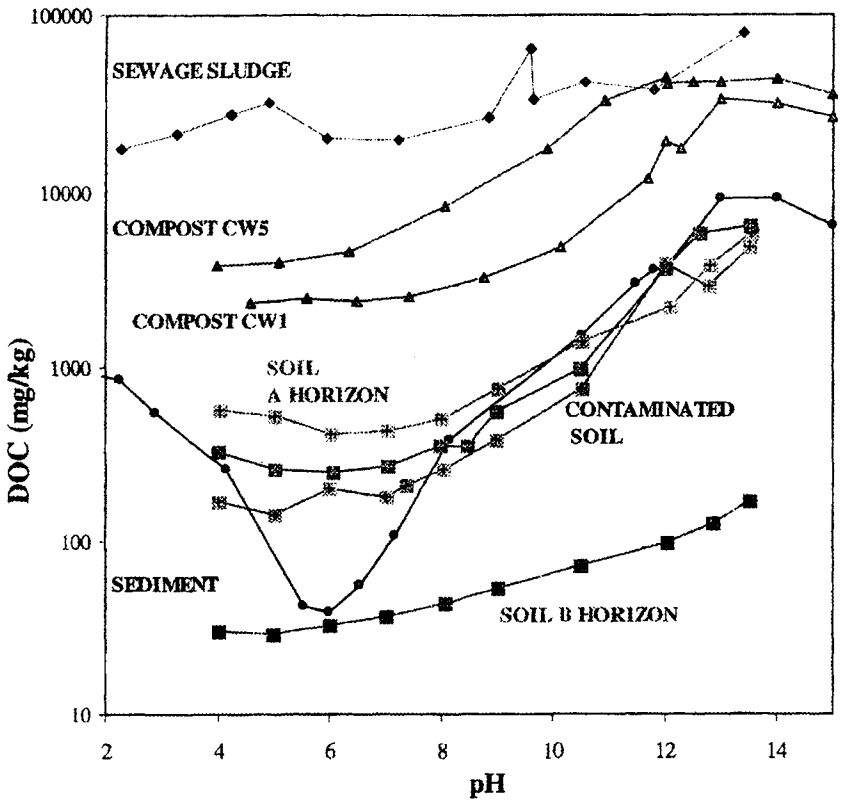


Figure III.1.10. Comparison of DOC as a function of pH for different bioactive materials illustrating the differences in response between fresh bioreactive materials and aged fully reacted materials (natural soil) (after EU project SMT4-CT96-2066).

provided by ENV 12920 (2003) "Methodology for the determination of the leaching behavior of waste".

It can be easily seen that the application and informative area of this test has considerable limitations, also for regulatory purposes, and is not relevant either to the full scope of waste materials (e.g. monolithic, organic, mixed organic–inorganic) or to the conditions of the environmental exposure. These, in general, display a much lower *L/S* ratio of infiltration water under the vadose zone conditions, and significant transformations of waste properties in time due to simultaneously occurring intrinsic processes of different kinetics induced by external factors. A leaching procedure for $L/S = 2$ has been developed in view of assessing waste for landfill. In case some form of infiltration reduction is applied, an *L/S* ratio of about 1 may only be reached in >1000 years (van der Sloot, 2000a). The transformations of waste properties within a much shorter time scale may cause dramatic changes in the leaching behavior of waste.

Nevertheless, this test is a valuable source of information on the contamination potential of waste at the moment of testing, and generally allows prediction of short-term

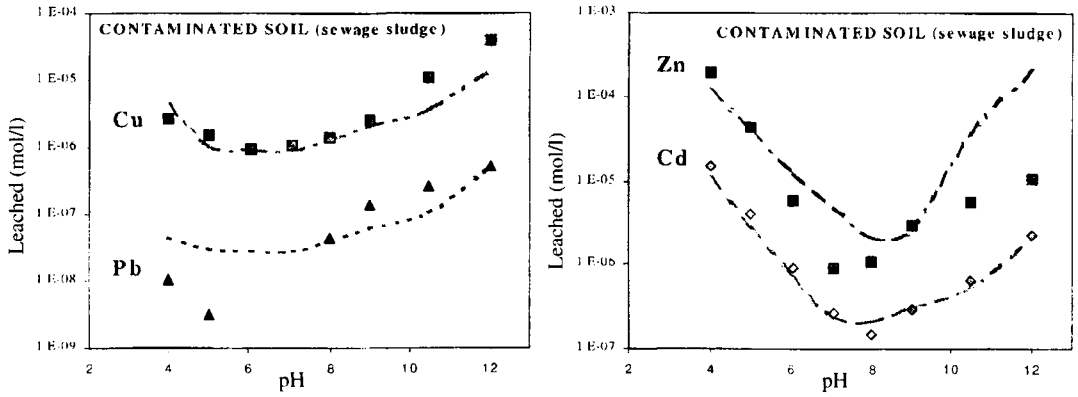


Figure III.1.11. Leaching behavior of Cd, Cu, Pb and Zn in a heavily sewage sludge amended soil. The main factors controlling metal mobility are the interaction of metals with particulate and dissolved organic matter (DOC). Geochemical speciation is modeled by ECOSAT computer program (after EU project SMT4-CT96-2066).

environmental behavior of waste in the wash-out (I) and dissolution (II) stages provided that no fast kinetically defined transformations occur within the time scale of these stages.

Leaching Tests EN 12457, 1–4 underwent in 2001 validation procedure of CEN/TC 292 (2001) in view of their possible use in a regulatory context, such as the EU Landfill Directive (EU, 1999); they were adopted as EU standards in 2002.

Construction with waste materials needs correct prediction of leaching behavior of cement-based solidified waste that has been studied in several research works (e.g. Kosson and van der Sloot, 1997; Tiruta-Barna et al., 2000, 2001). Compliance leaching tests for monolithic material (WI 292010, 2002; WI 292040) are now at the initial stage of development and anticipated to be ready for a Formal Vote in 2006. The proposed scope of this European standard is to determine the flow-through leaching behavior of these materials as a function of time. The test can be used to determine the dominant release mechanisms of inorganic constituents from regularly shaped specimens of monolithic wastes, including relatively water impermeable monoliths. It consists of a series of subsequent leachant renewal cycles, of which the contact time increases to reflect the predominant leaching mechanisms. At the development of the procedure, an extensive review of existing testing methods was utilized (CEN/TC 292/WG6, 2001). The assessment of the monolithic character of wastes is addressed in the draft EN standard WI 292031 (2002).

Dynamic leaching occurring in the anthropogenic (waste dump) and the natural vadose zone under the actual conditions of contaminant release and transport within the waste and in the underlying soil layer is addressed in the up-flow (prCEN/TS 14405 = WI 292034) and down-flow percolation simulation tests WI 292035 (Formal Vote and publication in 2003 for prCEN/TS 14405 and 2006 for WI 29035).

Recognition of the specificity of mining waste resulted in 2002 in the taking into consideration a preparation of a separate standard jointly with the CEN/TC 345 Soil Quality (CEN/TC 292, 2002d).

Another important direction for standardization is ecotoxicological testing of waste and different aspects of this issue (CEN/TC, 1999). The rationale behind this set of tests of different scope is that effects on living organisms goes through the liquid phase even in case of inhalation or ingestion, and that pH as a controlling factor of toxic constituents release in the environmentally accepted range 5–9 at low *L/S* (1–2) should be a basis for ecological testing (van der Sloot, 2000a). For this purpose, a modification of EN 12457 1 with manual pH control in the relevant pH window has been suggested as the most suitable one. In the waste, in which the role of dissolved organic matter is of importance, an upper boundary in the pH range reflecting the highest DOC and oxyanions (As, Mo, Sb, Se) and Cr (VI) mobility is considered to be relevant for ecotoxicity testing, while for predominantly inorganic waste a lower boundary in the pH range will reflect the highest mobility of metal cations (Pb, Cd, Zn, Ni, etc.).

The test on ecotoxicity (prEN 14735, 2003) aims to provide standardized test methods for ecotoxicological properties of raw waste and water extracts from waste that will describe the necessary steps to be performed before the ecotoxicological tests themselves, such as: taking the sample, transport, storage, preparation of raw waste sample and preparation of water extract to be tested. In a recognition of the applicability of other biological tests than those considered in the WI 292027 (2002), the extension to other applications and other biological tests by CEN/TC 262 is planned.

III.1.3.3.3. Further directions of test development and validation

These and other standards under development constitute further steps towards the harmonization of tests for the environmental risk assessment from waste. Though the systematic leaching behavior of different waste materials has been already well documented (van der Sloot et al., 1991b, 1994a,b, 1996, 1997, 2000; Eighmy and van der Sloot, 1994; van der Sloot, 1996, 2000a) and leaching tests are in wide use for regulatory purposes as a tool for the environmental risk assessment from waste, there is also awareness that a single test is not a reliable method for long-term risk assessment, considering possible transformations of physico-chemical parameters of a waste in time. To ensure good confidence in the tests for this purpose, more sophisticated dynamic and sequential testing schemes (or combinations of weak and strong extractions), and a need of the validation of leaching/extraction tests in relation to the actual field conditions have been suggested (Quevauviller et al., 1996; van der Sloot et al., 1997).

An evidence of discrepancies of different nature between singular regulatory tests, long-term risk assessment based on accelerated simulation tests or predictive models and actual field conditions reported by different authors (Fällman and Hartlén, 1994; Jansen-Jurkovičová et al., 1994; Meij and Schaftenaar, 1994; Meij and te Winkel, 2000) has been supported by the case study on powerplant FA surface pond (Upper Silesia, Poland) reported elsewhere (Twardowska and Szczepańska, 2002) and discussed in detail in the Chapter III.7. This typical high-volume waste disposal site was subjected to field validation of the results of laboratory leaching/extraction tests and long-term column experiments on FA leaching behavior under controlled conditions for environmental risk assessment. The study proved inconsistency of the laboratory leaching tests and the actual leaching behavior of trace metals, particularly when equilibrium conditions are dictated by kinetically determined reactions; the test results reflected entirely wash-out (I) and dissolution (II) stages, but did not comprise the delayed release (III) stage. Life-cycle monitoring or singular screening of waste profiles at well-defined dumping sites (by waste age and hydrogeochemical characteristics) for contaminant release to the infiltration water as a function of the primary (pH–Eh, ionic strength, ionic composition of solute) and secondary controlling factors (actual *L/S* ratio, water percolation conditions) along the vertical profile of an anthropogenic or natural vadose zone can be utilized in the development of the long-term predictive hydrogeochemical models based on the input data from standard testing and their field validation. The pH (and Eh) as a function of time-dependent (kinetically defined) processes appeared to be a key issue for a correct prediction of the leaching behavior of waste. In the European Standardization, the influence of pH is considered to be covered by the Leaching Behavior Tests prCEN/TS 14429 (2003); WI 292033 under the development by CEN/TC 292/WG 6 with a final target date 2003. The influence of the specific conditions of the *L/S* phase contact is to be tested by the Leaching Behavior Tests ENV 12920 (methodology for the determination of the leaching behavior of waste under specified conditions), prEN14405 = WI 292034 and WI 292035 (up-flow and down-flow percolation simulation tests), and WI 292010 (compliance leaching test for monolithic material). Nevertheless, due to a high degree of simplification, these tests do not characterize well kinetically defined processes of contaminant generation and leaching.

Another area that is still not well addressed in standardization activity and needs more attention is the leaching of organic and inorganic contaminants from mixed and pure organic waste (EN 12457-1, Annex A, 2002). The difference in release and immobilization mechanisms (e.g. sorption) makes the leaching pattern different for organic and inorganic contaminants. The same source points out also a significant difference in properties and mechanisms of release between more polar, relatively water-soluble compounds and non-polar, hydrophobic organic contaminants.

Partially, these issues have been considered in WI 292033 (2003) "influence of pH on leaching with continuous pH control" and WI 292XXX (2002) "measure for biodegradability of waste", where the difference of DOC release from fresh bioreactive material and aged fully reacted material as a function of pH (Fig. III.1.10), as well as interaction of metals with DOC as the main factor controlling metal mobility are illustrated (Fig. III.1.11). Nevertheless, much more attention should be paid to the leaching behavior of organic contaminants and to the interaction of organic–inorganic phases under different conditions, due to the abundance of mixed-phase waste.

III.1.3.4. Waste analysis

The discussion of methods of waste analysis are beyond the major scope of this chapter, though the European Standardization activity on characterization of waste comprises waste analysis and validation of analytical procedures as an integral part of standardization process. A number of standards on analytical procedures have currently received the status of an European standard: EN 13137 (2001) on determination of total organic carbon (TOC) in waste, sludge and sediments; EN 13656 (2002) on microwave-assisted digestion with hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acid mixture for subsequent determination of elements in waste; EN 13657 (2002) on digestion for subsequent determination of *aqua regia* soluble portion of elements in waste. Prior to the Formal Vote, the standards on waste digestion underwent a detailed validation procedure (Environment Institute JRC, 1999). Several standards concerning analysis of constituents in waste and eluates are in the last stage of voting before getting the status of National Standards of CEN member states, e.g. standards on determination of hydrocarbons in waste by gas chomatography (prEN 14039) and by gravimetry (prEN 14345), both were subject to validation procedure; also standards on calculation of dry matter (prEN 14346) and on determination of halogen and sulfur content, as well as oxygen combustion in closed systems (WI 292007 = prEN 14582). Analysis of eluates comprise European Standards 12506 (2003) on determination of pH, heavy metal ions, and anions Cl^-, NO_2^- and SO_4^-; EN 13370 (2003) on analysis of ammonium-(N), AOX (sum of adsorbable organic halogen compounds), conductivity, Hg, phenol index, TOC, CN-easy liberable, F Several standards on waste samples preparation (WI 292042) and pre-treatment (WI 292030), and determination of polychlorinated biphenyls (PCB) in waste (WI 292028) are in the initial stage of development.

Due to high mobility and high health and ecological hazards, much attention is paid to Cr(VI) determination in the environmental matter, though this task is considered difficult to handle because of instability of the oxidation states of Cr and the complex character of environmental samples (van der Sloot, 2000b; Jitaru et al., 2001). Analysis method for

determination of Cr(VI) in waste was published in 2003 (CEN/TR 14589, 2003). Target date for acceptance of a draft standard WI 292037 (2002) as European Standard is 2006. A non-destructive method of determination of waste elemental composition by X-ray fluorescence (XRF) was also accepted by CEN as a work item (WI 292038, 2002).

To date, a large number of different methods are available for the determination of the content of trace elements in different matrices. Most of them are designed for soil and sediment samples, and not for inorganic solid waste. These methods are often used at random and without proper justification, guidance and documentation, and considerable confusion exists in this area. An overview of the different methods, a discussion of the advantages and drawbacks associated with each method, along with the documentation on the comparative efficiency and the areas of application of various methods, in order to initiate a set of guidelines for the selection of methods for various purposes of waste analysis has been presented recently by Hjelmar and Holm (1999). The scope of an overview comprises brief discussion of principles and descriptions of standard methods and novel methods or methods under development based both on destruction of the solid matrix, among them of digestion with strong acids and oxidizing mixtures, decomposition of samples by fusion and analysis of digested and decomposed samples, as well as non-destructive methods such as XRF spectroscopy, neutron activation analysis (NAA) and other techniques. On the basis of comparison of the different methods, the application of various types of methods has been summarized and discussed in relation to the scope of the analysis and the different types of matrices and elements to be considered. This project thus provides a simple guidance for the selection of suitable methods for determining the contents of various trace elements in various solid matrices for various purposes.

In particular, if the purpose of the analysis is to perform mass balance calculations of specific elements in different matrices and media, the complete destruction of matrix, e.g. with use of HF in conjunction with other acids or non-destructive methods for the total content analysis have been suggested. Digestion with e.g. HNO_3 or aqua regia could be used for samples not containing silicates.

It has been stated that since in several regulatory systems the results of analysis of waste and soil are based on partial digestion, these results can be used for comparative purposes with a clear specification of digestion method and a labeling the results as "partial content" to avoid confusion and wrong conclusions.

The final conclusion of the review points out the disadvantages of the methods based on total digestion of the matrices, which consisted in using aggressive and potentially hazardous acids and small-size samples. Non-destructive methods for the analysis of the total content are not yet effective enough to be used as a sole method and thus "should be further developed to yield sensitive and accurate analytical results based on fast, simple, non-expensive and non-destructive methodology" (Hjelmar and Holm, 1999).

The question arises, whether a total content evaluation of an inorganic element is indeed of a crucial importance for environmental analysis and risk assessment from waste. The total or "nominal" metal concentration in a matrix does not give enough information on environmental risk, while contents of soluble metal species more closely reflects the bioavailable fraction (Gupta et al., 1996; Allen and Batley, 1997).

III.1.4. Evaluation of metal mobility in a matrix as a tool for risk assessment

The European Standardization activity in the area of Environmental impact assessment of waste is focused mainly on inorganic contaminants, in particular heavy metals and their leachability. An approach that is not yet addressed in the European Standardization activity is the evaluation of metal fractions of different susceptibility to release in the waste matrix with use of a sequential extraction scheme. A number of studies on application of chemical extraction as a decision-making tool clearly confirm the reliability of this method for evaluation of risk assessment from waste (Prudent et al., 1996), sediments (Kersten and Förstner, 1986; Förstner and Kersten, 1988; Tack and Verloo, 1996) and soil (Gupta et al, 1996; Houba et al., 1996; McGrath, 1996; Quevauviller et al., 1996; Ure, 1996; Twardowska et al., 1999). For site- and use-specific actual and potential risk assessment from waste, as well as for estimating long-term effects of the changing controlling factors on metal release and leachability, the identification of metal-binding strength in matrix is of fundamental importance for evaluation of their susceptibility to mobilization under different exposure conditions with respect to different risk receptors, of which humans (adults and children), farm animals and wildlife, soil organisms and groundwater should be specified.

Recently, many authors involved in the project on harmonization of leaching/extraction tests for environmental risk assessment emphasize a necessity for determination of metal fractions of different mobility as a requirement for risk assessment (Gupta et al., 1996; McGrath, 1996; Ure, 1996). For this purpose, sequential extraction schemes for distinguishing metal-binding fractions appear to be an extremely useful tool. The concept of these schemes is that elements occur in the soil or waste matrix in various pools of different binding strength, which can be assessed by different reagents.

Since 1973, more than a dozen sequential extraction procedures using different extractants and defining from one to nine extraction schemes, mainly to identify chemical "forms" of metal binding have been developed, among them those by Tessier et al. (1979) modified by Kersten and Förstner (1986), Zeien and Brümmer (1989), Kaszycki and Hall (1996) and Han and Banin (2001) are currently the most widely used for general or specific purposes. The chemical extraction sequences by many authors are still subject to arguments concerning the selectivity of extractants and the redistribution of metals among phases during fractionation (e.g. Tessier and Campbell, 1991a,b; Xiao-Quan and Bin, 1993; Tack and Verloo, 1996; Hall and Pelchat, 1999). The attempts of many authors are focused on using a sequential extraction procedure mainly for the identification of chemical associations of pollutants in different organic–inorganic and mixed matrices. The greatest advantage of the chemical extraction sequences, though, is a possibility to differentiate between the fractions of different binding strength onto particular matrix and to compare partitioning in different organic, inorganic and complex matrices (Twardowska and Kyziol, 2003). An extreme variety of waste materials with differing mechanisms of metal-binding needs to be tested for bioavailability, e.g. metal bonding onto material that is predominantly organic like fresh sewage sludge (e.g. Förstner et al., 1981), soil and solid waste particles that are predominantly inorganic (Förstner et al., 1981; Harrison et al., 1981; Lum et al., 1982; Twardowska et al., 1999), and complex material like municipal waste (Prudent et al., 1996). These materials vary with respect to

the fractions that are mobile thus reflecting differences in key metal transfer pathways from waste to risk receptors.

Of these pathways, groundwater is endangered by metal leaching from waste by percolating water; the food chain is considered the most important pathway leading from waste/contaminated soil to humans, farm animals and wildlife. Direct uptake is of importance for small children, grazing farm and wild animals, and soil organisms. The relevant fractions in waste or contaminated soil that reflect the health risk for the anthroposphere from these transfer paths are generally termed the mobile fraction (active = bioavailable and easily leachable), mobilizable (potentially bioavailable or leachable) and "pseudo total". The mobile fraction is a deciding factor for risk caused by leaching, mobile and mobilizable fractions reflect metal intake through the food chain, while pseudo total fraction is crucial for the direct ingestion of waste–soil particles under intestinal conditions. As extracting media for the mobile fraction, neutral unbuffered salt solutions are commonly used; mobilizable fractions are extracted with buffered and unbuffered complexing and chelating reagents, while for simulation of intestinal conditions, strong acid solutions are used (Gupta et al., 1996).

For the purposes of testing for binding strength of waste for metals, the optimum sequential extraction procedure should be simple both analytically and conceptually and display an order of a consecutive increase of binding strength. These are the properties shown by the most widely applied six-step sequential extraction procedure developed by Tessier et al. (1979) and modified by Kersten and Förstner (1986) for partitioning sediment samples, but which has also been used for different matrices, e.g. for soils (e.g. McGrath, 1996; Twardowska et al., 1999) or municipal waste (Prudent et al., 1996). Due to the variety of waste, in many cases it is rather difficult to identify the chemical forms of binding associated with each step. Nevertheless, the fractionation according to binding strength as a decisive parameter with use of this scheme ensures a very good confidence and repeatability. With respect to a certain group of materials (sediments and soils), the identification of major binding phases with use of this scheme is also possible. A growing number of extraction schemes and the advantages of this procedure as a useful tool for risk assessment from waste, clearly stresses the need for harmonization, identification of the areas of their applicability and standardization.

The need for standardization of methodology resulted in The Community Bureau of Reference (BCR) coordinating the development and validation of soil extraction schemes and in producing in 1995 two reference soils with certified extractable contents of a group of heavy metals (Ure, 1996). Also two Polish reference soils (PL-1 and BPGL-1) with certified extractable contents were prepared in parallel.

The metal aquatic toxicity testing for regulatory purposes requires consideration of metal species and a careful selection of the appropriate conditions for testing sparingly soluble substances that determine their bioavailability (Allen and Batley, 1997). In 1999, within the CEN/TC 292 *ad hoc* group on ecotoxicology of wastes has been established in order to provide standardized *test* methods as tools for the application of Annex III, Hazardous Waste Directive 91/689/EEC (EEC, 1991), which defines "ecotoxic" substances and preparations as the ones, which present or may present immediate or delayed risks for one or more sectors of the environment (CEN/TC 292, 1999). Ecotoxicity tests for raw wastes and water extracts from waste are currently under development; standard prEN 14735 (2003) describes preparation of waste samples for ecotoxicity tests.

III.1.5. Horizontal standardization

Recently, the initiative has also been undertaken with the aim of development within the CEN Environmental and related TCs, and external liaison bodies of horizontal standards for relevant EU Directives and thus to produce, where possible, one standard as opposed to several elaborated in a vertical manner (CEN BT, 2001).

Besides standards applicable specifically for waste, there is a need to develop horizontal and harmonized European standards that are suitable for a wide range of materials, including waste, soil, sludge, and treated biowaste, lead to equivalent results and permit to avoid unnecessary differences in standards and duplication of work. The development of horizontal standards is aimed to facilitating implementation of upcoming EU Directives on sludge, biological treatment of biodegradable waste, and on the soil monitoring, as well as of the Council Directive 1999/31/EC on the landfill of waste. For this purpose, the collaborative European project HORIZONTAL started at the end of 2002 (CEN/TC 292, 2002c). Part of the work within the project will focus on co-normative horizontal standardization of existing ISO and CEN standards developed by the relevant TCs for the same parameters. Another part will comprise pre-normative research required to develop new needed horizontal standards for these materials. The workplan includes horizontal standards on sampling, on hygienic, biological, organic and inorganic parameters, on mechanical properties and leaching behavior of the most frequent contaminants in waste, sludge, treated biowaste and soils in Europe, in view of the potential impact on human and animal health, plant uptake, soil function and groundwater quality. In particular, the project considers an evaluation of: (i) inorganic compounds such as heavy metal cations, oxyanions and nutrients (N, P); (ii) volatile to semi-volatile compounds (chlorinated compounds etc.); (iii) strongly sorbed, non-volatile, relatively low water-soluble compounds (polycyclic aromatic hydrocarbons (PAHs), PCBs and phthalates); and (iv) soluble non-volatile organic compounds such as oxygenated and heterocyclic compounds.

In the process of horizontal standardization, a number of tests developed for the characterization of waste are considered to be evaluated in relation to their implementation in the Landfill Directive, and suitability for sewage sludge, soil and biowaste.

III.1.6. Conclusions

In general, the current approach to the testing procedures for a short- and long-term environmental risk assessment from waste shows growing understanding of release mechanisms and factors controlling leaching behavior. This has resulted in developing testing schemes and scenarios based on the consideration of both intrinsic properties of waste material and external factors specific for the exposure conditions and interactions instead of a single regulatory test. The European standardization activity, which is directed to unification and harmonization of the numerous testing procedures, tends to simplification of the testing procedure based on the use of the observed geochemical similarity of the leaching behavior of waste and a limited number of parameters controlling the contaminants' release. Significant progress has been achieved in the development of a reliable testing procedure for prediction of short-term leaching behavior

within the wash-out (I) and dissolution (II) stages. Nevertheless, there are still considerable difficulties in the simulation of kinetically defined processes that in many cases determine long-term leaching behavior in the delayed release (III) stage, and the leaching behavior in the specific conditions of a liquid/solid phase contact (in particular, under vadose zone conditions). The current waste testing methods do not include site-specific evaluation of the environmental hazard, which should comprise interaction of waste with soil of the vadose zone into the waste testing procedures.

Another area that is not adequately addressed in standardization activity is the leaching of organic and inorganic contaminants from pure organic and mixed organic–inorganic waste due to the difference in the release and immobilization mechanisms. There is still limited progress in the harmonization and optimization of procedures for prediction of metal mobility and bioavailability in the waste matrix that is of a particular importance for site- and use-specific risk assessment from waste. The validation of laboratory data by field leaching studies for different solid wastes, their interpretation based on the understanding of the processes of contaminant generation and release, controlling factors and interactions under the actual conditions of exposure should ultimately lead to development of an optimized environmental evaluation scheme in order to make a correct decision concerning the life-cycle environmental sustainability of a waste site, which excludes both false-positive and false-negative errors.

The development of harmonized horizontal European standards suitable for waste, and for a wide range of other materials such as sludge, soil, and treated biowaste is anticipated to facilitate the European standardization and its implementation in the relevant regulatory fields governed by EU Directive on waste landfill and upcoming Directives on sludge, biowaste and soil.

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III.2
Agricultural wastes

Teodorita Al Seadi and Jens Bo Holm-Nielsen

III.2.1. Introduction

During the twentieth century agricultural production became more and more industrialized and the traditional production systems were gradually replaced by systems where mechanization, use of mineral fertilizers, pesticides, herbicides, concentrates, etc. led to intensification and concentration of agricultural production and not only increased the volume of the production but also changed the composition and the quality of the agricultural output.

Most agricultural wastes are valuable resources that should be recycled, used for industrial purposes and for energy recovery. If unsuitably handled and managed, agricultural wastes become an environmental problem and a hazard for human and animal health. The example of animal manure and how the perception of the value of animal manure changed during the last century, from a valuable natural fertilizer to a problematic excessive waste, as a consequence of intensive, industrialized agricultural practice, is a typical example (Wadman et al., 1987).

The management of agricultural wastes is considered today an important target in the global waste management strategy. Since 1990s the public has become increasingly concerned about the environmental impact of agricultural practices. As a result, the environmental and human and animal health consequences of today's agricultural practices are recognized, evaluated, and reflected into an increasingly restrictive legislative framework.

III.2.2. Agricultural wastes categories

A possible classification of the most common categories of agricultural wastes is shown in Figure III.2.1.

III.2.3. Main issues related to agricultural wastes and their utilization

Any kind of waste can become a hazard factor for humans, animals, and vegetation if its concentration in the environment is excessive. Water quality is affected if manure runs into

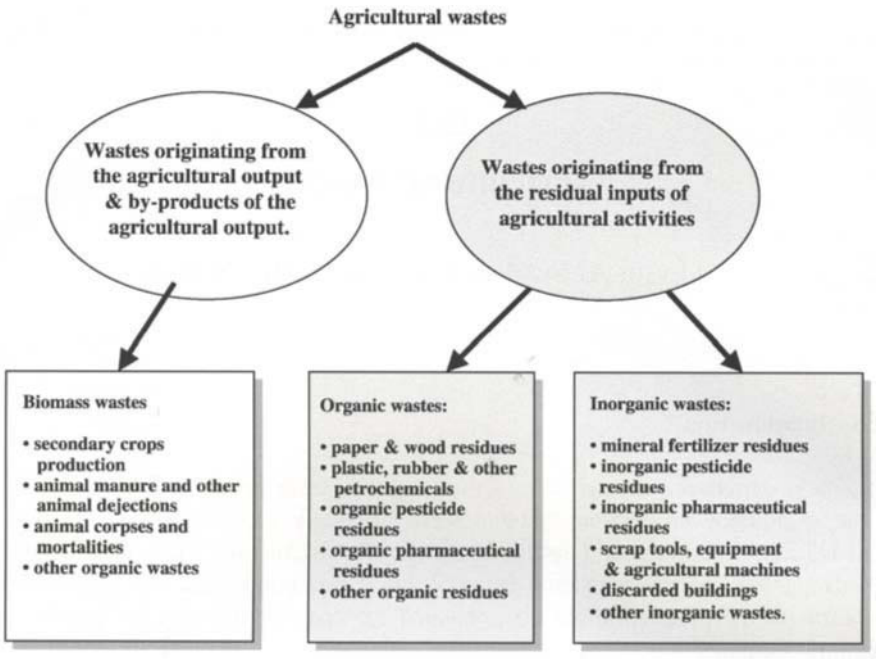


Figure III.2.1. Agricultural wastes.

water streams as a result of inappropriate and excessive land application, spillage, overflow, or deliberate dumping. The nutrients and the organic matter contained in manure can pollute the ground water by leaching or by runoff when manure is applied at rates that exceed crop fertilizer requirements. In such cases, arrangements should be made to move excess manure to other cropland, or to use it for other purposes (Bauder and Vogel, 1989–1990).

Agricultural practices can be an important source of groundwater pollution. The most frequently occurring groundwater contaminants are shown in Tables III.2.1 and III.2.2. Nitrates are one of the groundwater contaminants of concern in drinking water. High concentration in groundwater can cause methemaglobinaemia (blue baby syndrome). Sources of nitrates can be mineral fertilizers and animal manure that leach from grasslands and arable crops, liquids that percolate into the groundwater in areas with high concentration of animal manure, septic systems that are too close together or too close to the wells (Bauder and Vogel, 1989–1990).

Wastes of agricultural origin can be contaminated with crop and animal disease-causing organisms and chemicals, and with chemical and physical contaminants. Some of the main issues related to optimum utilization of agricultural wastes refer therefore to the control of chemical pollutants (organic and inorganic), breaking the chain of diseases transmission by inactivation of pathogens and other biological hazards and the removal of physical impurities. The quality control of these types of agricultural wastes, supported by regulations, is therefore essential in relation to their safe utilization and recycling for both the environment and human and animal health.

Table III.2.1. Sources of groundwater contamination (after Bauder and Vogel, 1989–1990).

Industrial operations
Mining
Drilling
Construction
Forestry
Disposal of industrial waste into landfills, pits, lagoons and deep injections wells
Agricultural
Pesticides
Mineral fertilizers
Animal manure
Soil erosion
Irrigation practices
Feed lots
Municipal
Landfills
Sewage treatment plants
Urban runoff
Underground storage tanks
Households
Improper disposal and use of cleaners, solvents, automobile products, septic tanks

Residual wastes originating from inputs of agricultural activities such as pesticides, fertilizers, or pharmaceutical residues are considered hazardous wastes, and their disposal and management must be done in accordance with the legal prescriptions.

III.2.3.1. Inorganic contaminants/heavy metals

The presence of heavy metals in agricultural wastes is of great concern due to their poisoning effect on humans and animals. Table III.2.3 shows an example of heavy metals content in animal manure.

The presence of heavy metals in manure and agricultural wastes occurs from natural and anthropogenic sources (metabolic wastes, corrosion of water pipes, consumer

Table III.2.2. Frequently occurring groundwater contaminants (after Bauder and Vogel, 1989–1990).

Organic hazards	Inorganic hazards	Microbial hazards
Pesticides (insecticides, herbicides, fungicides)	Heavy metals (Pb, Cu, Hg, Ba)	Coliform bacteria
Gasoline, petroleum derivatives and additives	Nitrate	Viruses
Chemicals in paints and solvents	Sulfate	
	Sodium	

Table III.2.3. Heavy metals in animal manure (after Danish Ministry of Agriculture and Fisheries, 1996).

Kind of manure	Number of samples	Dry matter (%)	Dry matter (mg/kg)				
			Pb	Cd	Ni	Cr	Co
Solid manure							
Cattle	9	19	0.50	0.07	1.04	0.42	0.13
Pigs	3	23	0.74	0.06	1.29	1.56	0.29
Poultry	5	44	0.96	0.37	5.46	1.82	0.23
Slurry							
Cattle	47	6.3	0.27	0.04	0.52	0.20	0.12
Pigs	31	3.8	0.13	0.02	0.55	0.41	0.05

products, etc.). Surface water can also be a source of contamination with heavy metals. Anthropogenic inputs of some metals in surface water systems may locally exceed natural inputs (Connell and Miller, 1984). Industrial effluents and waste sludge may substantially contribute to metal loading.

Excess metal levels in soils, surface and ground water may pose a health risk to humans and to the environment. Soil and aquatic organisms may be adversely affected by heavy metals in the environment. Slightly elevated metal levels in natural waters, for example, may cause the following sub-lethal effects in aquatic organisms such as: histological or morphological change in tissues, suppression of growth and development, changes in circulation, enzyme activity and blood chemistry, change in behavior and reproduction, etc. (Connell and Miller, 1984; Manahan, 2002). The presence of heavy metals in agricultural wastes used as fertilizer may transport dissolved heavy metals to agricultural fields. Although most heavy metals do not pose a threat to humans through crop consumption, some of them (e.g. cadmium) may be incorporated into plant tissue. Accumulation usually occurs in plant roots, but may also occur throughout the plant.

III.2.3.2. Persistent organic contaminants

Waste-derived products can contain persistent organic contaminants according to the origin of their base ingredients. Agricultural wastes can contain persistent organic contaminants such as pesticide residues, antibiotics, and other medicaments. Organic wastes from agro-industries and household wastes can contain aromatic, aliphatic, and halogenated hydrocarbons, organo-chlorine pesticides, polychlorinated biphenyls (PCBs), PAHs, etc.

The persistent organic compounds of xenobiotic origin represent a hazard to humans, flora, and fauna due to their toxicity and environmental adverse effect (e.g. ozone layer depletion). The hazard for humans, animals, and the environment is linked to their volatility, mobility/water solubility, persistence/low biodegradability and bioavailability that can cause dispersion of volatile compounds to the atmosphere, bioaccumulation and/or induced toxicity in plants (Al Seadi, 2001).

Numerous xenobiotic organic compounds are known to have estrogenic effect on vertebrates (xenoestrogens) or to be endocrine disruptors (Manahan, 2002). These compounds are considered to be responsible for decline in human male reproductive health and for a number of forms of cancer in humans (Danish Environmental Protection Agency, 1995). Chemicals reported to be estrogenic include, but are not limited to: organo-chlorine pesticides, PCBs, dioxins and furans, alkyl phenol polyethoxylates, phytoestrogens, etc. (Manahan, 2002).

In many countries there are regulations about the permitted limit values of persistent organic pollutants in different products, such as the Danish statutory order 49/20.01.2000-02-29 (Danish Ministry of Environment and Energy, 2000), similar regulations in the Netherlands, Germany and other countries, or the European Community Directives 80/778/EEC (EEC, 1980) and 98/83/EC (EC, 1998) concerning water quality for human consumption. Table III.2.4 presents an example from the Danish legislation concerning the limit values for persistent organic compounds in organic wastes utilized as fertilizers.

- *PAH: Polycyclic aromatic hydrocarbons.* Mainly found in smoke from incineration and the exhaust fumes from vehicles. They deposit on roofs and road surfaces, from where they are flushed into the sewage sludge systems by rainwater.
- *DEPH: Di(2-ethylhexyl)phthalate.* The compound is primarily used as a plastic softener, especially of PVC (e.g. for tarpaulins, toys, cars, and vinyl flooring). By washing, the substance ends up in the sewage system.
- *LAS: Linear alkylbenzene sulfonates.* Primarily used as surfactants in detergents and cleaning agents.
- *NP and NPE: Nonylphenol and nonylphenolethoxylates with 1–2 ethoxy groups.* Typically used as surfactants in detergents, cleaning agents, cosmetic products, and vehicle care products. They find their way into the sewage system via wastewater from laundries and vehicle workshops and from cosmetics in household waste and sewage.

The problem related to the control and management of the organic contaminants is that it is difficult to perform a screening of such a broad spectrum of contaminants at a reasonable cost. The most feasible way to deal with the problem refers to waste quality control.

The aerobic treatment/composting has a positive effect on reduction of the main persistent organic pollutants. The method is largely utilized today in composting systems

Table III.2.4. Example of limit values for persistent organic pollutants in Denmark from July 2000 (*Source*: Danish Ministry of Environment and Energy, 2000).

Persistent organic pollutant	Maximum limit values (mg/kg dry matter)
LAS	1300
PAHs	3
NPE	30[a]
DEPH	50

[a]The limit value for NPE is reduced to maximum 10 mg/kg dry matter from July 2002.

Table III.2.5. Animal by-products categories and conditions for anaerobic digestion treatment (after Sander Nielsen, 2003).

Category 1	Category 2	Category 3
All parts of animals that may contain TSE prions	Fallen stock, by-products not suitable for human consumption and all animal materials collected when treating wastewater from slaughterhouses	Parts of slaughtered animals and fish, suitable for human consumption
	Manure and digestive tract content	The same categories, unfit for human consumption, but posing no risk for animals and humans Food and catering waste
Must always be destructed by incineration	May be digested in biogas plants after pressure sterilization at 133°C for 20 min at 3 bar	May be digested in biogas plants after pasteurization at 70°C for 60 min
	Manure and digestive tract content may be digested without pre-treatment	Maximum particle size 12 mm

and in some cases in association with anaerobic digestion (AD), usually as a post-treatment step.

Recent studies proved that AD has a certain effect on reduction of these pollutants. The laboratory trials on the four main groups of organic contaminants (see Table III.2.5) show that a reduction of persistent organic contaminants occurs during anaerobic digestion. The reduction of LAS and NPE seems to be more effective than the reduction of DEHP and PAHs (Manahan, 2002). The issue still requires further research based on full-scale trials.

III.2.3.3. Pathogen contamination

Safe utilizations of animal manure and other agricultural wastes must not result in new routes of pathogen and disease transmission between animals, humans, and the environment. The main contaminants can be bacteria, viruses, intestinal parasites, and more recently TSE prions.

For many years it had been widely accepted and considered economically profitable to use animal by-products from slaughterhouses and fallen stock as feed. The acknowledgment that transmissible spongiform encephalopaties (TSE) may be spread by food and feed brought animal by-products to the attention of the European Commission. The attempts made over the years to guarantee food safety were this time concretized into an important decision to ban the use of animal by-products as feed. A comprehensive and strict veterinary regulation (EC) 1774/2002 came in force in May 2003 and is still in a state of continuing amendments. The Regulation 1774 categorizes animal by-products and defines obligatory processing methods and acceptable final use of the by-products, stipulating very detailed health rules concerning collection, processing, and final disposal

or use of animal by-products with the aim of preventing not only TSE but also other agents that may cause diseases in humans or animals.

According to the regulation 1774, animal by-products belong to three categories (Table III.2.5). Category 1 contains materials with the highest risk for public health, animals, or the environment and must always be disposed by incineration or in special cases buried in special landfills after pressure sterilization. Category 2 materials include animal by-products that do not fit into category 1 or category 3 as well as manure and digestive tract content. These materials may, e.g. be supplied for digestion in biogas plants after pre-treatment by pressure sterilization at 133°C at 3 bar for 20 min (manure and digestive tract content is exempted from pre-treatment). Finally, those animal by-products that would be fit for human consumption but, for commercial reasons, are not intended for human consumption, represent category 3 materials (Kirchmayr et al., 2003). Category 3 materials may be used in biogas plants after pasteurization at 70°C for 60 min. The use of category 3 materials for feed production is banned for the time being.

The EC Regulation 1774 will have a major impact on the future role of biological treatment processes for animal by-products and other wastes of biological origin (Braun and Kirchmayr, 2003).

Anaerobic digestion has a pathogen reduction effect due to the combination of temperature and retention time. The effect of anaerobic digestion on pathogen reduction in digested animal slurry compared to untreated animal slurry is shown in Table III.2.6. The most common pathogens are destroyed by thermophilic, at process temperatures around 53°C, during 1 h of guaranteed retention time.

A veterinary safe utilization of agricultural wastes implies some basic principles:

- *Livestock health control*: No utilization of animal manure and slurries from any livestock with health problems (zoonoses, transmissible spongiform encephalpathy (TSE), transmissible spongiform, etc);
- *Waste selection*: Hazardous waste types must be excluded from any utilization and canalized towards suitable, safe disposal methods (e.g. incineration);

Table III.2.6. Comparison between the decimation time (T-90) of some pathogenic bacteria through the biogas system and the untreated slurry system (after Al Seadi, 2001).

Bacteria	Anaerobic digestion		Untreated slurry system	
	Thermophilic (53°C) hours	Mesophilic (35°C) days	18–21°C weeks	6–15°C weeks
Salmonella typhimurium	0.7	2.4	2.0	5.9
Salmonella dublin	0.6	2.1	–	–
Escherichia coli	0.4	1.8	2.0	8.8
Staphilococcus aureus	0.5	0.9	0.9	7.1
Mycobacterium paratuberculosis	0.7	6.0	–	–
Coliform bacteria	–	3.1	2.1	9.3
Group of D-streptococi	–	7.1	5.7	21.4
Streptococcus faecalis	1.0	2.0	–	–

- *Pre-treatment*: Before utilization certain waste categories require controlled sanitation through thermal treatment (e.g. pasteurization at 70°C for 1 h, pressure sterilization, etc.);
- *Follow-up and regular control of pathogen reduction efficiency.*

III.2.3.4. Comments

The increased agricultural output, generated by the intensive, industrialized agriculture caused also an increasing of the amount of agricultural residues, wastes, and by-products. Valuable resources, when suitably managed and utilized, these wastes and by-products can be a threat to human and animal health and to food safety and create serious environmental pollution problems.

The mechanization of agriculture, the use of mineral fertilizers, pesticides, pharmaceuticals, etc. have simultaneously caused a change in the composition, the quality and the properties of the traditional wastes (e.g. animal manure) and has generated new kinds of wastes from the agricultural sector (pesticides residuals, pharmaceutical residuals, heavy metals, etc.).

Changing the perception of agricultural wastes from environmental problems to valuable resources is a matter of finding and implementing sustainable solutions for their safe collection, recovery, recycling, and utilization for agricultural, industry, or energy purposes.

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III.3
Agrochemicals: transport potential in the vadose and saturated zones

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III.3.1. Introduction

Modern agriculture became successful mainly due to the use of pesticides and fertilizers. Fertilizers contain large amounts of nitrogen, phosphorus and potassium associated with chloride, sodium and sulfate.

Earlier, pesticides had contained copper, mercury and arsenic salts. These caused damage to the soil structure and texture and the soil organisms, some of which can still be detected. In the 1960s, a transition to organic substances was made that had the effect of pesticides. These new substances are degradable and are formulated so that they when applied provide the wanted optimal effect.

Agrochemicals must be available for uptake by plants, i.e. must be sorbed on the plant itself or on solids, such as organic substances and clays. Once there, they are also subject to different types of chemical–microbiological reactions and can thus change their bonding and their health effects. They are also subject to different transport processes as solutes or fixed on particles through overland discharge, interflow and groundwater recharge. In between retardation, chemical–microbiological reactions and transport, conflicts of interest can build up that depend mainly on the weather conditions and are generally difficult to solve. For example, although the local precipitation should be known, it cannot be forecasted with the necessary accuracy either on a long or on a short term for any specific locality. Therefore, agricultural activities cannot be adapted to weather conditions to minimize the input of agrochemicals on water resources.

The way in which the agrochemicals are applied affects their availability for crops and neighboring compartments, like the atmosphere and the hydrosphere.

- In the agricultural fields, damage can occur to the soil organisms or the physical properties of the soil or
- Unwanted accumulations of the agrochemicals can develop in the plants.
- Trace gases (N_2O, CH_4, H_2S) emitted into the atmosphere can initiate unwanted chemical reactions and
- Pollutants (substances in unwanted concentration) such as eutrophying and toxic substances can enter the hydrosphere.

Though introduced to the environment in purpose, overdosed agrochemicals not utilized in accordance with the aim should be treated as wastes. Substantial amounts of residual agrochemicals are also disposed with packaging waste.

III.3.2. Pesticides in agriculture

In Germany, approximately 2000 pesticide compounds and around 300 active ingredients are approved for use; 80% are applied in agriculture. The pesticide market in Germany rose in the three decades from 1970s to 1990s from 10,000 to 30,000 t/a (Amann et al., 1989) or *ca.* 2.5 kg/(ha a) have been applied, as an average, in agriculture. Meanwhile, the amounts applied have fallen to 0.5–1 kg/(ha a). If it was assumed that the pesticides do not react during the underground passage, an infiltration of 200 mm/a of water produced pesticide concentrations of 1.3 and 0.3 mg/l in groundwater, respectively.

According to the Drinking Water Ordinance of the European Community, water used as drinking water may contain only 0.1 μg/l of any single active ingredient and a sum of 0.5 μg/l for all active ingredients. There are different reasons for this low limit:

- Pesticides are not natural products and therefore should not be in groundwater at all.
- The effects that pesticides might have upon health and life are inadequately known.
- Of the metabolites of the pesticides, less than 15% are known and there are indications that the toxicity of the metabolites could be even stronger than the mother substance itself and, simultaneously, the mobility of the metabolites increases mostly with decreasing molecular weight.

At the time when the limits were set for pesticides allowed in groundwater, the detection limit was fixed. The same procedure today could lead to lower limits.

The theoretical, maximum discharge of agricultural pesticides of 1.3 mg/l to groundwater and the limit of 0.0001 mg/l for drinking water show the high requirements that must be placed upon the pesticides with respect to:

- the intensity and rate of the sorption onto organic and inorganic particles,
- their decay with respect to the water flow underground and
- the metabolites produced and their mobility and toxicity.

These requirements, however, have been only partially fulfilled for optimal drinking water protection.

Most of the publications have dealt with the behavior of pesticides in soils (Edwards, 1966; Harris, 1969; Hayes, 1970; Adams, 1973; Haque and Freed, 1972; Führ and Mittelstaedt, 1979; Hellig and Gish, 1986) and only a few focused on the fate of pesticides in subsurface waters. Furthermore, most of the experimental investigations were conducted on a small scale (small-scale lysimeters, microcosms) (Bergström, 1990; Dickopf, 1994; Dörfler et al., 1994) and only a few have been performed relative to the field scale (Dickopf, 1994). Thus, the knowledge available concerning the behavior of pesticides in compartments adjoining the soil is limited. Yet it is known that in most middle and coarse grained aquifers and in fissured aquifers, there are high pesticide concentrations in groundwater. This contamination of the groundwater is still rising. Therefore, extensive efforts have been made, to gain a better understanding of:

- the retention capacity of soils for pesticides,
- the decay kinetics and the decay products of pesticides by applying ^{14}C-labeled substances and

- the propagation behavior of pesticides with and without bonding onto particles in the vadose (unsaturated) zone and aquifers.

III.3.2.1. Types of pesticides and their sorption onto solids in the soil

Preferentially, the pesticides applied today in agriculture belong to triazines, urea derivatives, phenoxy carboxylic acids, chlorinated hydrocarbons and carbamates. Lately, heavy metal sulfates have also been in use again. About 62% of the pesticides are applied as herbicides, 24% as fungicides and 7% as insecticides. The remainder refers to other applications. *Circa* 75% of the total amount of fungicides are applied in vineyards and *ca.* 75% of all herbicides are used in corn and grain fields. In using these pesticides, the timing of the application, relative to the growth stage of the plant and relative to the weather conditions, is decisive as to how effective and whether they will be transported by discharge into the adjacent compartments.

Above all, pesticides are adsorbed on the humates and clay minerals, which are predominantly abundant in the A- and B-horizons of the soil (Fig. III.3.1); both of these horizons are thin in temperate climates. In the non-weathered rock below these, adsorbents are mostly not as important for the sorption of pesticides; either they have been mechanically filtered (Seiler, 1988; Matthess et al., 1991; Klotz, 1994) or, as in the case of the humates, are subject to microbiological decay.

Most of the organic pesticides are subject to slow sorption kinetics on humic substances and clay minerals and develop a very strong binding on the humates. This leads in hilly terrains

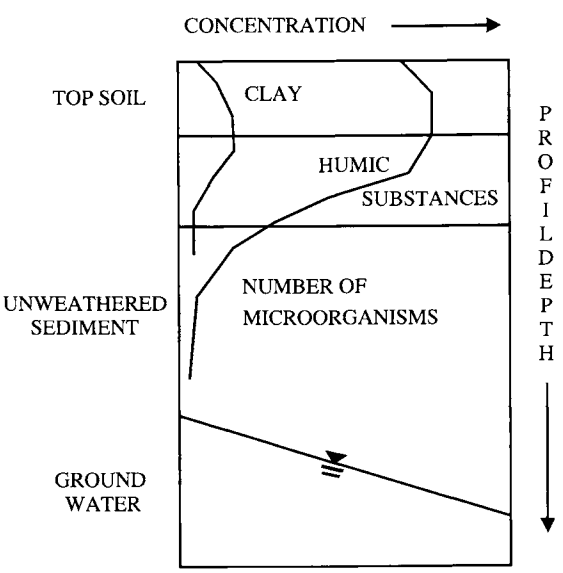


Figure III.3.1. Distribution of clay, organic substances and organisms in soil and unweathered rock.

- under groundwater recharge conditions with flow velocities of a few meters per year to a quasi-complete sorption and
- under bypass-flow velocities of a few decimeters to meters per day (see below and Chapter V.2.2), however, to a rapid transport of the pesticides out of the soil zone into the sediments with weak sorption properties or to surface water resources.

Sorption of pesticides is an important prerequisite for microbiologic degradation. This decay is especially efficient in biofilms that are in aquifers rather thin (less than a few tens of micrometers) and cover the particle's surface in soils, less in the unsaturated and the saturated zones. These biofilms contain a sufficiently high and specialized microbiologic community for pesticide degradation. Recent investigations show that below the soil zone there may develop a microbiological population, which could also cause such degradation (Dickopf, 1994; Seiler et al., 1996). Yet it requires an incubation period, to adapt to the changes in the chemical composition of subsurface water, which is much longer in the unsaturated than in the saturated zone. As to what degree of change and at which maximal concentrations this response is possible are not yet known.

The slow sorption of pesticides onto surfaces can be considerably disturbed by discharges as a consequence of precipitation. In hilly terrain, the precipitation producing discharges is spited at the land surface into overland discharge and the infiltration of seepage water. This seepage water is further divided into the fast bypass-flow, turning mostly into lateral flow, and the slow groundwater recharge. Such bypass-flow can make up 25–50% of the seepage water infiltration in unconsolidated sediments and mostly covers 40–50% in consolidated rocks. As a result, the discharge consists of two components with high (overland discharge and bypass-flow) and one component with slow flow velocities (groundwater recharge). Bypass-flow and overland discharge act opposite to a complete sorption of pesticides, if they were applied shortly before the precipitation event, and may transport pesticides as well as metabolites out of the soil. In contrast, the slow movement of the groundwater recharge favors the sorption of pesticides underground.

The high flow velocities of overland flow (several hundred meters per day) and interflow (from 0.5 m/d to several meters per day) also favor the transport of particles such as dissolved organic carbon (DOC) colloids and clay minerals, which can both have accretions of pesticides. However, the subsurface transport of clay minerals is generally less important than that of DOC, because clay minerals form very slowly as compared to DOC. The pool of DOC always has a better regeneration capability than that of the clay minerals and the particle sizes of the DOC are generally smaller than that of the clay minerals. Therefore, due to the existing pore size distribution in the sediments and in the soil, a total or selective retention of the large clay and only a partial retention of the small, colloidal particles take place (Matthess et al., 1991).

Due to the aforementioned and the generation of discharge in landscapes, it follows that after precipitation periods on hilly terrains, shock loads of pesticides repeatedly discharge (Fig. III.3.2). This occurs during the periods when agricultural pesticides are applied, as they are partially dissolved and partially bound to particles. Yet, even long after the pesticides were applied, such shock loads in surface waters can be clearly detected (Fig. III.3.2); at these times particle transport prevails.

The stated, particle favored run-off transport of pesticides into rivers and lakes decreases the pesticide concentration in the soil and thus reduces the direct input into

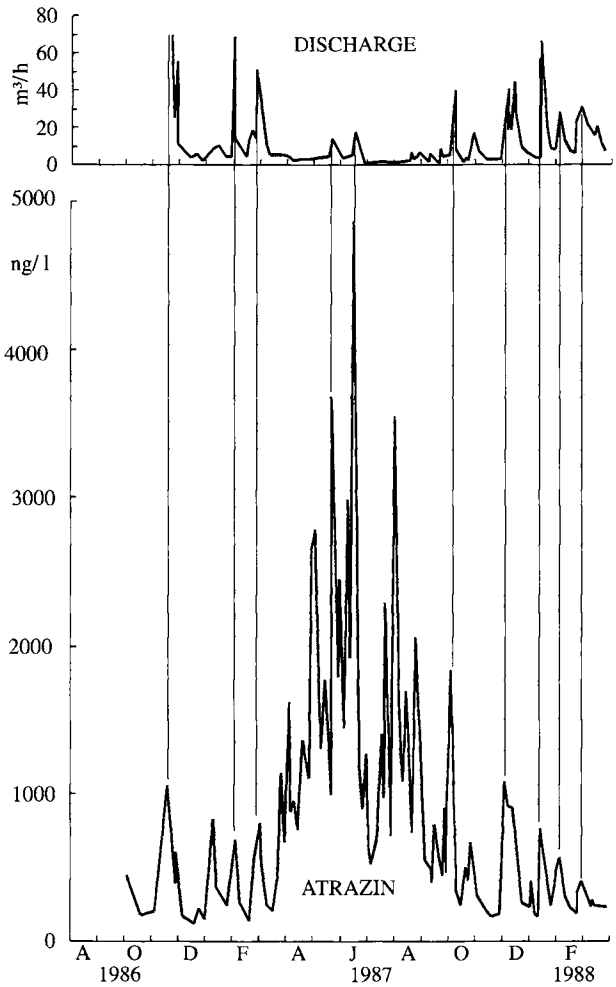


Figure III.3.2. Atrazine in the discharge of an upland stream.

the groundwater. However, the shock loads may re-enter the groundwater recharged, e.g. by bank filtration, if the surface water was not previously treated.

Batch laboratory tests consistently show that the sorption onto montmorillonites and illites is pesticide specific and much lower at neutral and basic pH values than at acidic pH ranges (Fig. III.3.3); only lindane is sometimes accreted onto montmorillonites at neutral pH values. For DOC, the sorption is almost the same at basic, neutral and acidic pH ranges (over pH 4), and becomes even stronger onto clay minerals.

An example for the migration of terbutylazine in subsurface waters with and without humates is shown in Figure III.3.4, as a result of laboratory tests (Dörfler et al., 1994); in this case, the flow velocities of the terbutylazine, which is involved in particle flow, are higher as compared to dissolved pesticides.

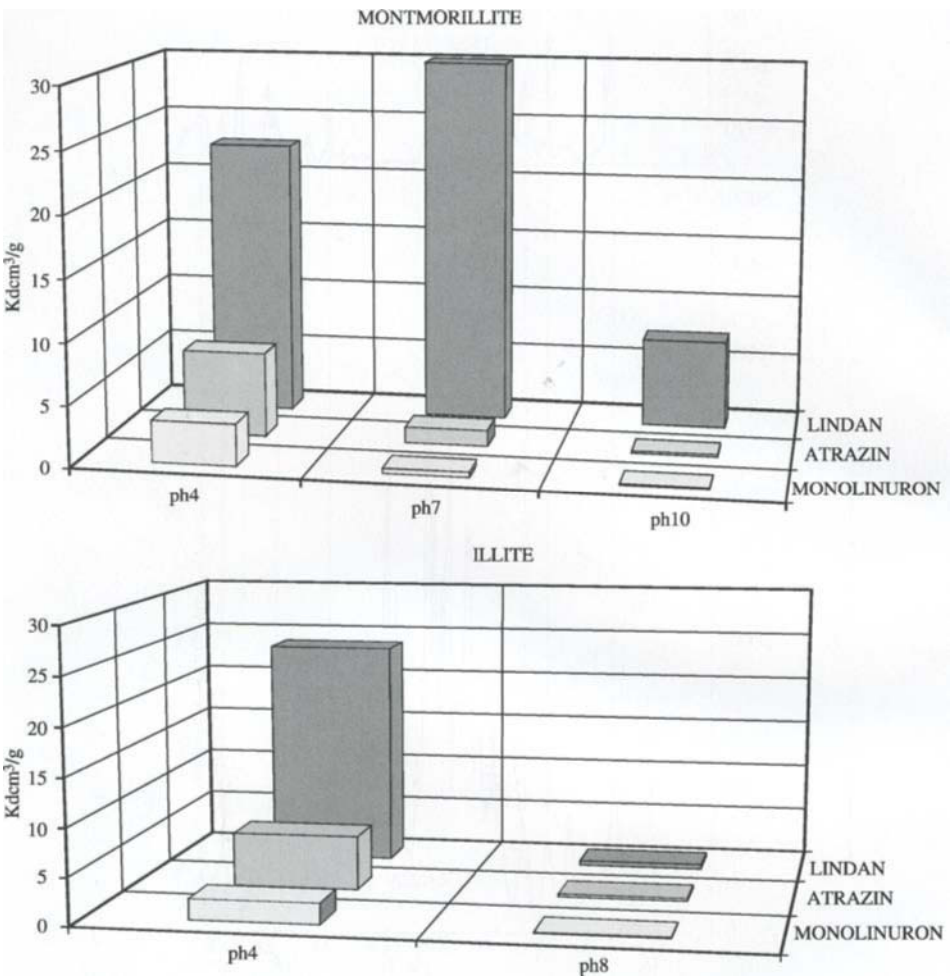


Figure III.3.3. Sorption of selected pesticides onto montmorillonite and illite at different pH values (Dickopf, 1994).

III.3.2.2. Migration of pesticides in the vadose and water saturated zone

Laboratory tests on the transport of pesticides (Dickopf, 1994; Klotz et al., 1995), in particular of atrazine, terbutylazine, lindane, diuron and monolinuron show that atrazine migrates in almost all sediments practically as fast as the water itself; its behavior is to a large extent independent of the hydraulic conductivity, the flow velocities and the compactness of the soil and sediment; all the other pesticides mentioned above show in laboratory experiments slower propagation velocities as compared to water flow with increasing:

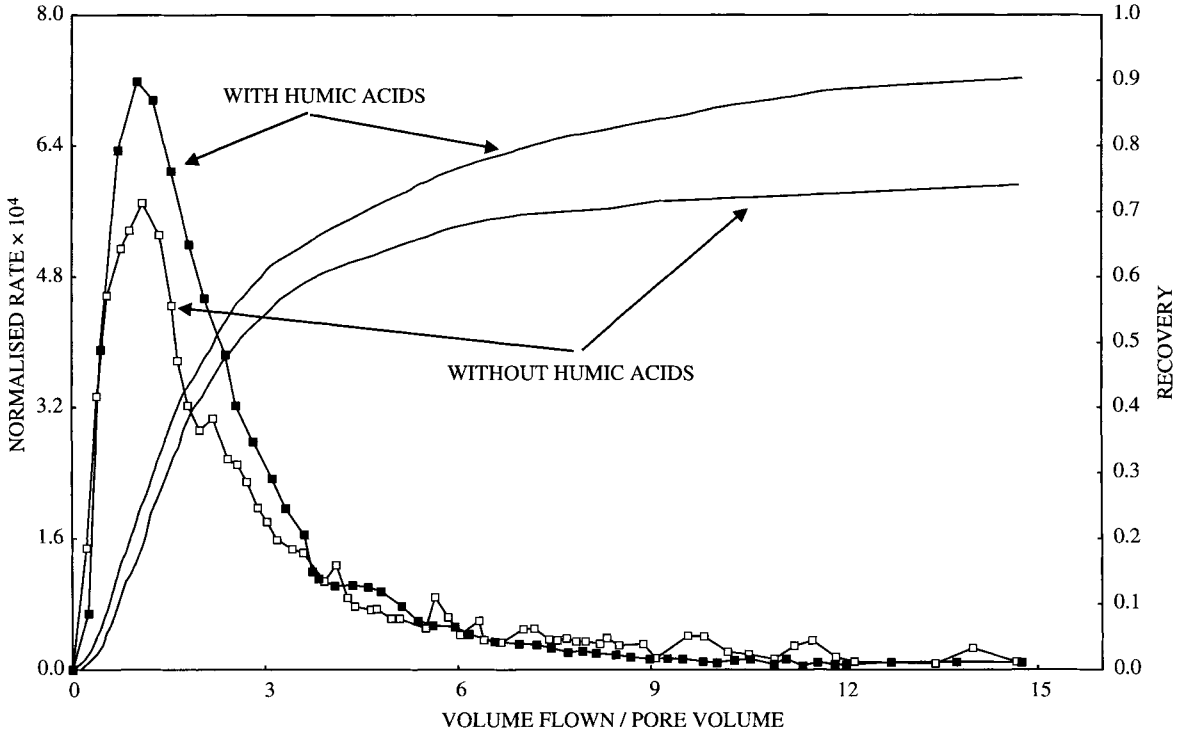


Figure III.3.4. Migration of terbutylazine with and without humates (Klotz et al., 1995).

- organic carbon contents in the sediments, since then the sorption increases,
- application quantities, since then the solubility is exceeded,
- compactness of the sediments and clay contents, since both increase the specific surface responsible for sorption processes,
- biomass fractions, which increase the incorporation in the biomass or the development of biofilms and
- with decreasing water contents and flow velocities, since then mechanical retention increases and sorption processes with slow kinetics quantitatively occur.

Examples for the influence of the effective flow velocity in the same aquifers (Quaternary gravels of the Munich Gravel Plain) upon the propagation velocities of different pesticides are shown in Table III.3.1 and Figure III.3.5. These field tests (Table III.3.1) were conducted without withdrawing groundwater, at effective flow velocities of 37 m/d and flow distances of 10 and 20 m with atrazine, lindane, monolinuron, diuron and a commercial atrazine, Gesaprim. As a non-reactive reference tracer, fluorescein was applied in parallel tests. In all the tests, no retardation of the pesticides was recorded, i.e. they seem to migrate as fast as the non-reactive tracer. Within the scope of the measurement accuracy, the total injected amount of the active ingredients was recovered (Seiler et al., 1995). In parallel laboratory tests on the same Quaternary gravel but flow velocities of only 3 m/d, the tests showed that migration of atrazine was not delayed with respect to the non-reactive reference tracer (tritium). Diuron, monolinuron, and to an even larger extent, lindane, all showed a flow retardation (Fig. III.3.5). These results demonstrate why a large range of retardation factors and K_D-values for most of the pesticides is reported. In order to create a better base for comparison, all indicated retardation factors required an exact description of the hydraulic boundary conditions and of sorption kinetics to which they refer.

Table III.3.1. Calculated recovery and retardation of selected pesticides in field tests in the Quaternary gravels of Dornach (Germany). The non-reactive reference tracer is fluorescein.

Pesticide	Flow path (m)	Recovery in % of the injection	Retardation
Atrazine	10	121	1.02
	20	104	1.02
Lindane	10	108	1.02
	20	48	1.02
Monolinuron	10	117	0.98
	20	104	1.00
Diuron	10	101	1.00
	20	96	0.99
Gesaprim	10	94	1.04
	20	97	1.00

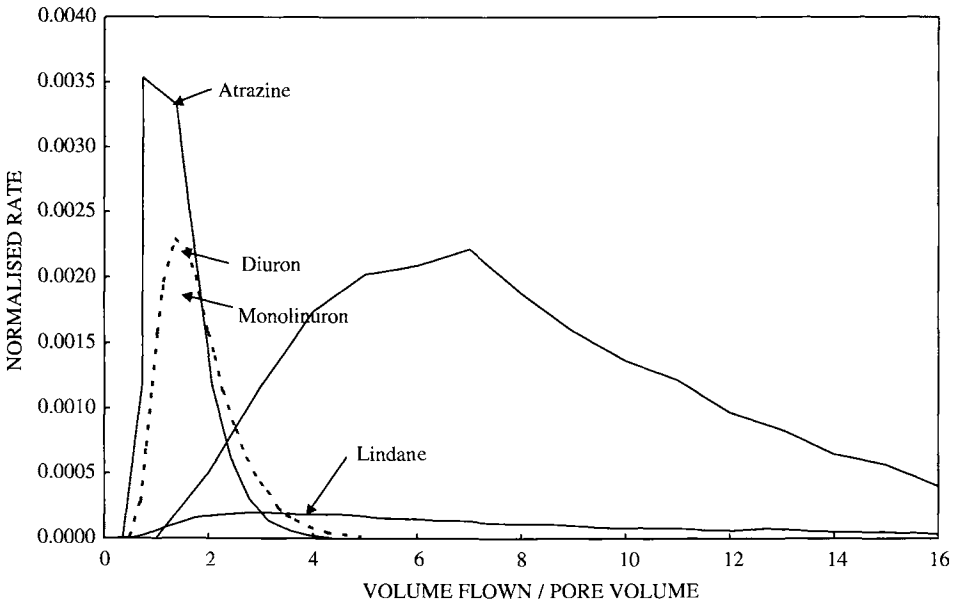


Figure III.3.5. Breakthrough curves for atrazine, diuron, monolinuron and lindane in Quaternary gravels. Laboratory tests; flow velocity 3 m/d (Dickopf, 1994).

III.3.2.2.1. Microbiological degradation of pesticides

The low concentrations of organic substances, the oligotrophy of the subsurface water in the sediments below the soil (Fig. III.3.1) and the primarily low microbiological population density of the solid surfaces lead to a decreased microbiological degradation of the pesticides in the vadose and the saturated zone. Another factor that can decrease the microbiological degradation efficiency is the low temperature of the underground water.

The mean underground temperature varies around the value of the mean annual air temperature; the amplitude of the seasonal temperature variations decreases with increasing observation depth and the phase shift of the temperature variations increases too (Fig. III.3.6). The neutral zone, below which in temperate climates noteworthy seasonal temperature variations of ± 0.1°C do not occur any more, is at 15–20 m below ground (Fig. III.3.6).

Generally, the degradation of pesticides can be described by first-order kinetics; in this case the half-life is a suitable measure for the mathematical description of the pesticide degradation.

The literature lists a large number of times for the half-life for pesticide degradation (Börner, 1967; Kohnen et al., 1975; Hamaker and Goring, 1976; Attaway et al., 1982; Scheunert, 1992); they cover a large range for most pesticides. This has different causes:

- It is not always sufficiently differentiated between mineralization (total degradation) and metabolization (partial degradation).
- A lack of data as to the degree of the metabolization achieved, which is sometimes even not possible to determine exactly without tracing the pesticide.

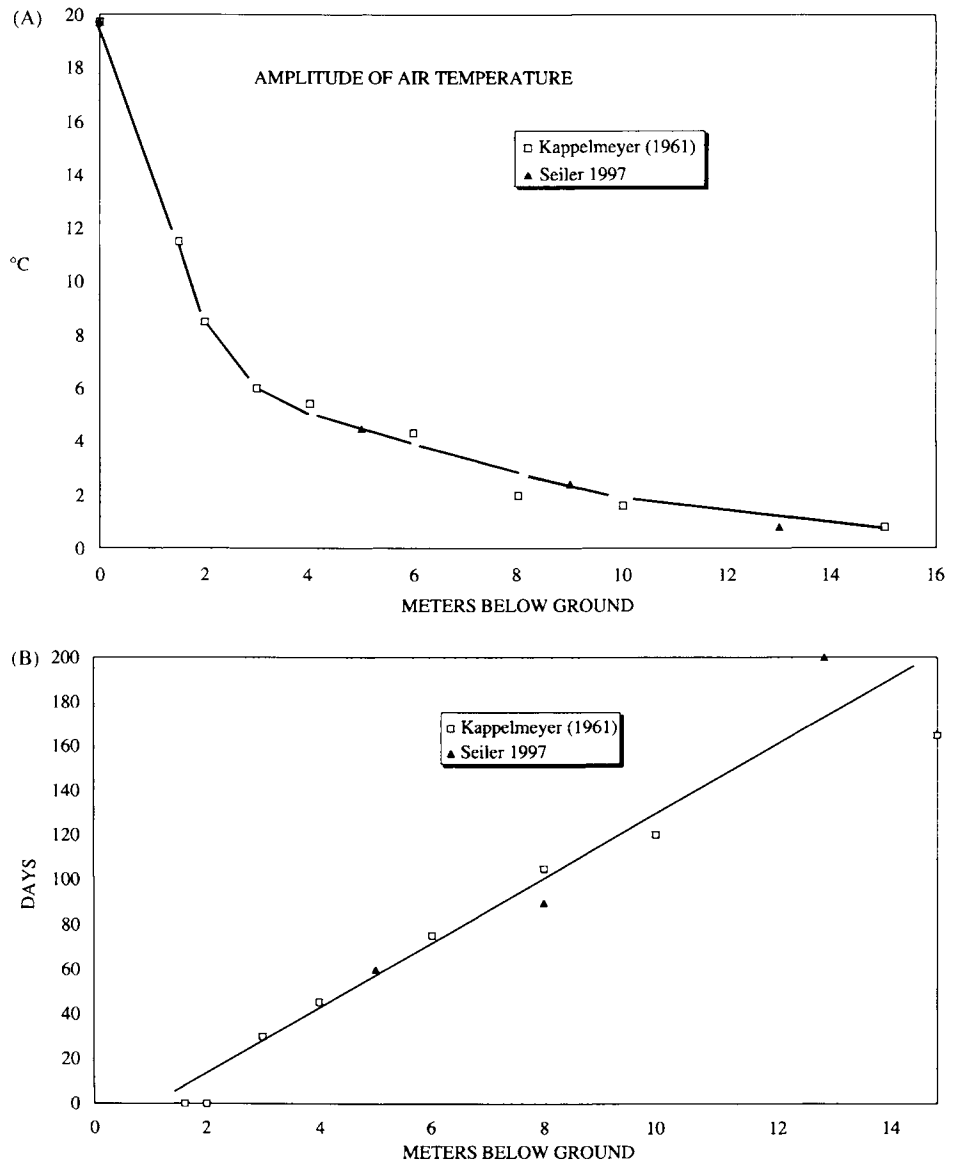


Figure III.3.6. Variations in the amplitude (A) and the phase displacement of the temperatures (B) in different depths below the ground surface as compared to the annual changes of the air temperature 1 m above the surface.

- The pH, temperature and environmental conditions under which the degradation experiment has been conducted, were different and frequently not well enough reported to allow reliable comparisons.
- Co-dissolved substances in the water may stimulate the metabolism.

- The influence of the relationship of the solution volume (V) to the sediment mass (m) upon the speed of the degradation processes is not taken into account.

The V/m ratio in batch experiments can strongly influence the experimentally determined value of the half-life for the pesticide degradation. Investigations with ethyl-parathion in a mix of Quaternary gravels (m) and carbonate groundwater (V) showed (Klotz et al., 1995) that the half-life decreases parallel to the V/m ratio (column curve in Figure III.3.7). In nature, the V/m ratio would be in the range of 0.1–0.15 cm^3/g, i.e. the half-life for the degradation of the ethyl-parathion would be extrapolated to about 10 days (Fig. III.3.7). In comparison, the half-life of the pesticide degradation in column tests (Figure III.3.7) is higher; here, the sorption kinetics relative to the flow velocity of the water plays a co-determining role.

How different the degradation behavior of the pesticides under different biotic, oxic and temperature conditions can be, can be instanced in several examples (Dickopf, 1994). However, these examples cannot be readily qualitatively or quantitatively transferred to other pesticides or even to those from the same substance family:

- Lindane has a much quicker degradation in oxygen-poor than in oxygen-rich environments (Fig. III.3.8).
- Atrazine is decomposed at practically the same slow rate whether or not the sediment and water have been subjected to sterilization.
- Pesticides from the same group behave differently under different degradation temperatures (Fig. III.3.9).

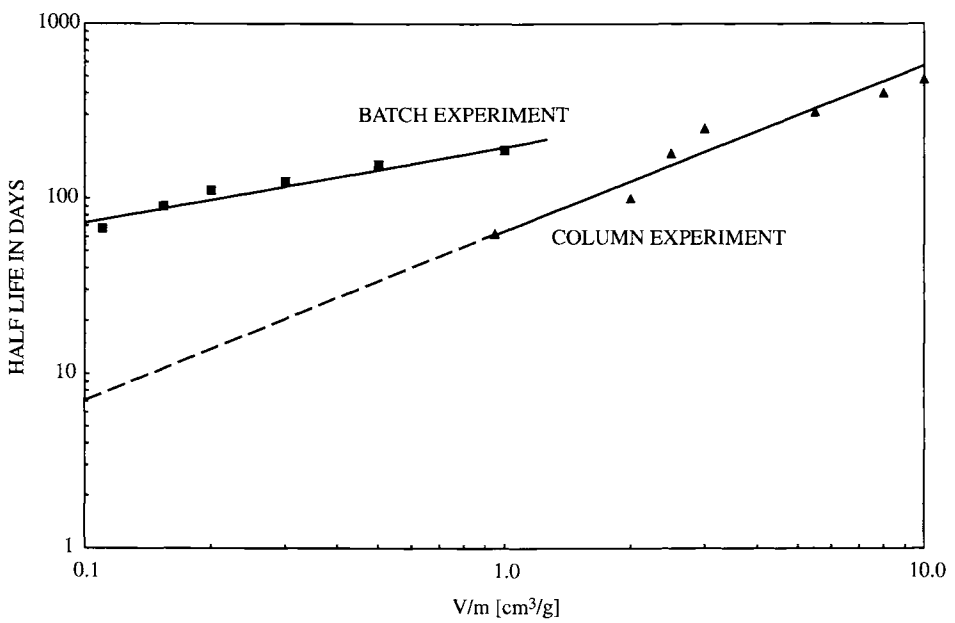


Figure III.3.7. Decrease of half-life of ethyl parathion vs. decreasing cumulative water loading, i.e. ratio of water volumes (V) to sediment mass (m) (Klotz et al., 1995).

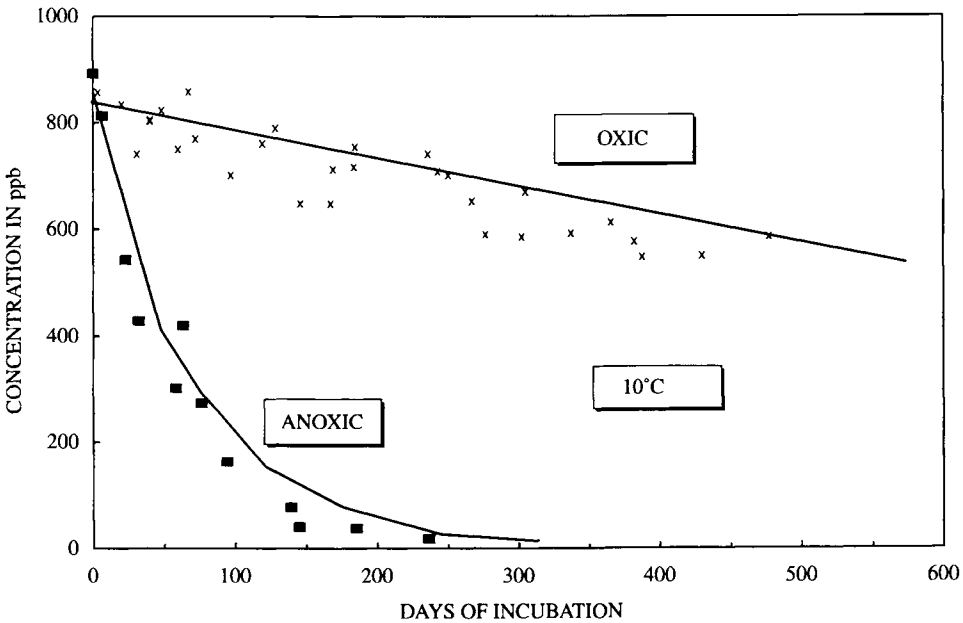


Figure III.3.8. The degradation of lindane under oxic and anoxic conditions (Dickopf, 1994).

Furthermore, degradation tests have shown that, e.g. nitrate- and sulfate-contaminated groundwater can bring about a higher degradation efficiency of the pesticides than uncontaminated groundwater (Fig. III.3.10).

There are still great uncertainties in the quantitative behavior of the pesticides and their impact upon the soil organisms. Due to this lack of understanding about the processes concerning most of the degradations, no reliable guidelines for the application of these substances can be formulated generally and mathematical calculations of the exposition of the pesticides in landscapes result in only rough estimates.

III.3.3. Nitrogen in agriculture

Nitrogen amounts to

4×10^{15} t in the atmosphere,
2×10^{15} t in the lithosphere,
1×10^{10} t in the hydrosphere,
5×10^{12} t in soils.

On the earth, annually 10–100 billion tons of biomass decomposes; thereby, nitrogen forms as ammonium and other compounds. At low oxidation numbers, nitrogen is strongly sorbed onto clay minerals and organic substances, at middle oxidation numbers it is volatile and at high oxidation numbers it is very water soluble. The volatile forms of nitrogen develop mainly during reduction processes

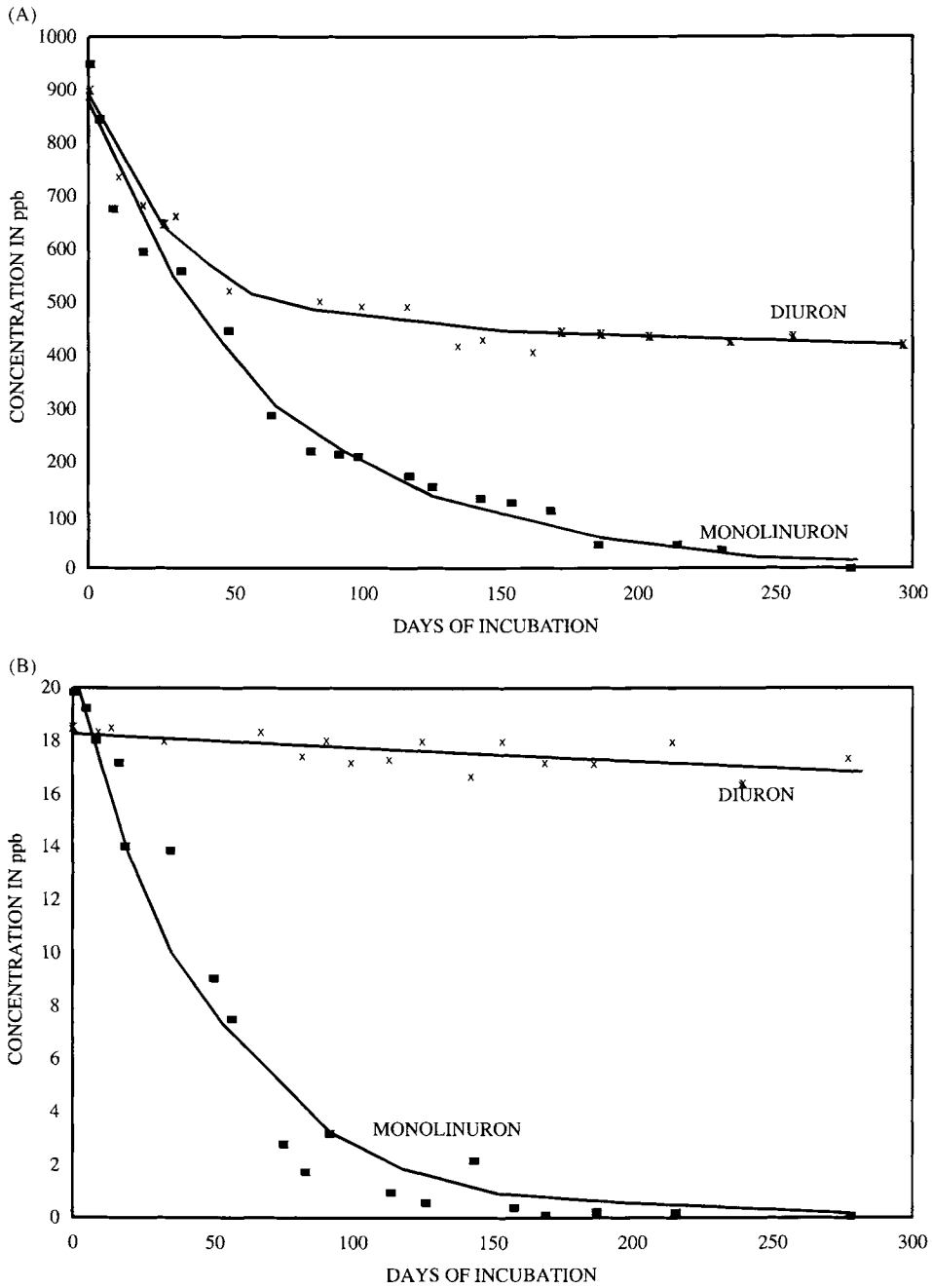


Figure III.3.9. The degradation of diuron and monolinuron at 20°C (A) and 10°C (B) (Dickopf, 1994).

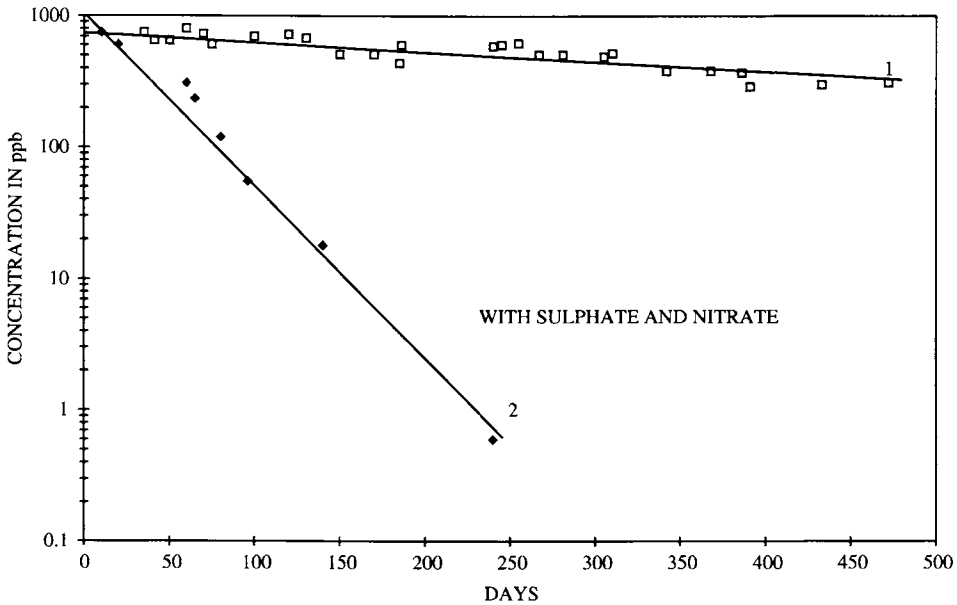


Figure III.3.10. The degradation of lindane in groundwater with normal chemical composition (top curve) and with elevated sulfate and nitrate concentrations (Dickopf, 1994).

such as denitrification; during oxidation processes such as nitrification or ammonification, this happens less. The volatile fraction of nitrogen can reach up to 15% of the inorganic nitrogen in the soil.

The natural nitrogen supply is not sufficient for the plant growth required in modern agriculture and thus, nitrogen as well as other nutrients must be added. Depending on the soil type, cultivation history and crop grown, currently, up to 255 kg/(ha a) of nitrogen are applied to agricultural crops; the natural decomposition of the organic substances in the soil and the nitrogen input from precipitation provide all together only *ca.* 15 kg/(ha a).

However, the oxidation and reduction processes that take place in this nitrogen pool in soil and underlying rock also produce unwanted release of material to the atmosphere as well as affecting water resources, life and health. These processes are microbiologically catalyzed and thus occur especially intensively in rocks and weathered formations with sufficient organic substance or sulfur in reduced form (pyrite).

During reduction processes such as denitrification, the trace gas N_2O forms, among others. This oxidizes to

$$2N_2O + O_2 \rightarrow 4NO \qquad \text{(III.3.1)}$$

In the presence of ozone, this reacts further to

$$3NO + O_3 \rightarrow 3NO_2 \qquad \text{(III.3.2)}$$

Nitrogen dioxide reacts then with atmospheric oxygen to

$$NO_2 + O \rightarrow NO + O_2 \qquad \text{(III.3.3)}$$

This reaction is favored by low temperatures and runs its course several times. If ozone and atmospheric oxygen occur together, ozone decomposes, but the nitrogen oxide contents do not change much over short and middle time periods. In contrast, oxidation processes produce nitrite and nitrate and both have high water solubility and can therefore enter the hydrosphere.

For infants and toddlers, excess in the total uptake of nitrate is responsible for the formation of nitrite, which can cause methemoglobinemia, resulting in an impairment of the oxygen uptake by the fetal red blood cells. The resulting cell damage can cause death. Adults can tolerate a higher nitrogen intake than infants and toddlers.

In determining the limits for the nitrogen uptake for people, the total nitrogen uptake through food and drink is essential: drinking water provides only a part of the total. In the European Community for the drinking water supply, the limit for nitrate is 50 mg/l, for nitrite 0.1 mg/l and for ammonium 0.5 mg/l. Long-term experience supports the validity of these limits that also contain a certain safety margin.

III.3.3.1. Average nitrogen input into the soil

The natural, i.e. anthropogenically uninfluenced nitrogen input from the atmosphere into the soil is 7 kg/(ha a). With respect to the 200 mm/a of infiltration this amounts to 3.5 mg N/l, which corresponds to 15.5 mg/l NO_3^-. In addition to this natural nitrogen input, on the average, the same amount comes annually due to the mineralization of organic substances. This is essentially caused by microorganisms, is strongly temperature dependent and at optimum in the summer. These natural sources of nitrogen are superimposed on the input of synthetic fertilizers, from large-scale livestock farming, burning fossil fuels, industrial production plus sewage. It is estimated that besides a biologically produced nitrogen amount of 500 million tons/a, there is an additional amount of *ca.* 50 million tons/a due to technical processes.

In agriculture areas *ca.* 255 kg/(ha a) of natural and synthetic fertilizers are applied, whereby the synthetic fertilizers are responsible for more than half of this input. Considering the application of fertilizers over the last 100 years, it rose from 1880 to 1940 from almost none to about 90 kg/(ha a) and by 1980 to about 255 kg/(h a). With this, plant production was increased by a factor of 3–5.

Urban areas and roads produce a nitrogen input of 0.9 kg/(ha a); household sewage produces 11 kg/(ha a). Both essentially drain through the receiving streams and may lead, in areas where groundwater is supplied by riverbank filtration, to a potential ground- and drinking water burden.

Older statistics from the Federal Republic of Germany concerning nitrate contents in groundwater shows that 6.5% of the consumers were supplied with drinking water exceeding 50 mg/l of nitrate and 4.0% had drinking water with a nitrite content of over 0.1 mg/l. These values have a rising trend even today. Very high nitrate and nitrite contents occur frequently in areas with intensively farmed crops such as vineyards and vegetables.

III.3.3.2. Nitrogen leaching in soils

If nitrogen enters the soil as ammonium nitrogen, it is optimally sorbed onto humic substances and clay minerals and can only become mobile through oxidation to nitrite or nitrate. In the root zone of arable lands, however, the oxidation processes are hindered by the reducing environments in the vegetation period and the little bacterial oxidation of ammonium by *Nitrosomonas* and *Nitrobacter* in this environment. On the other hand, nitrate also gets denitrified. Thus, the species of the nitrogen input, the organic and mineralogical composition of the rock and the chemical environmental conditions in the soil determine the extent of the N-retention, N-release and N-availability to the plants. These ratios undergo changes:

- Due to nitrogen input from the atmosphere in high oxidation numbers, i.e. nitrogen enters the soil in a mobile form.
- By the type of agriculture; there are long periods in the year with no active root zone and thus a reduction zone is missing. At these times nitrification is dominant.
- Finally, to increase the productivity of the soil, intensive nitrogen fertilization is carried out, which leads to strong nitrate leaching into the groundwater under unfavorable weather and agriculture conditions.

The three main processes are superimposed over others that also favor today's situation of nitrogen leaching in the soil:

- Plowing the soil facilitates aeration and oxidation processes occasionally prevail.
- The strongest groundwater recharge occurs in the vegetation free period. This is valid for our climate where groundwater recharge is the strongest in the winter; it is also valid in the tropics, where in the rainy season the fields lie fallow and are planted at the end of the rainy season and before the dry season.
- Soils with the highest groundwater recharge have the lowest clay content and thus the lowest inorganic retention capacity for nitrogen in low oxidation numbers.

The lowest nitrogen leaching in the soil occurs in areas with evergreens and natural stocks (Table III.3.2). In areas where crop rotation is practiced, it is dependent upon

- the soil structure and texture,
- the amount of rain,
- the seasonal change of the infiltration and the crop grown.

Nitrogen leaching ranges:

- in podsols from 5 to 20 kg/ha,
- in brown soils from 50 to 90 kg/ha.

It is modified by the uptake of crop from the soil that accounts for:

- fruits about 70 kg/ha and
- sugar beets about 300 kg/ha.

Data on these influencing factors based on detailed, long-term lysimeter observations, are available from Limburger Hof near Ludwigshafen (Pfaff, 1963) and from Weihenstephan (Amberger, 1976), as well as from pilot investigations in

Table III.3.2. Land use-dependent average nitrogen release in the Federal Republic of Germany (Wolters, 1982).

Agriculturally used areas without grasslands	25 kg/(ha a)
Grasslands	2 kg/(ha a)
Forest	2 kg/(ha a)
Wetlands, moor	2 kg/(ha a)

Nordrhein-Westfalen (Obermann and Bundermann, 1982) and in Fuhrberger Feld (Strebel and Renger, 1982).

Unfertilized lysimeters with conventional agricultural crop rotation show that high amounts of precipitation leached nitrogen much more than low amounts of rain (Table III.3.3). Considering the same substrate, there is a lower N-leaching at low than at high pH values; in this case the high proton supply has an impact upon the microbiologic efficiency of nitrification.

These values can only be conditionally used to calculate the nitrate input to groundwater, as they were obtained from lysimeters, mostly with disturbed texture and structure of soils and substratum. However, it can be clearly seen that:

- Nitrogen leaching from soils is higher in areas with high precipitation than in drier ones.
- At times there can be higher nitrogen release from fine-grained soils than from coarse-grained soils.
- More nitrogen is leached from the soil with high pH values than from the soil with low pH values.

The fact that more nitrogen is leached out of the same soil type at higher precipitation sums is closely connected to the fact that increase in the amount of oxygen goes along with increase in the precipitation amount, and thus an oxidizing environment is created for the nitrifying bacteria. The same holds true with respect to the pH value.

Table III.3.3. Nitrogen leaching from different soils at different precipitation sums and pH values.

Precipitation (mm/a)	pH	N-release (kg/(ha a))				
		Coarse sand	Sand	Loam	Humic loam	Silty loam
850	6.4	50	–	–	–	–
	7.2	–	–	–	72.8	–
	6.8	–	–	–	–	73.6
570	4.1	–	22	–	–	–
	7.6	–	30	–	–	–
	4.4	–	–	18	–	–
	7.0	–	–	25	–	–

During nitrification of nitrogen, which is accelerated bacterially, ammonia reacts to nitrite in the first reaction step:

$$NH_3 + 1.5O_2 \rightarrow NO_2^- + H_2O + H^+ \quad \text{(III.3.4)}$$

During the reaction, protons formation causes a drop in the pH value. However, microorganisms essential to this reaction (*Nitrosomonas*) cannot tolerate low pH values, so their activity would be limited. As ammonium is strongly sorbed, the corresponding mobility of the nitrogen is lacking in soils with high clay content; in coarse soils sorption is less important and the high seepage water velocities facilitate the proton export and thus the nitrification.

Generally, in Germany, more precipitation falls during the hydrological summer half-year than in the hydrological winter half-year. On the other hand, the evaporation in the hydrological summer half-year accounts for 2/3 to 3/4 of the annual evaporation, so that during the hydrological summer half-year less seepage occurs. As a consequence, nitrogen is stored in the hydrological summer half-year and gets mobile in the vegetation-free period.

Due to the nitrogen leaching in the hydrological winter half-year, there is a lack of nitrogen in the spring at the beginning of the vegetation period. In nature, this is not replenished until mineralization of the organic substances occurs; therefore, nitrogen fertilizers are applied mainly during this season. The soil though has also very low nitrogen retention at this time. As a result, there is a high loss of the nitrogen fertilizers into the seepage water during this season. The extent of these losses in the spring period depends upon the amount of nitrogen applied, but also upon the grain size of the sediment out of which the soil has developed (Table III.3.4).

Whether the nitrogen fertilizer is in the form of ammonium sulfate, calcium cyanamide, ammonium saltpeter or carbonate ammonium saltpeter is not particularly important.

The plant type may influence the nitrogen leaching since the plants can build up nitrogen deposits. Due to the environmental conditions in their root zone, the plants are also a deciding factor in the oxidation of the nitrogen to higher oxidation numbers.

Table III.3.4. Nitrogen application and release from two different soils (Pfaff, 1963).

N-fertilizer (kg/(ha a))	N-release (kg/(ha a))	
	Sand	Loam
Without	39	22
80	37	21
160	44	24
240	55	36
320	72	53

Depending on the soil use and plant type, the following retention series is given:

Fallow < vine < summer grains < winter grains < vegetables < root crops < grassland

However, this series of decreasing mean nitrogen leaching cannot be used to determine the expected groundwater charge with nitrates without further information. Other effective mechanisms are also of importance, such as:

- the type and time of application of the fertilizers and the type of crop,
- current and previous land use, especially the distribution from evergreens to deciduous land use,
- nitrogen losses due to denitrification by microorganisms.

Either organic or inorganic fertilizer can be applied, the soil always sorptively retains the ammonium fertilization, as long as oxidizing conditions in the root zone do not prevail or occur through a high groundwater recharge. Such oxidizing conditions occur in fallow periods, in which the soil is thoroughly leached of $N-NO_3^-$ by infiltrating precipitation and thus in the spring more fertilizer must be applied. Farming with intercrops is advantageous, since the soil is always covered with vegetation and has oxidizing conditions in the root zone for only short periods. This practice reduces the applied nitrogen fertilizer and contributes to groundwater protection. According to the field studies, the $N-NO_3^-$ concentrations in the groundwater were only half as high at the crop cultivation with intercrops as without, although the cultivation with intercrops required a larger amount of fertilizer (*ca.* 300 kg N/(ha a)).

Frequently, manure is spread on the soil during the fall or on the snow in the winter. This way of fertilizing allows the complete nitrate load and fecal microorganisms to enter the groundwater during the snowmelt, while applying organic fertilizer after snowmelt or after the rainy season provides optimal plant growth conditions.

Besides nitrogen fertilizer application, a liming of the soil is often carried out to reduce the acid content of the soil. Similar considerations are being made for forests. However, it is known that Ca-fertilization causes an increased release of the N from the soil, i.e. favors nitrate leaching.

Plowing grasslands play an important role in nitrogen leaching. If meadows are changed to crop fields, considerable nitrogen leaching starts. This nitrogen had been retained in the root zone of the plants before and gets released after plowing.

In a recent study, Hellmeier (2001) demonstrated by analyzing soil solutions and discharges that only in the effective root zone (0–90 cm below the ground surface) significant variations of nitrate and chloride concentrations occurred, which were not associated with respective nitrate consumption by the plants. In the unsaturated (vadose) zone below only trends of decreasing nitrate concentrations were observed since the application of nitrate fertilizers was reduced according to the demand of the plants (Fig. III.3.11).

The concentration variations reported by Hellmeier (2001) were found to be caused by the wash-out from the effective root zone through interflow that apparently predominated in the effective root zone (Seiler et al., 2002). This was observed in loess, as well as in sandy soils and sediments.

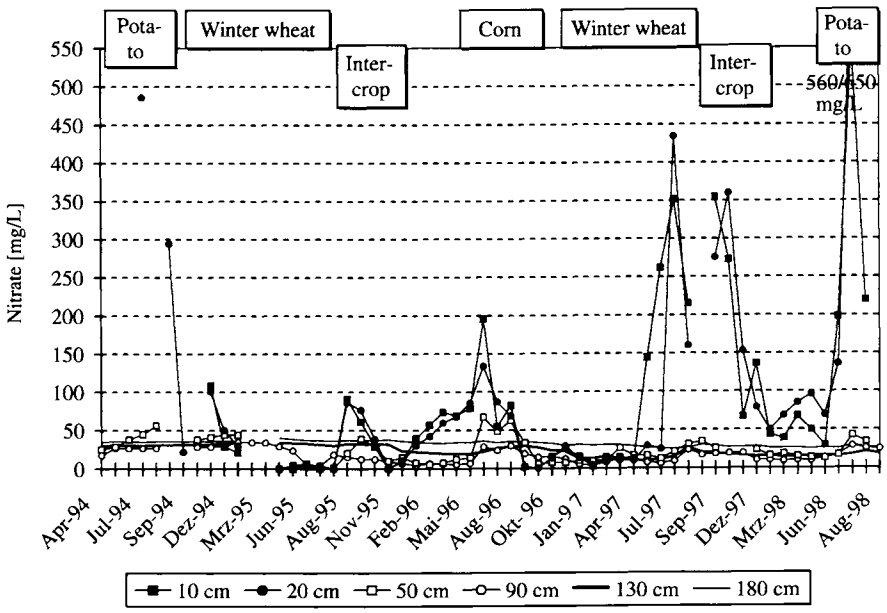


Figure III.3.11. The variation of nitrate concentrations in a soil profile of Scheyern (Upper Bavaria); nitrate peaks are the response to fertilizing (Hellmeier, 2001).

Considering the transport of DOC, nitrate and sulfate from the hilly area, Hellmeier (2001) stated (see Chapter V.2.2, Figure V.2.2.8) that, in general, the export of sulfate and chloride through surface run-off, interflow and groundwater recharge was of the same order of magnitude as determined by the analysis of discharge in creeks. DOC colloids were predominantly exported by the interflow, because within the effective root zone the mechanical filtration of particles was less pronounced as compared to the sediment beneath. Chloride and sulfate occur as dissolved, and DOC as suspended matter in the discharge components.

In the presence of chlorides and sulfates on one hand and DOC on the other hand, nitrates behave intermediately (see Chapter V.2.2, Figure V.2.2.8). Obviously nitrates are not only exported as a dissolved matter, but probably also as a DOC-bound matter.

III.3.4. Concluding remarks

Pesticides and fertilizers seriously affect ground and surface water quality if not adequately applied. Since one important pathway in agriculture areas is linked to discharges (overland runoff, inter-flow and groundwater-recharge) transporting agro-chemicals as solute or particle-bound matter, the application should be much more oriented on weather conditions and the soil in-homogeneities; rainy seasons mostly favor the export of agrochemicals as compared to the end of rain events or long before the rainy season. Repeated application of small amounts of agrochemicals according to the needs of

plants is preferable, as it would allow to adjust the agrochemical addition to the uptake by the crop and thus to reduce their losses.

The oxidation status of inorganic agrochemicals has a considerable influence on their export potential through discharge. It is potentially the highest in seasons without crops when significant soil aeration occurs, and the lowest in the vegetation period due to the reducing chemical environment and the storage function of the effective root zone. Both these factors that affect the mobility of agrochemicals can be regulated to the significant extent by seeding intercrops and by applying fertilizers according to plant needs and soil retention capacities. Pesticides also should be applied in much smaller quantities than usual and better repeatedly. Much more research is needed to elucidate the metabolisms as well as toxic effect and mobility of these substances. The routine pesticide tests do not satisfy the water protection requirements.

Also the kind of soil treatment and the crops itself contribute significantly to the transport of agrochemicals to surrounding compartments, resulting in hazardous concentrations in the aquatic environment and soils.

Taking into account the variety of factors influencing the mobility of agrochemicals, precision in farming probably could contribute much more to adequate environmentally friendly agricultural activities than usual ecological or intensive farming.

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III.4
Sewage sludge

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III.4.1. Introduction

Sewage sludge is a by-product of wastewater treatment at sewage treatment works. Effluents are received from industrial, municipal or rural sources. The sewage sludge is derived from primary, secondary and tertiary treatment processes (ANDERSEN-SEDE, 2001). In the Working Document on Sludge 3rd Draft (EC DG ENV, 2000), it is proposed to use the definition of sludge suggested by CEN (European Committee for Standardization): "mixture of water and solids separated from various types of water as a result of natural or artificial processes". *Sewage sludge* would then be "sludge from urban wastewater treatment plants". The suggested definition of *treated sludge* is that of "sludge, which has undergone one of the treatment processes...or a combination of these processes, so as to significantly reduce its biodegradability and its potential to cause nuisance as well as the health and environmental hazards when it is used in land". Sewage sludge belongs to the large group of *biodegradable waste (biowaste)* that means "any waste that is capable of undergoing anaerobic digestion or aerobic decomposition" (EC DG ENV, 2001).

Managing municipal and industrial waste presents a major challenge for today's society. Current approaches to waste management tend to focus on avoidance of waste generation and reutilization of waste products without adversely affecting the environment, rather than waste disposal, wherever feasible (EC DG ENV, 1999, 2001). Due to the progressive implementation of the Urban Waste Water Treatment Directive 91/271/EEC (EEC, 1991) in all EU Member States, and rise in the number of households connected to sewers, the annual generation of sewage sludge is constantly growing. The increase of the level of sewage treatment also adds to the amount of sewage sludge produced. In 1995–1998, in 5 of 14 EU Member States (Sweden, Denmark, Finland, The Netherlands and Germany) the percentile of population covered with the upgraded sewage treatment with biogen removal exceeded 70% (EUROSTAT, 2001). In other countries the level of sewage treatment is continuously increasing. Due to the combined effect of these factors, the annual generation of sewage sludge in the European Community is heading from some 5.5 Mt (million tons) in 1992, through 7 Mt in 1997 towards about 9 Mt by the end of 2005 (ANDERSEN-SEDE, 2001; Langenkamp et al., 2001a; EC, 2002). The current sludge production in 12 EU Member States (without Greece, Spain and Italy) ranges from 16 to 35 kg/person/a; in Greece it accounts

for 9 kg/person/a (Langenkamp et al., 2001a). The increasing trend of sewage sludge generation has been observed all over the world that prioritizes the issue of its environmentally sound and sustainable management. Sludge is rich in organic matter and nutrients such as nitrogen, phosphorus and potassium, and thus is an attractive material to be used in agriculture as a fertilizer or a soil improver. However, due to the original pollutant load of the treated sewage and processes involved in sewage treatment, sludge tends to concentrate heavy metals, organic contaminants and pathogenic organisms. The presence of toxic heavy metals and organic compounds, excess phosphorus and nitrogen, in addition to hygienic concerns, presents a challenge to wastewater treatment facilities in selecting appropriate technology and means of recycling or disposal of sludge, both from an economical and environmentally acceptable perspective (Harris-Pierce et al., 1995). Effects from these constituents may be immediate, or time delayed and non-linear (Van den Berg, 1993).

The primary objective of sludge management in the European Community is to utilize the opportunity of its beneficial use in agriculture. Simultaneously, the new regulations under development are focused on long-term protection of Community soils, to assure safety to human health and to the environment in view of the most recent scientific and technological progress. A focus on these objectives has resulted in a number of comprehensive state-of-the art review studies commissioned by the European Commission in several research centers, which on one hand, evaluate occurrence of contaminants in sewage sludge, potential risk from its use in agriculture and treatments for reduction of harmful substances and pathogens (ANDERSEN-SEDE, 2001; Carrington, 2001; ICON, 2001; Langenkamp et al., 2001a), and on the other hand, analyze background trace element and organic matter content of European soils and define short- and long-term actions for setting up a European Soil Monitoring System (Balze et al., 1999; Langenkamp et al., 2001b). Other feasible and environmentally friendly ways of sewage sludge utilization are also considered.

The evaluation of sludge quality presented here is largely based on these sources. On its background, the approach to the limit values of trace elements in soil and sewage sludge used in agriculture will be discussed, along with other options of this waste utilization.

III.4.2. Sludge quality

III.4.2.1. Occurrence and sources of pollutants

The physical separation, biological and chemical treatment of wastewater produce sewage sludge. Screenings, grit, scum, septic material, filter backwash and other wastewater solids are all found in sludge. They provide additional solids to the sludge from primary, secondary and tertiary treatment processes. The chemical composition of municipal sewage sludge can vary greatly, depending on the composition of wastewater, and applied wastewater and sludge treatment processes. As sewage sludge sequesters hydrophobic compounds, concentrations of pollutants in this material reflect the flow of chemicals in a contemporary society (Hale et al., 2002). Sources of pollutants in urban wastewater (UWW) that become subsequently enriched in sewage sludge are shown in Figure III.4.1.

Before disposal or recycling, sludge is subject to undergo one or several treatment processes such as thickening, dewatering, stabilization, disinfection and thermal drying, in

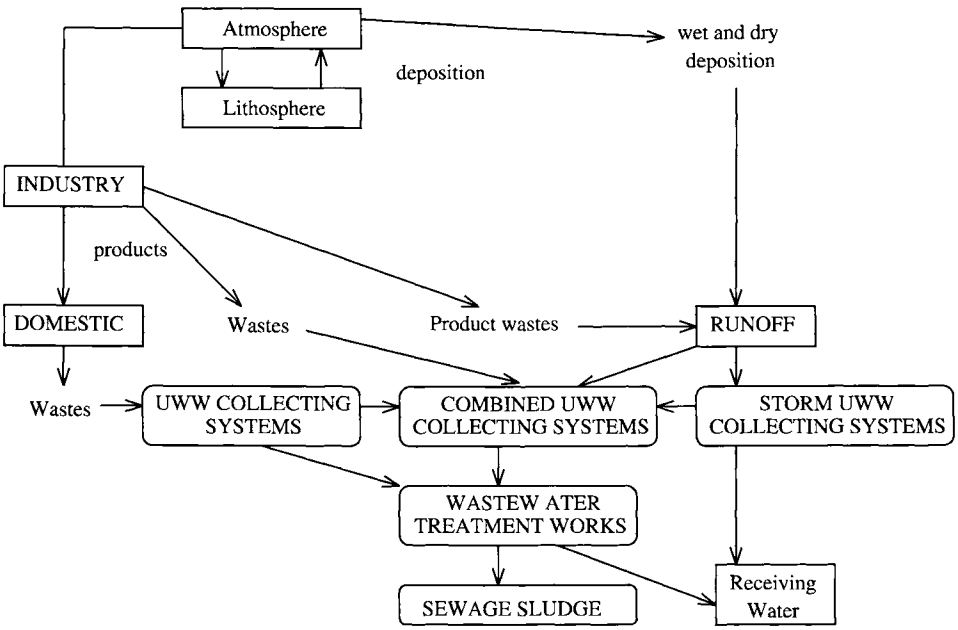


Figure III.4.1. Source of pollutants in urban wastewater and sewage sludge (ICON, 2001, modified).

order to reduce water content, biodegradability and improve hygienic properties. Apart from the enrichment of above-mentioned constituents of agricultural value (organic matter, nitrogen, phosphorus, potassium, and to a lesser extent, calcium, magnesium and sulfur), sewage sludge is significantly enriched in organic pollutants, trace metals and pathogens. The EC study performed by ICON (2001) formulates the type and loads of both organic and metal pollutants in wastewater (sewage) treatment systems and consequently in sewage sludge as a complex function of:

- size and type of conurbation (commercial, residential, mixed);
- plumbing and heating systems;
- domestic and commercial product formulation and use patterns;
- dietary sources and feces;
- atmospheric quality, deposition and run-off;
- presence and type of industrial activities;
- use of metals, and other materials in construction;
- urban land use;
- traffic type and density;
- urban street cleaning;
- maintenance practices, for collecting systems and stormwater control;
- accidental releases.

The pollutants that through the wastewater treatment process accumulate in sewage sludge, thus posing a potential risk to the environment, represent three major groups:

- potentially toxic elements (PTEs) that include heavy metals: Cd, Cr(III) and Cr(VI), Cu, Hg, Ni, Pb, Zn, Ag, platinum group metals (PGMs) and metalloids (As, Se);
- organic pollutants;
- pathogens.

III.4.2.2. Heavy metals

The heavy metal content in sewage sludge has been of major concern for many years. Heavy metals in UWW (sewage) tend to be associated with suspended solids and are partitioned into the sludge during treatment. Conventional sewage treatment removes 60–72% of cadmium (Cd), 28–73% of chromium (Cr), 45–70% of copper (Cu), 20–70% of nickel (Ni), 54–73% of lead (Pb) and 40–74% of the zinc (Zn) from the influent and consequently enriches sewage sludge with these metals. A wide range of metal concentrations may be present in sludge, due to differences in sewage metal concentrations. Contents that exceed common values indicate substantial contamination from industrial sources (Weber et al., 1984; Wong et al., 2001). An EC report prepared by ICON (2001) differentiates three major sources of PTEs entering the wastewater (sewage) treatment plant and sewage sludge as the target recipient: (1) domestic, (2) commercial/industrial and (3) urban run-off (Table III.4.1). The degree of uncertainty in the estimation of proportion of the particular sources in the metal load accounts for $\geq 50\%$ of the total inputs of Cr, Ni and Zn, 20–40% of Cu, Hg and Pb and $< 20\%$ of Cd.

Commercial/industrial inputs are estimated to be the major sources of Hg, Cr and Cd, and are considered to be responsible for up to 60% of these metals enrichment in wastewater and sewage sludge. Identified domestic sources contribute particularly significantly to the loads of Pb, Cu, Zn and Ni (up to 50–80%), while up to 20–40% of the total load of Cd, Pb, Zn is supplied with run-off (mass balance of Zn, Ni and Cr has been incomplete due to difficulties in identifying and evaluating part of the sources). The share of these sources in the total load may vary in a broad range, depending on the structure and significance of the industry. In some areas, the proportion of non-point metal input may be dominating, e.g. in the primary industrial areas of historically high long-term emission.

Table III.4.1. Estimated load of potentially toxic elements (PTEs) from different sources entering urban wastewater (UWW) system in the EU countries (% of the total input) (after ICON, 2001).

Heavy metals (PTE)	Sources (% of total input)		
	Domestic	Commercial/industrial	Urban run-off
Cd	20–40	30–60	3–40
Cr	2–20	35–60	2–20
Cu	30–75	3–20	4–6
Hg	4–5	50–60	1–5
Ni	10–50	30	10–20
Pb	30–80	2–20	30
Zn	30–50	5–35	10–20

The provisional metal source balance presented in Table III.4.1 is valid for the EU area, but may substantially differ from other areas with diverse economy, climatic conditions and urban infrastructure.

Limit values for metal content in sewage sludge from wastewater treatment plants have been set in the EU Sludge Directive 86/278/EEC (1986). A more stringent new draft regulation has been proposed by EC DG ENV, 2000. These regulations define sewage sludge and soil quality for the protection of soil when sludge is applied to agricultural land. The reported contemporary metal content in the sewage sludge from wastewater treatment plants (WWTPs) in the EU Member States vary in a broad range, generally within an order of magnitude (Table III.4.2). These metal contents appear to be well below the limit values.

The EU reports (ANDERSEN-SEDE, 2001; ICON, 2001) point out the general declining trend in metal concentrations in wastewater and sewage sludge in the EU Member States over the past two decades (up to 10% for Ni, 40–50% for Cr, Hg and Pb, and up to 60% for Cd), which is attributed mainly to efficient trade effluent controls, optimization of technological processes and overall structural changes in industrial production.

Data on sewage sludge quality in the EU Accession countries and available data for some other countries (e.g. Israel) show that concentrations of the most heavy metals fall within the range reported for the EU and all the data, including the priority hazardous substances Cd and Hg, are below the limit values set by the EU regulations in force and as a draft. Average content of Hg is within or only slightly above (Czech Republic) that in the EU, while Cd appears to be more problematic, and in Latvia, Slovenia and Poland its

Table III.4.2. Range and average metal content in sewage sludge vs. limit values in the EU (in mg/kg d.m.) (after ICON, 2001; ANDERSEN-SEDE, 2001).

Heavy metal	Concentrations in sludge		EU limit values for sludge		EU limit values for soil	
	Mean[a]	Range[b]	86/278/EEC	EC DG ENV (2000)[c]	86/278/EEC	EC DG ENV (2000)[c]
Cd	2.2 (2.8)[d]	0.4–3.8	20–40	10	1–3	0.5–1.5
Cr	79 (141)[e]	16–275		1000		30–100
Cu	337	39–641	1000–1750	1000	50–140	20–100
Hg	2.2	0.3–3	16–25	10	1–1.5	0.1–1.0
Ni	37	9–90	300–400	300	30–75	15–70
Pb	124	13–221	750–1200	750	50–300	70–100
Zn	863 (1222)[f]	142–2000	2500–4000	2500	150–300	60–200

[a]Arithmetic mean from data reported for 13 countries: Austria, Denmark, Finland, France, Germany, Greece (Athens), Ireland, Luxembourg, Norway, Poland, Sweden, The Netherlands and UK.
[b]EU Member States only.
[c]The Working Document on Sludge, 3rd Draft (2000).
[d]Data without parenthesis exclude Poland: the mean Cd content in Polish sludge is 9.9 mg/kg d.m.
[e]Data without parenthesis exclude Greece: the mean Cr content in sludge from Athens is 886 mg/kg d.m.
[f]Data without parenthesis exclude Poland and Greece (Athens): the mean Zn content in Polish sludge is 3641 mg/kg d.m., in Greece (Athens) 2752 mg/kg d.m.

average concentrations in sludge about twofold exceed the EU range: in Latvia and Slovenia these values are above 7 mg/kg d.m. (ANDERSEN-SEDE, 2001) in Poland 9.9 mg/kg d.m. (ICON, 2001), in Israel (one plant) 10.7 mg/kg d.m. (Avnimelech and Twardowska, 1997).

The PTEs listed above that include Cd, Cr(III) and Cr(VI), Cu, Hg, Ni, Pb, Zn, Ag and metalloids (As, Se) are considered to be the priority inorganic pollutants in the EU, the USA and Canada. Their contents in biosolids and soil are regulated and extensively tested, while other metals detected in sewage sludge that may be potentially harmful to risk receptors such as soil biota and grazing animals are not well quantified and evaluated with respect to safe application in agriculture. Hargreaves and Hale (2002) suggest quantifying in biosolids a number of other unregulated metals, such as Al, Ag, Ba, Be, Bi, Mo, Fl, Sb, Sr, Th, Ti and V.

Recently, due to the significant expanding of the commercial use of the PGMs that includes Pt, Pd, Rh, Ru, Ir and Os, mainly in vehicle exhaust catalysts for reduction of atmospheric emissions of CO, hydrocarbons and NO_x from internal combustion engines, and in minor amount (6–12%) in anti-neoplastic drugs used in hospitals for cancer treatment, these metals have appeared in municipal wastewaters. Approximately 70% of Pt is transferred to the sewage sludge. Reported concentrations of Pt in sludge from two WWTPs in Munich (Germany) were in the range 86–266 μg/kg d.m. (ICON, 2001).

Rose and Swanson (2002) report also the concentration of medical radioisotopes (I-125, Ir-192, Sm-145 and Cs-137 with half-lives of 60 days, 74 days, 320 days and 30 years, respectively) in sewage sludge exemplified in three WWTPs in the New York area. According to these authors, the potential of posing a threat to human health from such sludge transformed to biosolids for land application may occur, as these isotopes have half-lives longer than the time of sludge digestion process.

III.4.2.2.1. Source control

Analysis of status and further development of source control of PTEs in the European community was carried out for EC Directorate General – Environment by ICON (2001).

For efficient source control, identification and quantification of sources of PTEs, and the development of a complete mass balance from each source are required. In the EU up to now, though, for a high proportion of major PTEs, sources are not yet identified and there is a substantial uncertainty in the mass balance, the highest for Cr, Ni and Zn ($\geq 50\%$), lower for Cu, Hg and Pb (20–40%) and the lowest for Cd ($< 20\%$). Despite these uncertainties, efforts to reduce metal discharges to sewer systems resulted in significant decrease of metal contents in the sewage sludge. Effective implementation of effluent controls, technology optimization and change in industrial structure in the EU Member States have also contributed to the decrease in metal content in sewage sludge. ICON (2001) reports reduction of input concentrations of Cd to WWTPs in the UK and Sweden during 1992–1998 by 60%, Cr, Hg and Pb by 40–50%, Zn and Ni by 10% and no change in Cu inputs that reflects the share of industrial sources in these countries in the total input load.

Besides large industrial installations that are subject to rigorous waste control standards, discharge of metals plays significant role in small commercial, artisan enterprises such as vehicle workshops and washing facilities, metal processing and

goldsmiths, and also health establishments and hotels/catering, which are also supposed to comprise a major proportion of the incomplete information and unidentified inputs of metals to UWW systems (Table III.4.1). Metal loads discharge to sewer systems from small business enterprises is more difficult to control. Compulsory wastewater pretreatment before discharge and inspections of the premises may markedly reduce the input of metals from artisan activities to the sewer system and to the sewage sludge. As has been shown in case studies (ICON, 2001), reduction of Zn, Cu and Pb may reach up to $< 10\%$, Cr and Ni up to 0.5% and Cd up to 40% of the total metal load entering WWTP.

Reduction of metals from domestic sources and run-off is particularly problematic and feasibility of its control is limited. According to ICON (2001), the principal sources of metals in domestic wastewater are body care and cleaning products, pharmaceuticals, liquid wastes (e.g. paints) and plumbing (Cu and Pb source). The referred report sees a way of reducing these metal inputs in a participation of homeowners in voluntary collection schemes for liquid waste. It, though, seems that the only practicable way of efficient reduction of metal inputs from households is the minimization of metal contents in the household products by manufacturers.

III.4.2.3. Organic pollutants

III.4.2.3.1. Occurrence and sources

The studies of ICON (2001) and Langenkamp et al. (2001a) for the EC reviewed about 150 literature sources published in the last decade, in addition to older literature reviews that cover a period since late 1970s. Data on the occurrence of organic pollutants in sewage sludge were collected and discussed with respect to basic toxicological issues, transfer pathways and risk assessment. In both referred EC review studies (ICON, 2001; Langenkamp et al., 2001a), a limited number of available data on organic pollutants in sewage sludge (generally, within the range from < 10 to several tenths of samples for each of 3–4 countries) is evident. This reflects the lack of routine testing due to analytical difficulties and costs, and lack of standardized methods of analysis, as well as the lack of an agreement on the kind and number of specific substances to be tested in a group of chemicals (e.g. data for PAHs comprise from 8 to 18 compounds, for PCBs 6–7 congeners) that limits the comparability of data.

Sewage sludge was found to carry the highest load of organic contaminants among fertilizers. Organic micropollutants, or xenobiotics, are widespread in the environment as a result of human activities such as industry, agriculture and traffic (Berset and Holzer, 1995). They are persistent in nature and concerns exist regarding their toxicity and the tendency for some of them to bioaccumulate through the food chain (Jones et al., 1995). Through the UWW systems they enter the wastewater treatment facilities and finally sewage sludge; the residue level of organic pollutants increases from raw to digested sludge. Organics found in sewage sludge include, but are not limited to, adsorbable organic halogen compounds (AOX), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Seven PCDDs, 10 PCDFs and 12 PCBs are jointly referred to as dioxin-like compounds; this term is currently in a wide use (e.g. WHO, 1999; Larsen et al., 2000; US EPA, 2000a; Van den Berg et al., 2000). According to ICON (2001), due to

introduction of source and emission controls on persistent organic contaminants in the 1980s, significant reduction of industrial inputs of these compounds to sewers (up to >90 to >99%) and consequently decrease of their concentrations in sewage sludge in the EU Member States occurred. The current contents of persistent organic contaminants in this waste result mainly from:

- background inputs to the sewer from normal dietary sources;
- background inputs by atmospheric deposition due to contemporary remobilization/ volatilization from soil and cycling in the environment (PCB, PCDD/F, PAH);
- atmospheric deposition from waste incineration (PCDD/F);
- atmospheric deposition from domestic combustion of coal;
- the limited biodegradation of organic contaminants during sludge treatment;
- the increase of the concentration of these compounds in sludge due to volatile solids destruction during sludge treatment.

In countries, where controls on industrial combustion and incineration emissions are unsatisfactory, these processes, along with small consumers (household and trade activities) and the production of chlorinated pesticides are the principal sources of persistent organic contaminants (PAH, PCB, PCCD/F) in sludge.

Other widespread organic contaminants in sewage sludge originate from their domestic and commercial use and comprise detergent residues, nonylphenol and nonylphenol ethoxylates with one or two ethoxy groups (NPE), surfactants – linear alkylbenzene sulfonate (LAS), and di-2-(ethylhexyl)phthalate (DEHP) used in plastic manufacture. Many other emerging organic compounds identified in sludge create problems due to their persistence in soil or during sewage or sludge treatment, or toxic effects, e.g. organotins (such as mono-, di- and tributylin MBT, DBT and TBT) (Langenkamp et al., 2001a); commercial chlorinated paraffin (a large group >200 formulations) used as plasticizers in plastics, extreme pressure additives, flame retardants, sealants and paints; brominated diphenyl ethers (PBDE), increasingly used as flame retardants in furnishing, textiles and electrical insulation; polychlorinated naphthalenes (PCNs) originated from waste incineration or landfilling of items containing PCN; quintozene (pentachloronitroenzene); nonvolatile silicone polymers polydimethylsiloxalanes (PDMSs) used in lubricants, electrical insulators and antifoams; nitro musks (chloronitrobenzenes) that are components of perfumed cosmetic products; endogenous estrogens (17β-estradiol and estrone) and synthetic steroids that are ingredients of oral contraceptives; pharmaceutical compounds used in medical and veterinary practice; or polyelectrolytes based on polyacrylamide and cationic copolymers and used for sludge treatment as dewatering aid (ICON, 2001). The list of organic pollutants occurring in sewage sludges reflects current trends in their production and use. A comprehensive literature review by Drescher-Kaden et al. (1992) concerning organic pollutant residues with proven or suspected toxic effects detected in German sewage sludge in 1977–1992, cited in both recent EC review sources (ICON, 2001; Langenkamp et al., 2001a), refers to 332 compounds, of that 42 of them were present regularly, mostly in the range from mg/kg to g/kg d.m.

Concentration range and mean contents of major groups of organic contaminants in sewage sludge from different European countries in 1989–1996 collected in the review studies accomplished for the EC by ICON (2001) and Langenkamp et al. (2001a) are presented in Table III.4.3.

Table III.4.3. Occurrence of selected organic contaminants in sewage sludge in 1989–1996 vs. limit values (MCL) proposed by EC DG ENV (2000) (after ICON, 2001; Langenkamp et al., 2001a).

Organic compounds	Country (sludge treatment)[a] [number of samples/ WWTPs tested]	Years[b]	Concentrations (mg/kg d.m.)[c]			MCL[d]
			Mean[e]		Range	
Halogenated organics (AOX)	Denmark [NA]	1995	200	NA	75–890	500
	Germany [NA]	1994–1996		196–206	NA	
Linear alkylbenzene sulfonates (LAS)	Denmark (V) [26, *19*]	1993–1995	6500	455–530	11–16,100	2600
	Germany (And) [*8*]	NA, –2000		NA	1600–11,800	
	Germany (Ae) [*10*]	As above		NA	182–452	
	Italy (And) [*1*]	1996–1997		NA	11,500–14,000	
	Norway [36]	NA, –2000		54	<1–424	
	Spain (And) [*3*]	As above		NA	12,100–17,800	
	Spain (Raw) [*2*]	As above		NA	400–700	
	Switzerland (And) [*10*]	As above		NA	2900–11,900	
	UK (And) [*5*]	As above		NA	9300–18,800	
D(2-ehylhexylphtalate) (DEHP)	Denmark [29]	1993–1995	20–60	24.5–38	3.9–170	100
	Norway [55]	1989 +		58–83	<1–1115	
	Sweden [27]	1989–1991		170	25–661	
Nonylphenol and ethoxylates (NPE)	Denmark [29]	1993–1995	26	NA–8	0.3–537	50
	Norway [55]	1989 + [b]		136–189	22–2298	
	Sweden [60]	1989–1993		82–825	23–7214	
	UK [NA]	NA		330–640	NA	
Polycyclic aromatic hydrocarbons, total (PAH)	Denmark 18 PAH [29]	1993–1995	0.5–27.8	NA	<0.01–8.5	6[f]
	Germany 6 PAH [124]	NA, –2000		NA	0.4–12.83	
	Germany 16 PAH [88]	As above		NA	0.25–16.28	
	Norway [36]	NA, –2000		3.9	0.7–30	

(*continued*)

Table III.4.3. (Continued)

Organic compounds	Country (sludge treatment)[a] [number of samples/ WWTPs tested]	Years[b]	Concentrations (mg/kg d.m.)[c]		MCL[d]
			Mean[e]	Range	
	Sweden 6 PAH [NA]	NA, –1997	1.6	NA	
Polychlorinated biphenyls, total (PCB)	Germany 6 PCB [NA]	1989–1996	0.154–0.34	NA	0.8[g]
	Norway 7 PCB [36]	NA, –2000	0.0422	0.017–0.10	
	Sweden 7 PCB [27]	1989–1993	0.113–0.1	0.0006–7	
	USA [NA]	–1998	NA	0.21 (98.P)	
Polychlorinated dibenzo-dioxins and -furans (PCDD/F) (ng TEQ/kg d.m.)	Austria [NA]	NA, –1999	14.5	8–38	100
	Denmark [9]	1993–1994	NA	10.3–34.2	
	Denmark [NA]	NA, –1999	21	0.7–55	
	Germany [NA]	As above	20–40	0.7–1207	
	Germany [NA]	1994–1996	17–22	46–56 (90.P)	
	Spain [NA]	NA, –1999	64	NA	
	Sweden [14]	1989–1991	20.5 (50.P)	5.7–115	
	Sweden [NA]	NA, –1999	20	0.02–115	
	Sweden [36]	NA, –2000	6.26 (50.P)	3.0–68.8	
	UK [NA]	NA, –1999	NA	9–192	
Organotins					
MBT	Switzerland [4]	1988–1990	NA	0.10–0.97	NA
DBT	Switzerland [4]	1988–1990	NA	0.41–1.24	
TBT	Switzerland [4]	1988–1990	NA	0.28–1.51	

[a]Sludge treatment: (V), various; (And), anaerobically digested; (Ae), aerobic process; (Raw), non-treated.
[b]–2000, data before 2000; 1989+, data after 1989.
[c]Concentrations in mg/kg d.m., except for PCDD/F, given in ng TEQ/kg d.m.
[d]Proposed EU 2000 (3rd draft) limit concentrations in sewage sludge used in agriculture (EC DG ENV.E.3/LM, 2000).
[e]Mean concentration values: left column – for the several EU countries (after ICON, 2001); right column – for each specific country.
[f]Sum of 11 compounds: acenaphtene, phehahthrene, fluorine, fluoranthene, pyrene, benzo(b + j + k)fluoranthne, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-c,d)pyrene.
[g]Sum of six congeners PCB 28, 52, 101, 138, 153, 180; WWTP, wastewater treatment plant; NA, not available; 50.P and 98.P, 50 and 98 percentile of a compound concentration, respectively.

The highest enrichment in sewage sludge shows the surfactants LAS and nonylphenol NPE that also significantly exceed the proposed EU concentration limits for sludge to be used in agriculture. The data for LAS prove that these compounds are not completely degraded during mesophilic anaerobic digestion, which is the principal commonly used sludge stabilization process, thus their high accumulation in the anaerobically digested sludge. The LAS concentration range in aerobically digested or untreated sludge appeared to be visibly narrower.

The broad concentration range and variations in toxic organics content are also of concern, in particular that the variations observed within one waste treatment plant can be greater than the differences in concentration range between different plants (Langenkamp et al., 2001a). High maximal concentrations and broad concentration range are characteristic also for DEHP. PAHs in some reported cases exceed the rigorous proposed EU limits, both with respect to mean and maximal contents.

Source and emission control on combustion and incineration emissions and production of certain chlorinated pesticides, as well as the ban on use of PCB resulted in efficient reduction of persistent compounds such as PAH, PCB and PCDD/Fs in the primary industrial/commercial sources, up to >90 to $>99\%$, and consequently caused an adequate decline of input to sewage sludge from these sources. The contemporary principal inputs of these contaminants to the environment, and also to sewage sludge, have shifted to much less controllable sources such as small consumers including households and surface run-off or remobilization/volatilization of background (historical) contaminant loads from soil (ICON, 2001). Also long-lived applications of industrial chemicals such as PCBs (e.g. electrical equipment) may emit them to the environment during use and disposal for a long time (Breivick and Alcock, 2002; Breivick et al., 2002). Generally, the reported actual concentrations of PCDD/Fs and PCBs in sewage sludge in the EU countries appear to be safely below the precautionary limits proposed by the EC.DG.ENV.E3/LM, 2000 (3rd draft). Nevertheless, due to the aforementioned environmental cycling of these chemicals, their occurrence in wastewater and in sewage sludge cannot be neglected.

High concentrations of PAHs in sewage sludge are particularly problematic; flue gases from traffic account for one of the major sources of PAH release to the environment. Measurements of 16 PAHs content in dust particulates suspended in the ambient air in the vicinity of gasoline stations, car parks, bus terminals and along the roads, conducted in 2000 in the thickly populated industrial Silesia Land, Poland, showed high and variable concentrations of these compounds, many times exceeding standards and off-road background contents (Table III.4.4). Therefore, this source can contribute significantly to the elevated contents of PAHs in the sewage sludge.

Besides AOX, LAS, NPE, DEHP, PAH, PCB, PCDD/F and TBT that are considered as priority organic pollutants and thus received relatively much, but still not enough attention, there is a limited data on the environmental behavior, fate and risk associated with a number of organic compounds occurring and accumulating in sewage sludge during waste treatment process, e.g. with hormone steroids, both natural, as estrone (E1), 17β-estradiol (E2) and estriol (E3), and synthetic, as 17α-ethynylestradiol (EE2) and mestranol (MeEE2) that belong to a group of endocrine disruptors. Estrogenic steroids were reported to occur in influents to sewage treatment plants in different countries (UK, Italy, Canada, Brazil, Denmark, Japan, Germany) in concentrations

Table III.4.4. Mean concentrations of selected PAHs in the ambient air in the vicinity of gasoline stations, car parks, bus terminals and along the roads in 2000 in Silesia Land, Poland (after Klejnowski et al., 2002).

Statistical parameter	Concentration (ng/m^3)											
	BaA		BbF + BkF		BaP		CHR		INP + DbahA		∑16 PAH	
	S	W	S	W	S	W	S	W	S	W	S	W
Mean	49.5	36.2	19.3	74.6	88.2	116.2	96.8	98.9	76.0	87.2	1427	1558
Minimum	0	0	0	0	0	0.5	0	0	0	0	568.0	643.5
Maximum	376.8	209.9	398.0	398.2	463.9	407.3	604.8	320.9	228.8	396.5	3609	2240
Standard deviation	63.6	46.8	63.3	114.7	83.9	107.0	105.5	72.1	40.9	75.6	467.6	359.6

BaA, benz(a)anthracene; BbF + BkF, benzo(b)fluoranthene + benzo(k)fluoranthene; BaP, benzo(a)pyrene; CHR, chrysene; INP + DbahA, indeno(1,2,3-cd)pyrene + dibenz(a,h)anthracene; ∑16 PAH, sum of 16 PAHs; S, summer; W, winter.

ranging from < 1 up to several tenths ng/l. Their removal rate during sewage treatment, partially due to adsorption on sludges was found to be high and for different estrogens and treatment plants varied within the range from 61 to $> 99\%$, thus their considerable enrichment in sewage sludge can be anticipated (Ying et al., 2002a). In the sludge dry matter from German WWTPs, several estrogenic endocrine disruptors, 17α-ethinylestradiol (EE2), 4-*tert*-octylphenol (OP), 4-nonylphenol (NP) and bisphenol A (BPA) were found in significant concentrations: up to 280, 13.3, 560 and 32 mg/kg d.m., respectively (Gehring et al., 2003). Studies on occurrence of about 100 of human and veterinary pharmaceuticals in the influents and effluents from WWTPs showed decrease from μg/l to ng/l range during the treatment process that suggests their adequate enrichment in sewage sludge. The fate of these compounds in wastewater and sewage treatment process is not well understood (Schrap et al., 2003).

Other authors (Cloup et al., 2003) report frequent occurrence of biocides at ppb level in sewage sludge from 12 WWTPs, of these permethrin and tributylin contents were the highest with a mean 98 and 148 ppb d.m., respectively. Water run-off was considered as the main source of permethrin, diuron and carbendazin, and the industry as a complementary source of diuron. Biocides are widely applied as disinfectants for public/private areas and in veterinary hygiene, as wood/masonry preservatives and conservators in non-alimentary finished products.

While PCBs, due to past restrictions on their use and improved industrial source control decline as chemicals of concern, unrestricted and unregulated polybrominated diphenyl ethers (PBDEs), among them penta-BDE mixture that serves as flame retardant additive in polymers used, e.g. in polyurethane foam for furniture, thermoplastics for electronics and in textile back coatings, have become environmentally problematic. In North America that consumes over half of the world's production of PBDEs and 98% of penta-BDE, these compounds have been detected in all compartments of the environment, in animals and humans, exhibiting persistence and bioaccumulative properties similar to PCBs. PBDE concentrations appeared to be also the highest in North American sewage sludges (typically over 1 mg/kg), while content levels elsewhere (in the EU, UK, Australia, New Zealand and Hong Kong) were much lower. One of the sources of PBDE enrichment in sewage sludge is considered to be urban dust (Hale et al., 2002).

Besides xenobiotic organic compounds of different kinds that enter to the sewage sludge through wastewater, there is also a purposeful introduction of such substances in the sludge treatment process. Polyelectrolytes based on polyacrylamide and cationic copolymers are used extensively in this process to aid the mechanical dewatering process. This results in high concentration of these compounds in sludge, in the range 2500–5000 mg/kg. Acrylamide is a common monomer associated with polyelectrolytes. They are reported to be potentially toxic to humans and have a carcinogenic effect. This caused their withdrawal from use in Japan and Sweden and restrictions in Germany and France. In many other countries polyelectrolytes in sludge treatment are used unrestrictedly (ICON, 2001).

These examples show that sewage sludge is a sink for many organic compounds. Their persistence in the environment, the exposure and possible effects on the environment and human health are not yet thoroughly understood.

III.4.2.3.2. Source control

The EC review study prepared by ICON (2001) summarizes the relative importance of contemporary sources of the major groups of organic contaminants in sewage sludge, as well as reduction opportunities for these compounds (Table III.4.5).

The major problematic organic compounds of high relevance to the industrial/commercial and domestic sources comprise detergent surfactants and residues (LAS and NPE), DEHP that originates from the production and use of finished products from PVC, such as floor and wall plastic coverings and textile prints, and pharmaceuticals. The source control of these compounds at the producer side is considered possible mainly through limitation of LAS surfactants and NPE use by substituting them in detergent formulations and DEHP in plastic manufacture. At the consumer side, the use of these chemicals is planned to be reduced through eco-labeling and extensive information about advantages and disadvantages of currently used chemicals and their prospective substitutes. Human and veterinary pharmaceuticals occurrence in the sewage sludge can be partially limited through the collection system for unwanted drugs, as well as through segregation and pretreatment of hospital, medical center and laboratory effluents. Financial incentives for encouraging municipalities and household owners to remove lead piping in the areas with soft water and to remove old lead paints have also been recommended.

Due to aforementioned efficient control of PAHs and PCDD/F emission from the industrial sources, and a ban on PCB use, surface run-off becomes the major source of these compounds in wastewaters and consequently in sewage sludge. This source is generally difficult to control. A substantial reduction of PAH emission to the environment from traffic sources can be achieved through rigorous technical control of exhaust gases in

Table III.4.5. Major sources and possibility of control of organic contaminants entering urban wastewater and sewage sludge in the EU Member States (after ICON, 2001).

Organic contaminant[a]	Manufacturing/ commercial		Run-off		Domestic	
	Relative importance	Opportunity to reduce	Relative importance	Opportunity to reduce	Relative importance	Opportunity to reduce
LAS	H	M	L	L	H	M
NPE	H	M	L	L	H	L
DEHP	H	M	L	L	M	M
PAH	L	L	H	L	L	L
PCB	L	L	H	L	L	L
PCDD/F	L	L	H	L	L	L
Pharmaceutical	H	M	L	L	H	M

H, high; M, moderate; L, low.

[a]LAS, linear alkylbenzene sulfonates; NPE, nonylphenolethoxylates; DEHP, di(2-ethylhexyl)phtalate; PAH, polycyclic aromatic hydrocarbons; PCB, polychlorinated biphenyls; PCDD/F, polychlorinated dibenzo-*p*-dioxins and dibenzo-*p*-furans.

cars and other motor vehicles and withdrawal of old vehicle fleets not adequately equipped to meet the requirements.

Development of the sustainable urban drainage with individually assessed and implemented low- and high-tech solutions has been considered as effective method of pollutant input from the run-off source, along with increasing control on emissions to water, air and land, and a close monitoring and control for connection of small users, hospitals, dental and medical practices, garages and car washes to the UWW systems.

III.4.2.4. Pathogens

The report by Carrington (2001) for the EC DG ENV (EC Directorate General – Environment) points out the variability of the quantity and species of pathogens with time and location depending upon local circumstances and the current population health (Table III.4.6).

These data show that for safe use of sewage sludge on the agricultural land, a reduction of at least 10^4 of added *Salmonella* and the destruction of viability of *Ascaris* ova is required, which means that the level of pathogen content in sewage sludge should not exceed the ambient levels in the environment. This level of hygienization is demonstrated by WWTPs, which treat sewage sludge by advanced processes listed in Table III.4.7. Conventional treatment processes do not sufficiently reduce the risk of pathogen transmission and thus must be restricted with respect to sludge applied to land.

Monitoring of treated sludge for the presence of pathogens is considered impracticable. For evaluation of sludge quality, use of surrogate organisms such as *Escherichia coli* and *Clostridium perfringens* commonly found in sludge that have similar resistance to treatment as pathogens is suggested. The recommended numbers of *E. coli* in treated sludge should be ≤ 1000 per gram (d.m.), and of *C. perfringens* ≤ 3000 per gram (d.m.).

Hygienic requirements are considered in the EU both by the regulations in force (EEC, 1986) and in the Working document on sludge (EC DG ENV, 2000). According to this document, the advanced sludge treatment process shall be initially validated through a 10^6 reduction of a test organism such as *Salmonella senftenberg* W 775. The treated sludge shall not contain *Salmonella* sp. in 50 g (wet weight) and

Table III.4.6. Typical concentrations of microorganisms (wet weight) in untreated sewage sludge (after Carrington, 2001).

Microorganisms	Species	Concentration range (cells/g)
Bacteria	*E. coli*	10^6
	Salmonella	10^2–10^3
Viruses	Entero-	10^2–10^4
Protozoa	*Giardia*	10^2–10^3
Helmints	*Ascaris*	10^2–10^3
	Toxacara	10–10^2
	Taenia	5

Table III.4.7. Advanced hygienization treatments of sewage sludge (after Carrington, 2001).

Process	Parameters
Windrow composting	Batches of sludge (± bulking agent) to be kept at 55°C for 4 h between each of three turnings, followed by a maturation period to complete the composting process
Aerated pile and invessel composting	The batch to be kept at a minimum of 40°C for at least 5 days and for 4 h during this period at a minimum of 55°C. This to be followed by a maturation period to complete the composting process
Thermal drying	The sludge should be heated to at least 80°C for 10 min and moisture content reduced to $< 10\%$
Thermophilic digestion (aerobic or anaerobic)	Sludge should achieve a temperature of at least 55°C for a minimum period of 4 h after the last feed and before the next withdrawal. Plant should be designed to operate at a temperature of at least 55°C with a mean retention period sufficient to stabilize the sludge
Heat treatment followed by digestion	Minimum of 30 min at 70°C followed immediately by mesophilic anaerobic digestion at 35°C with a mean retention time of 12 days
Treatment with lime (CaO)	The sludge and lime should be thoroughly mixed to achieve a pH value of at least 12 and a minimum temperature of 55°C for 2 h after mixing

the treatment shall achieve at least a 10^6 reduction in *E. coli* to less than 5×10^2 CFU/g.

For biowaste that is a much broader group of organogenic waste and comprises also sewage sludge, in the EC Working document on biowaste, 2nd draft (EC DG ENV, 2001), as test organism for the hygienic requirements, *Salmonella streptococchi* and *C. perfringens* have been selected. Biowaste is deemed to be sanitized if *S. streptococchi* is absent in 50 g of compost/digestate and *C. perfringens* is absent in 1 g of compost/digestate. Both documents are widely discussed and the final decisions concerning hygienization criteria are to be approved.

The US federal rules (US EPA, 1993) pertaining to pathogens in land-applied sewage sludge are technology based and no risk assessment was performed. A study commissioned by the US EPA and by the National Research Council of the National Academy of Sciences and released in 2002 (NRC, 2002) found that there is uncertainty about the potential for adverse human health effects from exposure to biosolids and recommended a new survey of pathogens in sludges, reassurement of risks based on more recent methodology including pathogens, and development of improved pathogen detection methods and indicator organisms (Hanlon, 2002; Harrison and McKone, 2002).

III.4.3. Sludge treatment technologies and management

III.4.3.1. Sludge treatment technologies

The problem of sludge management is neither simple nor cheap. Increasingly stringent regulations and new technologies to meet quality demands, e.g. progressive implementation of the Urban Waste Water Treatment Directive 91/271/EEC (1991) in all Member States of the EU, have resulted in the production of greater sludge quantities and types. Solids processing and disposal account for a significant proportion of the costs associated with the operation and maintenance of a WWTP. Hence, cost-effective, environmentally sustainable options must be sought.

Before utilization or disposal, sludge has to undergo one or several treatment processes aimed to reduce its water content and fermentability, and to hygienization. The steps of sludge treatment are presented in Table III.4.8.

Sludge processing methods generally should consider the following:

- sources, quantities and characteristics of the wastewater;
- best available treatment technologies;
- regulatory, public health and environmental considerations;
- performance and costs.

A comprehensive short description of existing sewage sludge treatment processes can be found in the EC study (ANDERSEN-SEDE, 2001). The details of treatment technologies are widely presented in the relevant technical literature and guideline sources are not addressed in this chapter, and only their environmental aspects are discussed here.

Table III.4.8. Sludge treatment processes (after ANDERSEN-SEDE, 2001).

Steps	Types of processes	Objectives
Conditioning	Chemical conditioning Thermal conditioning	Sludge structure modification Improvement of further treatment
Thickening	Gravity thickening Gravity belt thickener Dissolved air flotation	Obtain sufficient density, strength and solids content to permit hauling for further disposal process Reduce the water content of the sludge
Dewatering	Drying beds Centrifuging Filter belt Filter press	Reduce the water content of the sludge
Stabilization and/or disinfection	Biological processes: *Anaerobic digestion* *Aerobic digestion* *Long-term liquid storage* *Composting* Chemical processes: *Lime treatment* *Nitrite treatment* Physical processes: *Thermal drying* *Pasteurization*	Reduce the odor generation Reduce the pathogen content of the sludge
Thermal drying	Direct Indirect	Highly reduce the water content

III.4.3.2. Effect of wastewater and sludge treatment on contaminants content and transformations

III.4.3.2.1. Heavy metals

Heavy metals enrichment in sludge depends on their content in influent to WWTP and efficiency of treatment processes. Metal transfer to sludge occurs during primary and secondary sedimentation as physico-chemical processes of gravitational separation of mineral particulate matter and microbial biomass, and metal uptake by flocks of microbial biomass during biological treatment step. Process of metal transfer from wastewater to sewage sludge is well described by existing empirical and mechanistic models. In general, 60–80% of most metals are transferred to the sludge except Ni that is removed in a lesser proportion (~40%) due to high solubility (ICON, 2001).

The wastewater treatment process determines metal content in sewage sludge, as practically no changes of metal load occur during sewage treatment, except of a minor loss of soluble metals during thickening and dewatering with removed water. In contrast, metal concentration in sludge increases proportionally to the decrease of its volume due to dewatering, but decreases after chemical treatment processes proportionally to the chemicals added.

III.4.3.2.2. Organic contaminants

Organic contaminants show much higher propensity to transformations during physical, chemical and microbiological treatment of the sludge that results in their loss, decomposition or formation of new compounds. The mechanisms of these processes include (ICON, 2001):

- volatilization;
- biological degradation;
- abiotic/chemical degradation, e.g. hydrolysis;
- extraction with excess liquors;
- sorption onto solid surfaces and association with fats and oils.

Many organics in wastewater are lipophilic and readily sorbed onto sewage sludge. Hydrophobic organic contaminants on wastewater have different affinity to sorption onto sludge solids during primary sedimentation process. Sorption potential and therefore enrichment in sewage sludge of individual compounds can be estimated by the octanol–water partition coefficient (K_{ow}) as low for $\log K_{ow} < 2.5$, medium for $2.5 < K_{ow} < 4.0$ and high for $\log K_{ow} > 4.0$.

Considerable part of volatile organics of high volatilization potential (Henry's law constant $Hc > 10^{-3}$ l/mol m^9), e.g. benzene, toluene, dichlorobenzenes in the wastewater and in sewage sludge may be lost in aeration/agitation process during wastewater treatment, and during thickening and dewatering when transferred to sludge.

Sewage treatment was estimated to biodegrade during the activated sludge process about 80% of LAS and of the endocrine disruptor 4-nonylphenol polyethoxylate (NP_nEO), although 97–99% degradation was also reported. About 15–20% of LAS accumulates in the raw sewage sludge. Microbial degradation of NP_nEO causes formation of relatively lipophilic metabolites NP_1EO and NP_2EO that also enrich the raw sewage sludge (ICON, 2001). Studies have found that alkylphenol ethoxylate (APE) metabolites are more toxic than the parent substances and possess the ability to mimic natural hormones by interacting with an estrogen receptor (Ying et al., 2002b). The alkylphenols 4-nonylphenol and 4-*tert*-octylphenol are known to be formed under anaerobic conditions, probably from long chain anionic tensides. In digested sludge a distinct increase of the concentration of bisphenol A, a monomer of polycarbonates and epoxy resins, have also been noted recently (Tennhardt et al., 2003).

Mesophilic anaerobic digestion may cause destruction of about 20% of the residual surfactants, and transformation of approximately 50% of NP_nEO metabolites into NP. Destruction efficiency may be enhanced by increasing digestion temperature and retention time (ICON, 2001). Nonetheless, there is strong evidence that although APEs are highly treatable in conventional biological treatment facilities, anaerobic conditions retardate

biotransformation of APE metabolites and enhance their persistence (Marcomini et al., 1989; John et al., 2000; Ying et al., 2002b).

The potential to biodegrade during anaerobic digestion was found to relate to the size of alkyl side chains. Lower molecular weight phthalate esters and butyl benzyl phthalate are completely degraded in 7 days of anaerobic digestion at 35°C and thus are removable by the conventional process of anaerobic digestion. Compounds with larger C-8 groups such as di-*n*-octyl and DEHP are much more resistant to anaerobic microbial degradation (ICON, 2001).

Aerobic thermophilic treatment appeared to degrade APEs and their metabolites much faster than in anaerobic conditions (Banat et al., 2000; Ying et al., 2002b). Also phthalate esters (DEHP) are rapidly destroyed under aerobic conditions, thus their >90% reduction occurs in 24 h already during wastewater treatment in the activated sludge process. Under aerobic psychrophilic conditions, a high concentration decrease rate was observed for several estrogenic phenolic xenobiotics and natural and synthetic steroids (Tennhardt et al., 2003).

Thermophilic aerobic digestion process of stabilization during composting has the potential to biodegrade relatively persistent organic compounds in sludge. It has been reported that composting and sludge storage for 3 months provide similar reduction for organic compounds as does mesophilic anaerobic digestion. A relatively new enhanced treatment process of thermal hydrolysis conditioning prior to conventional anaerobic stabilization is supposed to enhance the efficiency of removal of organic contaminants from sludge, though the effects of this process are to be yet investigated (ICON, 2001).

Some surfactants, e.g. fluorinated compounds are known as resistant to biodegradation, and also to heat, acids, bases and oxidizing/reducing agents and thus are of high environmental concern. Recent studies on biodegradability of non-ionic and anionic fluorinated surfactants during aerobic and anaerobic treatment in 80 WWTPs proved that fluorinated alkylethoxylates, perfluorinated alkylsulfates and carboxylates biodegraded with formation of metabolites, while methyl ethers of fluorinated alkylethoxylates appeared to be resistant either to anaerobic or aerobic biodegradation (Schröder and Meesters, 2003). Though perfluorinated alkyl acids (PFAs) in wastewater and sludge were found to be not the sole source of these compounds entering the environment (Tolls and Sinnige, 2003), their proven high potential for persistence, bioaccumulation and toxicity (accumulative risk for children and adults greater than 10) (Purdy, 2003; Windle et al., 2003) suggest the need of better insight into the potential hazard and control of PFAs from different sources, including sewage sludge.

A number of other compounds that have propensity to partition onto sludge particulates show different biodegradability during the wastewater/sewage treatment process; data regarding the fate, behavior, degradability and toxicity of some of them are sparse and yet need to be investigated. The activity of endogenous estrogens and synthetic steroids is reported to be reduced by 90% during wastewater treatment; only <3% has been transferred into sewage sludge (ICON, 2001). The data on removal rates of different estrogens (E3, E2, EE2 and E1) during treatment in different WWTPs show though a broader range of efficiency, from 61 to 99.9%, and seasonally even from 7 to >99%. The reason behind this large difference is unclear. There are suggestions that activated sludge treatment process can consistently remove over 85%

of E2, E3 and EE2, but the removal performance of estrone (E1) appears to be less and more variable (Ying et al., 2002a).

Pharmaceutical compounds are often lipophilic and potentially bioaccumulative. A wide range of removal rates (7–96%, mean > 60%) of these substances during wastewater treatment has been reported. Many commonly used pharmaceuticals are soluble and/or readily biodegradable, though for many of them predicting fate and partitioning during wastewater treatment is not possible due to lack of data. The information on the fate and behavior in the treatment process of the large number (>200) of commercial chlorinated paraffins and nitro musks is also sparse, similarly as for the brominated diphenyl ethers (PBDEs) and PCNs of high toxic activity. Polymethylsiloxanes (PDMSs) were found to exhibit high persistency, though no bioaccumulation or significant environmental toxic effect has been observed. Polyelectrolytes based on polyactylamide used extensively in sludge treatment to aid dewatering and thus showing high enrichment in treated sewage sludge are reported to be carcinogenic (ICON, 2001). Knowledge about TBTO organotins presence and fate in sewage sludge is not yet satisfying (Langenkamp et al., 2001a).

Extensive studies on the biodegradation and transformations of a large group of emerging compounds during wastewater/sludge treatment are required to evaluate the significance of their release to the environment from these processes.

III.4.3.3. Waste utilization and disposal

Three main options for bulk management of treated sludge are considered at present, with different preference (e.g. Figure III.4.2): use in agriculture, incineration and landfilling. There are also other minor sewage sludge recycling routes that are close either to

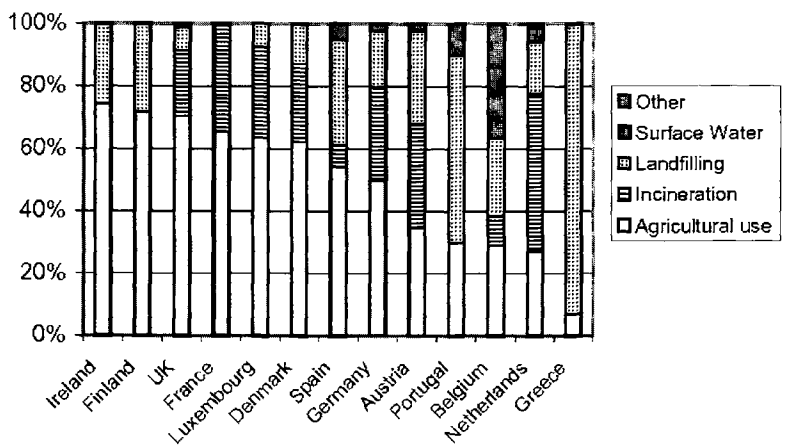


Figure III.4.2. Forecast of sludge utilization in the EU Member States by the year 2005 (after ANDERSEN-SEDE, 2001).

agricultural use (forestry and silviculture, land reclamation and revegetation) or presenting alternative solutions to combustion processes.

III.4.4. Use of sewage sludge in agriculture

III.4.4.1. General approach

The dramatic increase of sewage sludge generation in the EU that is estimated to reach nearly 9 Mt by the end of 2005 (Balze et al., 1999; ANDERSEN-SEDE, 2001; EC, 2002) brings about the increasingly difficult issue of its optimum disposal to all the acceptable outlets. The EU, through the existing Sewage Sludge Directive 86/278/EEC (EEC, 1986) being currently under revision that resulted in the development of Working documents on sludge (EC DG ENV, 2000) and biowaste (EC DG ENV, 2001) seeks ways to encourage the use of sewage sludge in agriculture and to regulate its use in such a way as to prevent harmful effects in soil, vegetation, animals and humans (EC, 2002). This is demonstrated in the increasing stringency of regulations concerning sewage sludge and soil quality, and in commissioning a number of feasibility studies on trace elements and organic matter contents in sewage sludge and European soils. Currently, at Community level the reuse of sludge in agriculture accounts for about 40% (EC, 2002). By 2005, forecasted agricultural use of sewage sludge in the EU should reach about 55% of the overall sludge generation. In Ireland, Finland, UK, France, Luxembourg, Denmark and Spain it will comprise over 60% of total. Predicted incineration rate will reach 23% and landfilling about 19% of total (Fig. III.4.2) (ANDERSEN-SEDE, 2001). Thus, agricultural use is going to be the dominant disposal outlet in the EU Member States.

In the USA, more than half of the 6.4 Mt of treated sewage sludges known also as biosolids are used as soil amendment (Harrison and McKone, 2002); agricultural use of biosolids shows increasing trend (Goldstein, 2000; Hanlon, 2002; NRC, 2002).

Another means of disposing sewage sludge in a way similar to agricultural use is its utilization in forestry, silviculture and green areas, and in degraded land reclamation.

III.4.4.2. Application of sewage sludge and soil protection

Soils are recognized as a finite, increasingly scarce and non-renewable resource. Their varying biological, chemical and physical properties should be protected and preserved in order to maintain ecological multifunctionality of soils. The protection of soils is and should be a principal objective of environmental policy that has been particularly stressed in the report by the European Soil Bureau to the EU-DG.ENV (Balze et al., 1999).

It is generally agreed that application of sewage sludge as a soil conditioner and fertilizer may supply plant needs for nutrients like nitrogen, phosphorus and organic matter, all necessary for plant growth and reproductive success. On the other hand, contamination of sewage sludge with pollutants often causes a low acceptance of this material. Among these pollutants, the presence of significant amounts of metals in sewage sludge is well established, which causes concern that long-term application of sewage

sludge (biosolids) may contaminate soil, edible crops and groundwater (Balze et al., 1999; Wang et al., 2001).

III.4.4.3. Heavy metals in soils

III.4.4.3.1. Background contents

Soil contamination with heavy metals is a result of several processes including atmospheric pollution, the use of contaminated water for irrigation, phosphate containing fertilizers, and other materials used in farming, such as sewage sludge and composts applied as fertilizer. Sludge exhibits larger heavy metal concentrations than soils. This is of particular interest when the sludge is applied to land as a soil amendment. The natural heavy metal content of soils depends on the parent material from which they were derived by alteration processes (soil formation). Highly variable proportions of heavy metals such as Zn, Cd, Cu, Cr, Pb, Ni, etc. occur naturally in most soils (Kabata-Pendias, 2001) that need to be considered when evaluating the potential impact of metals on soils. Table III.4.9 provides some data on the background concentrations of metals found in soils in different countries.

Detailed knowledge of the background concentrations of heavy metals in soil, resulting mainly from geogenic factors, is indispensable for a reliable evaluation of soils in relation to the environmentally safe waste disposal options. Trace elements in soils have been a subject of research for decades. Extensive studies on the background levels of trace elements have been carried out in the different parts of the world (e.g. Kabata-Pendias, 2001; Yamasaki et al., 2001). Nevertheless, knowledge on the background levels of metals in soils, also in most European countries, at the beginning of the new Millennium appeared to be inadequate or scarce, despite existence of the Soil Profile Analytical database within the European Soil Database. Besides, there were problems with linking available metal concentrations data to the geographical soil map and with compilation of data from different countries and sources, which resulted from different understanding of the term "background levels" and variations in sampling and analytical methods. Data were also scarce on the spatial deposition of metals through land application or management of sewage sludge.

This situation was the basis for commissioning by the EC DG.ENV to the European Soil Bureau (ESB) a study on trace element and organic matter content of European soils. Within this study, the available information was elicited, the needs for standardization ascertained, the major gaps in data being filled and a harmonized European Soil Monitoring System set up using as a basis existing soil monitoring systems in the European countries (Balze et al., 1999; Langenkamp et al., 2001b, 2003). The mapping of trace elements in soils and establishment of a Geochemical Baseline for Europe is in a final stage. At this stage, the establishment of a common framework through the harmonization, introduction of standard methods and integration of the concept of bioavailability into the regulatory system become crucial. A novel idea for soil protection in Europe is a development of the EU Soil Thematic Strategy linked with a possible systematic approach provided by the European Integrated Environment and Health Monitoring System (Bidoglio, 2003). The build up of a Global Integrated Environment and Health System would have been a target for the next decades of this Millennium.

Table III.4.9. Natural background concentrations of metals in agricultural soils (after Kabata-Pendias, 2001).

Countries	Soil	Cd		Cr		Cu		Hg		Ni		Pb		Zn		As		Mo		Se	
		From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean
Australia	Sand			1.4–3.5									57	39–86				2.6–3.7			
	Loess			13–30	16																
	Clay				24																
Canada	Sand	0.10–1.8	0.43	2.6–34.0				0.01–0.7	0.06			2.5–47.5	10			1.1–28.9	5.8	0.4–2.5	1.5	0.1–0.32	0.27
	Loess	0.12–1.6	0.64													1.3–16.7	4.8				
	Clay							0.02–0.78	0.13	3–98	23	1.5–50	16.5	15–20				0.93–4.7	1.7	0.13–1.67	0.43
	Different															< 1–30	5.8				
Japan	Sand															1.2–6.8	4.0				
	Different			3.5–810	50	5–176	34	0.08–0.49	0.28		28	5–189	35			0.4–70	11	0.2–11.3	2.6		
France	Different							0.03–0.5	0.4												
Germany	Sand													40–76							
	Loess					14–31								58–100							
	Clay					16–70								40–50						0.8–0.3	0.3
	Different			9–57	28			0.025–0.35	0.09		19	15–68								0.09–0.45	0.27
Greece	Different							0.033–0.1													
Italy	Different			20–307	95						14	4–81	26				16	0.4–2.2	0.9		
Netherlands	Sand								0.04												
	Clay							0.45–1.1													
Norway	Different							0.02–0.35	0.19							0.7–8.8	2.5			0.15–2.32	0.78
Poland	Sand	0.01–0.24	0.07	2–60	12	1–26	8.0			1–52	8	8.5–23.5	16	7–150	30	0.5–15	2	0.2–3.0	1.5	0.06–0.38	0.14
	Loess	0.24–0.36	0.30	21–35	29	8–54	19			7–70	19	14–32	26	20–130	50			0.6–3		0.17–0.34	0.23
	Clay	0.04–0.80	0.27	14–80	38					10–104	25	13–52	25			1.4–10	4.5	0.1–6.0	3	0.18–0.6	0.3
	Different			4–68	20			0.02–0.16	0.06	1.3–68	9					0.1–10.3	3.3				
Russia	Sand		0.32			1.5–29	11							4–57	30			0.3–2.9	1.5	0.05–0.32	0.18
	Loess					11–36[a]	25							40–55	50			1.8–3.3	2.2		
	Clay				51	4–21	12							9–77	35			0.6–4	2.0		
	Different							0.06–0.29	0.1									0.8–3.6	2.2		
Spain	Different							0.03–0.37	0.15								8.4				
Sweden	Different							0.004–0.99	0.06											0.17–0.98	0.39
UK	Sand			5–360	42					3.5–110	20					5.1–6.8				0.15–0.24	
	Loess											24–96[a]	63	67–180[a]	125						
	Clay	0.49–0.61					37											0.7–4.5	2.5		
	Different				69	11–323	23	0.01–0.09	0.03		23	15–41	29			4–95	16.3	1–5	1.2		0.21
USA	Sand	0.08–0.47	0.21	3–200	40	1–70	14	0.01–0.54	0.08	< 5–70	13	< 10–70	17	5–165	40	< 0.1–30	5.1				0.5
	Loess	0.13–0.55	0.27	10–1000	55	7–100	25	0.02–0.32	0.06	5–30	17	10–30	19	20–110	60	1.7–27	7.7	0.75–6.4	2.5	0.02–0.7	0.26
	Clay			20–150	65	7–70	29	0.0–0.90	0.13	5–50	21	10–70	22	20–220	70			1.2–7.2	4.1	0.1–1.9	0.5
	Different					3–300	26									< 1–93	7	0.8–3.3	2.0		

[a]Alluvial soils.

III.4.4.3.2. Regulatory limit values for heavy metals in sludge and soils

High concentrations of heavy metals in sewage sludge applied to land may pose a risk of accumulation through the food chain. However, not all metals in all soils, also the loads added to soil with sewage sludge pose the same hazard to the food chain. The differences between regulatory limit values for metal concentrations in biosolids and in soils within European countries, North America and New Zealand are remarkably high (Tables III.4.10 and III.4.11) and reflect the differences in approaches and protocols adopted to establish these values in view of soil protection.

These protocols for acceptable risk assessment can be summarized as below (after Amlinger, 1998):

- risk assessment based on no observable adverse effect levels (NOAELs);
- precautionary limitation or no net degradation (NND), adequate to a single safe threshold value – predicted no effect concentration (PNEC) or to a single predicted effect concentration (PEC);
- best available technique (BAT);
- hybrid systems utilizing toxicity assessments or embodying soil protection without quantifying risk.

Limit values of metals in biosolids and soils where biosolids are to be applied refer to a single total metal concentration. Among these regulations is *Directive 86/278/EEC (1986)*, currently under revision, which specifies the conditions under which sewage sludge can be used in agriculture within the European Union. On setting these limits, the maximum admissible concentrations in food and foodstuffs were determined after considering metal uptake by plants and crops, and metal phytotoxicity and zootoxicity data available at that time. In the EU, risk assessment for metals in the framework of the Existing Substances Regulation is based on a single PNEC or PEC value for soil organisms throughout Europe derived from total concentrations. The more stringent standards imposed by the national regulations by EC Member States are also allowed (Van den Berg, 1993).

In Canada, the responsibility of managing sewage sludge treatment and disposal lies within each province. In March 1996, the Ontario Ministry of Environment and Energy issued a set of *Guidelines for the Utilization of Biosolids and Other Wastes on Agricultural Land* (MOEE Ontario/MAFRA, 1996) that established limit values for 11 metals in sludge and soils, generally below the lower limit values for sludge and within the lower limit values for soils established by the EEC Sludge Directive (1986). Also in Québec standards have been set for acceptable levels of heavy metals in sludge and in fertilized soil. Only the total quantity of metals in the non-specified soils is considered in these standards, similarly to one given in the majority of other regulations (Tables III.4.11 and III.4.12).

In New Zealand, regulatory limit values of metals in biosolids are markedly below the lower values, while for biosolids-amended agricultural soils standards are mostly close to the highest values set by the EEC Sludge Directive (1986) and the European national regulations.

In 1993, the US Environmental Protection Agency published *Part 503 – Standards for the Use and Disposal of Sewage Sludge* (Goldstein, 1993; US EPA, 1993) and the US federal regulations governing sewage sludge (biosolids) land application were

Table III.4.10. Limit values for heavy metal concentrations in sewage sludge/compost in the EU, Canada, USA and New Zealand (mg/kg d.m.) (after Amlinger, 1998; Polish Directive of Minister of Environment on Sewage Sludge, 1999; EC DG ENV, 2000).

Country	Regulations	Cd	Cr_t	Cr(VI)	Cu	Hg	Ni	Pb	Zn	As	Co
EC/sewage sludge											
(86/278/EEC)	Lower limit	20	–	–	1000	16	300	750	2500	–	–
	Upper limit	40	–	–	1750	25	400	1200	4000	–	–
EC DG ENV.E3	Short term	10	1000		1000	10	300	750	2500	–	–
3rd Draft (2000)[a]	Medium term (~2015)	5	800		800	5	200	500	2000	–	–
	Long term (~2025)	2	600		600	2	100	200	1500	–	–
Austria	ON S 2200[b]										
	Class I[b]	0.7	70	–	70	0.7	42	70	210	–	–
	Class II[b]	1	70	–	100	1	60	150	400	–	–
	Class III[b]	4	150	–	400	4	100	500	1000	–	–
Belgium	Min. f. Agric.	1.5	70		90	1	20	120	300	–	–
Denmark	Sew. sludge	0.8	100	–	1000	0.8	30	120	4000	–	–
Finland	Trigger values[c,d]	3	300	–	600	3	100	150	1500	50	–
	Target values 1998[c,d]					1		100			
	Fertiliz. growing media				100	0.2	60	60	150	10	
France	Sew. sludge/ind. waste[e]	20	1000	–	1000	10	200	800	3000	–	–
	From 2001	15									
	From 2004	10									
Germany	M to Kl. I[b]	1.5	100	–	100	1	50	150	400	–	–
	M to Kl. II[b]	2.5	200	–	200	2	100	250	750	–	–
	RAL GZ 251[b]	1.5	100	–	100	1	50	150	400	–	–
	Blauer Engel[b]	1	100	–	75	1	50	100	300	–	–
	Biowaste ordinance I[f]	1	70	–	70	0.7	35	100	300	–	–
	Biowaste ordinance II[f]	1.5	100	–	100	1	50	150	400	–	–
Greece[d]		–	–	–	–	–	–	–	–	–	–
Ireland	Sew. sludge, agric. use	20	–	–	1000	16	300	750	2500	–	–
Italy	DPR 915/82	10	500	10	600	10	200	500	2500	10	–
	Ann. 748/84 green comp.	1.5	–	0.5	150	1.5	50	140	500		
Italy[d]		1.5	–	100	1.0	75	100	300	–	–	–

Luxembourg[d,g]	Recommended	20	1000	–	1000	16	300	450	2500	–	–
	Limit values	40	1750	–	1750	25	400	1200	4000	–	–
The Netherlands[h]	Compost	1	50	–	60	0.3	20	100	200	15	–
	Compost (very dean)	0.7	50	–	25	0.2	10	65	75	5	
Portugal[d]		–	–	–	–	–	–	–	–	–	–
Sweden[d]		2	100	–	600	2.5	100	100	800	–	–
	Guideline of QAS	1	100	–	100	1	50	100	300		
Spain	Decr. 1310/1990 pH > 7[d]										
	pH > 7[d]	40	1500	–	1750	25	400	1200	4000	–	–
		20	1000	–	1000	16	300	750	2500		
	B.O.E. n'm. 131, 06.1998	10	400	–	450	7	120	300	1100	–	–
United Kingdom	Sew. sludge/pasture land	–	–	–	–	–	–	1000	–	–	–
	UKROFS fertil. org. farm.	10	1000	–	400	2	100	250	1000	–	–
Poland[d]	Direct. Min. Envir. 2002:										
	Agricultural use	10	500	–	800	5	100	500	2500	–	–
	Non-agric. land reclam.	25	1000	–	1200	10	200	1000	3500	–	–
	Plants f. comp., land stab.	50	2500	–	2000	25	500	1500	5000	–	–
Canada[d]		20	–	–	–	5	180	500	1850	75	150
USA[d,i]	EPA/high quality	39	(1200)	–	1500	17	420	300	2800	41	
	EPA/others	85	3000	–	4300	57	420	840	7500	75	
	Composting Counc. 1996	39	–	–	1500	17	420	300	2800	41	
	Rec. USDA-Min. f. Agric.	21	–	–	–	–	–	–	–	54	
New Zealand		15	1000	–	1000	10	200	600	2000	–	–

[a]In parallel, limit values for amounts of heavy metals, which may be added annually to soil are given, based on a 10-year average (g/ha/yr) – numerically a triplicate of adequate limit values.
[b]Referring to 30% o.s.
[c]Soil improver and compost products.
[d]Limit values for application of sewage sludge.
[e]Cr + Cu + Zn max 4000 mg/kg d.m.o.
[f]Related to maximum application rate of 20 and 30 t d.m./ha.
[g]In preparation: values referring to RAL GZ 251.
[h] > 20% o.s. in d.m.
[i]For all organic waste.

Table III.4.11. Limit values for heavy metal concentrations in the soil comparing the EU, Canada, USA and New Zealand (mg/kg d.m.) (after Smith, 1994; Amlinger, 1998; Polish Directive on Sludge, 1999; EC DG ENV, 2000).

Country	Regulations	Cd	Cr	Cu	Hg	Ni	Pb	Zn	As	Mo	Se
EC/soil amended with sludge											
(86/278/EEC)	Lower limit	1.0	100[a]	50	1.0	30	50	150	–	–	–
	Upper limit	3.0	150	140	1.5	75	300	300	–	–	–
EC DG ENV.E3	$5 \leq pH < 6$	0.5	30	20	0.1	15	70	60	–	–	–
3rd Draft (2000)	$6 \leq pH < 7$	1.0	60	50	0.5	50	70	150	–	–	–
	$pH \geq 7$	1.5	100	100	1.0	70	100	200	–	–	–
Austria	ON L 1075	1.0	100	100	0.7	60	100	300	–	–	–
Belgium	Flanders[b,c]	1.2	78	109	1.3	55	120	330	–	–	–
	Wallonia[b]	1.0	100	50	1.0	50	100	200	–	–	–
Denmark		0.5	30	40	0.5	15	40	100	–	–	–
Finland[b]		0.5	200	100	0.2	60	60	150	–	–	–
France[b]		2	150	100	1.0	50	100	300	–	–	–
Germany[d]	Clay	1.5	100	60	1	70	100	200	–	–	–
	Loam	1	60	40	0.5	50	70	150			
	Sand	0.4	30	20	0.1	15	40	60			
Greece		–	–	–	–	–	–	–	–	–	–
Ireland		1.0	–	50	1.0	30	50	150	–	–	–
Italy		3.0	[e]	100	2.0	50	100	300	–	–	–
Italy[b]		1.5	–	100	1.0	75	100	300	–	–	–
Luxembourg[b]	Recommended	1.0	100	50	1.0	30	50	150	–	–	–
	Upper values	3.0	200	140	1.5	75	300	300	–	–	–
The Netherlands[b]		0.8	100	36	0.3	35	85	140	29		
Portugal		–	–	–	–	–	–	–	–	–	–
Sweden[b]		0.4	30	40	0.3	30	40	75	–	–	–
Spain	1310/1990 $pH > 7$[b]	3.0	150	210	1.5	112	300	450	–	–	–
	$pH > 7$[b]	1.0	100	50	1.0	30	50	150	–	–	–
United Kingdom[b,e]		3.0	400[f]	135[g]	1.0	75[g]	300	300[g]	50	4	3
	UKROFS	2.0	150	50	1.0	50	100	150	–	–	–

Poland	Agricultural use soils										
	Heavy	3	100	75	1.5	50	80	180	–	–	–
	Mean	2	75	50	1.2	35	60	120	–	–	–
	Light	1	50	25	0.8	20	40	80	–	–	–
	Non-agricult. use soils										
	Heavy	5	200	100	2	60	100	300	–	–	–
	Mean	4	150	75	1.5	45	75	220	–	–	–
	Light	3	100	50	1	30	50	150	–	–	–
Canada		2.0	–	–	0.5	18	50	185	7.5	2.0	1.4
USA[h]											
EPA Part 503 Rule	Soils – upper limit	19.5	1500	750	8.5	210	150	1400	20.5	9	50
EPA: risk-based concentrations (RBC)	Soils – residential area	39 n	Cr(III) 78,000 n, Cr(VI) 390 n	2900 n	23 n	1600 n		23,000 n	23 n	390 n	390 n
	Soils – industrial area	510 n	Cr(III) 100,000 n, Cr(VI) 5100 n	38,000 n	310 n	20,000 n		310,000 n	310 n	5100 n	5100 n
New Zealand		3.0	600	140	1.0	35	300	300	–	–	–

[a]Planned.
[b]Limit values for application of sewage sludge.
[c]Soil with 10% clay and 2% OM.
[d]Compost ordinance.
[e]Cr(VI) 3 mg/kg and Cr(III) 50 mg/kg.
[f]Preliminary.
[g]Soil pH 6.0–7.0.
[h]EPA Part 503 Rule and EPA Region III risk-based concentrations (n – non-carcinogenic).

Table III.4.12. Classification of organic substances with respect to their behavior in soils (source: Langenkamp et al., 2001a, cit. after UMK-AG, 2000).

Substance	Mammalian/human toxicity (acute)	Ecotoxicity	Water solubility	Persistence	Concentration levels[a]
AOX (summative parameters)					High, indicator
LAS	Medium	Aquatic high, terrestrial medium, bioaccumulation high	High, enhances mobility of other pollutants	Medium	High
DEHP	Low, suspected estrogenic effect	Aquatic medium/high, terrestrial low, bioaccumulation high	Low	Medium	High
Nonylphenol	Medium, suspected estrogenic effect	Aquatic high, terrestrial medium, bio accumulation high	Low	Medium	High
B(a)P single substance, PAH	Carcinogenic, mutagenic, teratogenic	High, bioaccumulation high	Low	High	High
PCBs, single substance/summative parameters	Medium, tumor promoting, immunotoxic	Aquatic high, terrestrial high, bioaccumulation high	Low	High	Low and declining
PCDD/Fs, single substance/ summative parameters	High, carcinogenic	Aquatic high, terrestrial high, bioaccumulation high	Low	High	Low
TBT, tributylin oxide	High	Aquatic high, bioaccumulation high, endocrine effect	Medium	High	High

[a]In the EU Member States. In other countries may be different, depending on generation and source control.

promulgated. The rules provide minimum risk-based standards for chemicals, among them for nine inorganic elements. To develop the standards, a risk assessment that examined 14 pathways of exposure to people, agricultural crops, livestock and selected environmental receptors was performed. These standards may be supplemented by stricter state and local rules (Goldstein, 1993, 2000; Harrison and McKone, 2002). Compared to limit values in force in the EU and other countries, general similarity of the US standards for high quality biosolids (Table III.4.11) and strikingly higher values for amended soils (except Pb), up to an order of magnitude (Table III.4.12) illustrate the difference of the US EPA approach to the target risk receptor, which is human, while ecological multifunctionality of soils is not adequately addressed in these rules.

On setting almost all these standards, little account was made for the possible effects of metals on the soil microbial population (McGrath et al., 1995; Weissenhorn et al., 1995). Alarmingly, studies initiated since the beginning of the last decade of 20th century have revealed adverse effects due to metals on soil microbial populations and their activities at concentrations close to EC limits for sludge application (Wild et al., 1990; Wang and Jones, 1994; Witter et al., 1994; Weissenhorn et al., 1995). A lack of long-term data and experiments aimed at assessing the effects of metals added to soils in sewage sludge over extended periods of time were also noted (McGrath et al., 1995), though since then a considerable progress in this area has been achieved (McGrath et al., 1999, 2000, 2003; McGrath, 2002). In some cases, environmental damage has been noticed years after a previously thought safe material had been used on the soil.

In the last decade, it has became obvious that criteria and standards regarding the maximum permitted concentrations of metals in soils virtually in all regulations (Table III.4.11), which are based on measurements of total concentration as determined by acid digestion, may not provide the best indication of its bioavailability. Numerous investigations have revealed that the total metal content neither correlates with its availability to crop plants and soil organisms, nor does it show how the metal is bound in the soil (e.g. Hooda and Alloway, 1994; Badilla-Ohlbaum et al., 2001; Ginoccio et al., 2001; Allen, 2002a,b).

It has also become evident that the reliance of the current standards on risk assessment methods consistent with the guidelines developed in late 1980s (Directive 86/278/EEC) and early 1990s (U.S. EPA, Part 503), and relying on a sewage sludge/soil survey dating from these periods are now outdated. Controversies surrounding both the practice of land application and the science behind the regulations, as well as evidences of adverse health effects of sewage sludge use (NRC, 2002), along with the prospects of a significant increase of sewage sludge generation and use in the nearest future, moved both the European Commission and US EPA to commissioning broad expert studies in 1999–2002 in order to update an information on current status of pollutants in sewage sludge and soils and to review current scientific knowledge concerning pollutant transfer mechanisms in the different environmental compartments and in the food chain, aiming to assess the possible risk to the environment and human health in accordance with this knowledge. Most of the studies commissioned by the European Commission have been discussed in this chapter. The comprehensive analysis of advances in risk assessment since the establishment of the Part 503 Rule, evaluation of EPA's approach to setting chemical and pathogen standards and conclusions suggesting integration of chemical and pathogen risk assessment have been presented in the study performed for US EPA by the Committee on

Toxicants and Pathogens in Biosolids Applied to Land of the National Research Council of the National Academy of Sciences. In particular, aggregate exposure assessments with special consideration to risks from long-term low-level exposures, as well as short-term episodic extremes have been recommended (NRC, 2002).

Reviews of reference sources on mechanisms affecting metal transfer in soils, also amended with sewage sludge, have brought to the conclusion that among the factors influencing metal mobility and bioavailability to plants, soil microorganisms and other soil biota, pH level of the soil is the most important; the role of binding to organic matter and mineral fraction in metal accumulation in the upper layer of the soil is also of crucial importance. Soil organic matter together with clay minerals makes up the most of cation exchange capacity (CEC) that has been considered to be a key parameter determining the metal sorption by soil (Balze et al., 1999; ANDERSEN-SEDE, 2001).

The common awareness of inadequacy of existing soil quality standards based on total metal concentration values leads to the revision of old standards in order to development of new ones that intend to adopt recent sound scientific information to derivation of relevant Environmental Quality Criteria (EQC), which define safe concentrations of chemicals in soils that would not affect the structure and function of terrestrial and boundary ecosystems both in short- and long-term span. In more recent regulations including Working document on sludge (EC DG ENV, 2000), limit values are related to the parameters considered critical for metal mobility and bioavailability in soil: pH (EC Working document on sludge) or soil type reflecting organic matter (OM) and clay mineral enrichment, e.g. German Compost Ordinance and Polish regulations (Table III.4.12).

III.4.4.3.3. Novel concepts of risk assessment for metals in soils

It, though, becomes evident that incorporating into regulatory values the parameters influencing metals mobility is not enough for prevention of heavy metal risk for soil and for boundary ecosystems and that the science-based EQC, besides chemical processes, should consider also physiological aspects for reliable predicting metal bioavailability and toxicity (Janssen et al., 2003). A generic definition of "bioavailability" of chemicals of concern *refers to a fraction of the total contaminant mass in soil/sediment available to receptor organisms, including human and ecological organisms* (Adriano, 2003; NRC, 2003). Metals and metalloids bioavailability approach deals with kinetic processes of *lability* transformation while their total mass remains unchanged. Metal lability, partitioning and its relation to bioavailability in terrestrial ecosystems, risk assessment and risk management have been widely discussed in relevant comprehensive publications (Gupta et al., 1996; Adriano, 2001, 2003; Allen, 2002a,b; NRC, 2003); some basic terms and processes are summarized here briefly.

The bioavailability of metals depends on chemical form of their occurrence in soils or *speciation*. Soils are dynamic systems, in which a very unstable equilibrium exists between the labile bioavailable fraction, the mobilizable fraction (potentially bioavailable, moderately leachable and partly active) and immobile, strongly bound inactive fraction. Ecological risk assessment is a fundamental consideration to evaluate the effects of metals in soil specific to risk receptors dependent upon the magnitude, frequency and duration of exposure. Exposure assessment is based on the direct interactions of soil organisms and plant roots with bioavailable heavy metal fractions. The human health risk assessment

should thus take into account several pathways, of which the food chain via plants plays the major role, either directly through food crops or indirectly via farm animals. Additionally, the direct ingestion of soil particles by small children and grazing animals (when dissolution of metals in strongly acidic intestinal fluids takes place) should be considered. The risk of metals in soil to hydrosphere, mainly to groundwaters, depends predominantly on the leaching process, where the vertical metal transport through the vadose zone and its further migration in saturated zone result both in the mobilization of the labile metal fraction and its immobilization due to pore solution–soil interaction during transport. It can be thus concluded that the key role in protection of ecological soil function and attenuation of metal uptake through food chain plays science-based predicting metal bioavailability and toxicity to sensitive soil organisms (microbes, invertebrates) and plants.

The most labile and readily bioavailable fractions are represented by the soluble metal components occurring in soil pore solution as free ions or soluble complexed ions (ion pairs or complexed with humic ligands), ions that are weakly adsorbed on exchange surfaces in soils or bound by carbonates. Biogeochemical mobilization/immobilization processes of different kinetics that determine metal *partitioning* between aqueous and solid phases of different binding strength comprise desorption/adsorption, dissolution/precipitation, complexation, redox reactions and complex processes termed as weathering and fixation in immobile phases (e.g. in humins, crystal lattice). These processes are influenced by a variety of chemical, physical and biological factors, such as pH, dissolved and solid-phase organic matter and its chemical speciation, carbonate and metal oxide (Fe, Al, Mn) content, sulfides, clay minerals, secondary phases, redox potential, time-related weathering transformations, microbial sequestration/oxidation, etc. The variability of factors controlling the binding strength of soils for metals and partitioning process are largely a consequence of difference in soil properties (Adriano, 2001, 2003; Allen, 2002a,b; Impellitteri et al., 2002; Yin et al., 2002; NRC, 2003).

The partitioning may be modified in the rhizosphere and within the digestive tract of soil-dwelling organisms. It may change over time because of natural or anthropogenic processes, e.g. as a consequence of the application of sewage sludges to soil (Allen, 2002a). The modifications in metal partitioning in sewage sludge-amended soil may occur partly due to probable presence in sewage sludge of non-humic ligands that come from proteins and other biological macromolecules, which were considered to be a possible explanation of observed much higher concentrations of strong ligands in wastewater effluent compared to those in natural organic matter in river water (Sarathy and Allen, 2003). Similar relation may occur also between ligands in sewage sludge and soil.

Schematics of bioavailability processes in soils exemplified in metal uptake by plants are depicted in Figure III.4.3.

Phase (A) comprises metal partitioning and its release to soil solution: Phase (B, B′) involves transport of metal to the target organism in soluble, colloidal and particulate form. Phases (C) and (D) delineate bioavailability processes. Phase (C) involves metal passing through organism–soil/pore solution interface that constitutes a biological membrane, which serves also as a bio-filter for contaminants (Adriano, 2003; NRC, 2003). In plants, metals pass through the roots membrane (McLaughlin, 2002). Intestinal metal uptake and internal metal partitioning that involve digestive fluids have been considered to be a dominating metal exposure route for invertebrates, in particular for hard-bodied ones, though dermal uptake has been found in some cases to correlate better (Allen, 2002a,b,

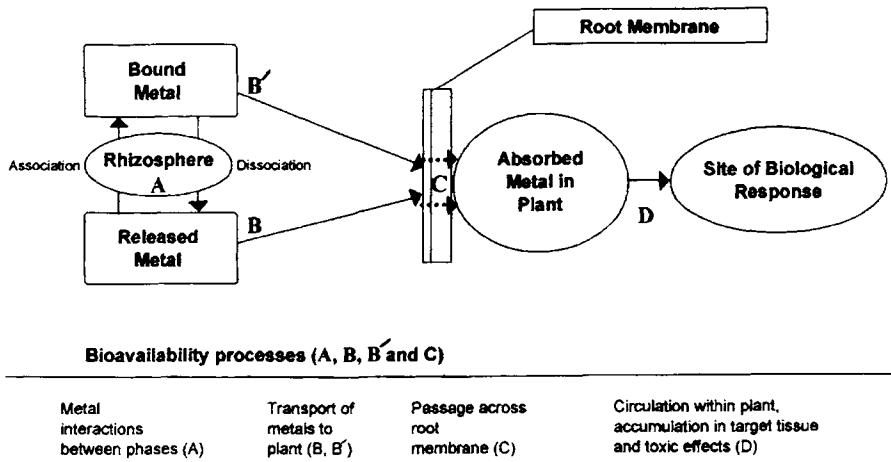


Figure III.4.3. Bioavailability of heavy metals in soil exemplified in plants (after Adriano, 2003; modified from the NRC, 2003).

Peijnenburg, 2002). Also some recent reports (Vijver et al., 2003a,b) support a conclusion about predominance of a dermal uptake by soft-bodied species. Phase (D) delineates assimilation of a metal in the organism and its biological response at the site of toxic action (Peijnenburg, 2002; Adriano, 2003).

It is clear that while metal mobility and bioavailability to plants and organisms in soils are determined by the kinetic processes and depend on the variable physical and chemical soil properties and different uptake mechanisms, risk assessment based on a single value and total metal concentration alone leads to false-positive or false-negative estimation of risk to site-specific terrestrial ecosystems. There is thus a must to develop regulatory programs and predictive models that consider metal bioavailability. Such programs are of particular importance in view of inevitable world's increase of anthropogenic impact on the terrestrial ecosystems in the 21st century due to growth of sewage sludge generation in parallel with increase of its use as soil amendment, as it has been already observed in the EU and in the USA.

As more definite evaluation of bioavailability becomes available, it should be incorporated into soil screening levels, criteria and soil quality standards, with a general aim to protect specific sites, specific processes, or life support functions within the terrestrial ecosystems based on prediction of actual effects. Although to date bioavailability-based approach is gaining wide acceptance, at present the understanding of factors that control bioavailability of metals in soils in the short and long term is still incomplete. The consideration of both chemistry and biology is the major requirement to advance developing sufficiently robust predictions of metal bioavailability in soils that can be incorporated into the regulatory programs (Allen et al., 2002; Schoesters et al., 2003).

Recently developed models for predicting metal concentrations in plants and soil organisms using soil property measurements seem to be promising, also for biowaste-amended soils, in particular the development and adaptation to the terrestrial systems of the aquatic biotic ligand model (BLM), which combines chemical speciation models with

more biologically oriented models. BLM has given rise to mechanistic understanding of the partitioning and uptake kinetics for metals from soils and enabled to evolve information on the relationship of appropriate soil parameters and organisms' responses (Cheng and Allen, 2001; Di Toro et al., 2001; Allen, 2002a,b). BLM development, principles and the potential of BLM approach are discussed in detail by Janssen et al. (2003). Novel models describing trace metal concentrations in the earthworm, *Eisenia andrei*, and in selected cultivated plants have been proved to have a considerable potential to be used in predicting metal bioavailability to soil organisms in polluted and sewage sludge amended soil. Model parameters quantify biological phenomena important for metal bioavailability, while soil variables quantify relevant soil chemistry characteristics. Of four metals studied (Cd, Cu, Pb and Zn), the model appeared the most accurate in describing Zn behavior (Saxe et al., 2001).

Through the application of the BLM principles, it becomes possible to facilitate the collection of the necessary data to evaluate the relationship between soil parameters and organisms responses and to predict the bioavailability of metals in different soils (terrestrial BLMs or t-BLMs) that would meet the needs of industry and regulators (Allen and Santore, 2003; Schoesters et al., 2003).

In parallel to development of soil BLMs (e.g. Allen and Santore, 2003; Peijnenburg et al., 2003; Van Gestel and Koolhaas, 2003), the current extensive research activities are focused on evaluation of mechanisms of time-dependent changes in metal speciation, and on the dynamic nature of bioavailability resulting from changes in input to the environment or in modifying factors (e.g. Hiemstra et al., 1996; Yin et al., 1997; Kinniburgh et al., 1999; Allen and Ponizovsky, 2003; Gustaffson et al., 2003; Ponizowsky et al., 2003; Ponthieu et al., 2003; Shi et al., 2003). Process kinetics and underlying mechanisms are of particular importance for long-term prediction of metal uptake in anthropogenically affected (e.g. sludge amended) soils.

The chemical methods of metal speciation by sequential fractionation developed in the last two decades to estimate chemical forms of binding, and particularly single extractant procedures (with use DTPA, EDTA, acetic acid, and the mineral acids HNO_3 or HCl) to assess metal bioavailability, appear to fail to precisely identify chemically specific soil fractions and to correlate them with bioavailability, thus their usefulness for these purposes is limited (Sauvé, 2002, 2003). Sequential chemical extraction is a useful tool for identification of operationally defined soil pools of different binding strength and metal mobility. For defining bioavailability (phases C and D – Figure III.4.3), i.e. the rates of metal supply from soil/pore solution through biological membrane (phase C) to the chosen biological endpoint (phase D), other approaches are needed. Soil-solution free metal ion activity as a parameter to estimate bioavailability and the free ion activity model (FIAM) based on this parameter offer a promising alternative approach, though further integrated chemical and biological research are required to explain biological responses and to combine them with chemical determination of free metal ion activities (Allen, 2002a,b; Sauvé, 2002).

In this case, a novel method of diffusive gradients in thin films (DGT) simulating metal passage through organism–soil/pore solution interface offers an excellent tool to quantify metal bioavailability (Zhang et al., 2001; Fitz et al., 2003; McGrath et al., 2003). Besides, it was found of importance also to segregate and consider separately metal uptake (phase C) and metal toxicity, i.e. toxicological bioavailability based on internal recirculation and

storage processes of the metals assimilated, resulting in transport to the target sites of toxicity (phase D) (Adriano, 2003; Peijnenburg et al., 2003).

At present, extensive studies on the determination of toxicity thresholds of metals for plants, microbes and invertebrates have been carried out, both in view of practical application of equilibrium partitioning and bioavailability concepts (e.g. Zhang et al., 2001; Criel et al., 2003; Fitz et al., 2003; Peijnenburg et al., 2003) or using more conservative PNEC (Smolders et al., 2003) or ecological soil screening levels (ECO-SSLS) approach (Checkai et al., 2003).

III.4.4.3.4. Effect of sewage sludge on metal bioavailability in amended soils

Metal enrichment in sewage sludge, high organic matter content of possibly partly different nature than that of natural origin (Sarathy and Allen, 2003), and instability of sewage sludge that undergoes "aging" transformations over time, influence the properties of amended soils, which results in alteration of the fractionation with respect to binding strength for metals, partitioning of metals to the soil, their bioavailability to microbes, soil animals and plants and further transfer through the food chain.

Even when the soils are greatly enriched, some metals (e.g. As, Cr(III), Hg and Pb) have been shown to sorb to and bind to solid phases in soil and soil colloids, removing the metals from pore solution and rendering them unavailable to higher trophic levels. They may also be retained in plant roots. Although plants are able to uptake certain metals, phytotoxicity may maintain plant concentrations of these elements (B, Cu, Mn, Ni and Zn) below safe levels for animals. When heavy metal concentrations in plant tissue are maintained at levels deemed safe for animals by one or more of these processes, the food chain is said to be protected by a "soil–plant barrier". This soil–plant barrier has been found to be effective for the heavy metals of concern in sewage sludge, with the exception of Cd, Mo, Se, and possibly Co, which are readily adsorbed and translocated to food-chain plant tissue (Chaney, 1980). Evidence indicates that Mo, Se and Co seldom occur in large enough concentrations to cause problems.

It would seem that Cd is the heavy metal of most critical concern, and that its content in sewage sludge is one of the key elements in determining whether or not the sludge is useable in agriculture (EC DG ENV, 2000). The uptake of cadmium by plants varies greatly from crop to crop and this should be reflected in agricultural management practices. In addition, plants are capable of taking up and concentrating relatively large amounts of Cd without, or practically without, harm to themselves. However, these high concentrations may render the plants unsuitable for human consumption.

Despite extensive experimental efforts, there is still a controversy over the possible long-term effects of sludge applications and leaching, in particular over the antithetic "sludge protection" thesis that launches the sludge adsorption properties in controlling metal lability and bioavailability and "time bomb" thesis stressing the hazard of metal release due to organic matter decomposition after terminating sewage sludge application (Chang et al., 1997). The recent studies rather do not support the "time bomb" concept based on the assumption that the major binding phase in sewage sludge is organic matter. There is an evidence that the substantially increased Cd binding associated with biosolids application is not limited to the organic matter but to the great extent results from the sorptive properties of Fe and Mn inorganic phase in sludge, thus the alteration in soil metal

chemistry and phytoavailability is of a more persistent nature (Ryan et al., 2002). On this basis the authors concluded that reduction in phytoavailability justifies comparatively high limit values for Cd in sludge-amended soils established by the US EPA as adequately protective for human health and the environment (see Table III.4.12).

Research focused on competitive role of Zn in sewage sludge at normally low Cd:Zn ratio and the effect of Zn–Fe–Ca malnutrition in the consumers' diet showed that low Cd and low Cd:Zn ratio in biosolids reduce phytoavailability in aerobic soils and inhibit food-chain transfer and bioavailability of Cd, preventing Cd risk to consumers, regardless of the fraction of diet grown on biosolids-amended soils. It was found though that risk to humans from Cd uptake by crops should be considered at high Cd:Zn ratios, as well as for rice or tobacco grown on paddy soils, also when normal geochemical low Cd:Zn ratio occurs, in particular at low Zn–Fe–Ca diet (Chaney et al., 2002).

Long-term studies by McGrath et al. (2000) indicated that sludge application in the UK arable soils resulted in an increased bioavailability and crop uptake of Cd. Data reported by other authors confirmed Cd enrichment in soils amended with sludge, in particular labile ($>10\%$ Cd_t) and bioavailable forms (up to $>5\%$) (Afyun et al., 2003), sharply increased Cd content in maize and wheat shoots grown in such soils (Hylander and Souta, 2003; Green and Tibbett, 2003), and Cd bioaccumulation in herbivorous invertebrates, though considerably lesser mobility of Cd than of Zn in the food chain soil–plant (wheat)–aphid was observed (Merrington et al., 1997; Green and Tibbett, 2003).

The long-term field trial of clay loam soil in Sweden, which received sewage sludge biennially for 41 years, appeared to accumulate 92% of input load of Cd in topsoil 17 cm thick. Compared to unamended soil, soluble Cd was 20 times higher, and its concentration in straw about 2 times higher, with no significant trends over time. Direct measurements and scenario simulations with use of a model called SLAM to illustrate trends in Cd availability during sludge application and its following cessation demonstrated that the environmental behavior of this system according to "sludge protection" or "time bomb" concept depends on Cd input rate, sludge/soil sorption capacity and the proportion of inorganic binding phase in the total sorption capacity of sludge, with pH as a major controlling factor (Bergkvist and Jarvis, 2003; Berkvist et al., 2003). In the light of the presented data, the "time bomb" concept seems to be unrealistic unless a drastic pH change occurs, while the extent of "sludge protection" function is determined by Cd partitioning.

These results that give an evidence of possible reduction of safety level mostly due to overloading a specific system with Cd, suggest higher precaution and lesser generalization with respect to risk from Cd in different sludge-amended soils. Recently developed simple model for predicting Cd concentrations in wheat grain using regulatory total limit concentrations of Cd in sludge-amended soils modified by the factors affecting bioavailability in different soils (soil pH) and incorporating a cultivar term into the model seems to be promising (McGrath et al., 2002).

Zn is another metal that should be strongly considered due to abundance in sewage sludge, higher bioavailability and transfer in food chain, despite of far lesser toxicity than Cd (McGrath et al., 2000). On the other hand, Zn presents the principal potential risk from phytotoxicity and adverse impact on soil microbes (McGrath, 2002; McLaughlin, 2002). Investigations of temporal and management-induced changes in the sewage sludge-derived Zn in a sandy pasture soil showed 5–7-fold increase of mean Zn concentrations in

pasture roots and 6–8 higher Zn content in the herbage, at scarcely 12–42% higher total Zn concentrations in sludge-amended soil than in unamended one. A substantial proportion (19–17%) of Zn load reached the shallow groundwater over the 4 years' application of sludge. Very high Zn mobility was found to be compatible with high soil solution concentrations in the amended low-pH soil (Speir et al., 2003). Long-term (6 years) experiments on acidic soil amended with metal-spiked sewage sludge confirmed similar much higher proportion of Zn enrichment in the mobile and mobilizable fractions, and in pasture herbage than in control soil, and strong effect of pH on Zn bioavailability (McLaren and Clucas, 2001, 2003). Sewage sludge derived Zn was found to readily biomagnify in the food chain exemplified in the soil–wheat–aphid system: concentrations in sap feeding herbivore appeared to be 1.4–2.4 times higher than in the shoots (Merrington et al., 1997; Green and Tibbett, 2003).

Other potentially dangerous elements (PDEs) in sewage sludge-amended soils also received attention of researchers. In general, Ni seems to behave similarly to Zn. Long-term (6 years) experiments with use of acidic soil treated with unspiked and spiked by Cu, Ni and Zn sewage sludge, were reported to show stable (at least 3 years long) higher proportion of all three metals enrichment in mobile and mobilizable phases and substantial increase of Ni and Zn concentrations also in herbage cover in spiked sewage sludge. This observation suggests insufficiency of "aging" for simulating actual kinetics of equilibration processes and thus possible erroneous predictions based on parameters measured on "aged" material. The pH control by liming resulted in declining Ni and Zn concentrations in herbage that confirm pH to be a major factor controlling Ni availability to plants (similarly to Zn), while Cu concentrations in herbage cover appeared neither to be significantly affected by sludge applications, nor by pH control measures (McLaren and Clucas, 2001, 2003).

The change of Pb content in maize (grain and shoots) was found insignificant as a consequence of the application of biosolids to clay and sandy soils of pH 5.7 up to total rate 50 t/ha over a period of 5 years (10 t/ha year) that confirms strong sorption of Pb by soil colloids and weak translocation to aboveground tissues. Though, even this low rate of biosolids caused an increase of total Pb concentration in both soils and downward movement in sandy soil. This leads to the conclusion that biosolid application may lead to elevated Pb accumulation in soils, up to maximum regulatory levels (Oliviera et al., 2003).

There is considerable variance in the metal content of different plants and different plant parts. For example, most vegetative parts, particularly leaves, are moderately high in metals, while seeds, nuts and fruits are normally low. It has been found that both crop yields and metal concentrations in soil become greater with increasing sludge loadings. The latter correlation suggests a complex system of microbial action, solubility and diffusion.

Observations of effects of a high dose (388 t/ha) sewage sludge application in clay and sandy tropical soils within 1 year before the first plantation of grass (*Bracharia brizantha*) on Cr, Cu, Ni and Zn concentrations in soil, grass biomass and metal uptake seem to be of interest, and can be summarized as follows: (i) the addition of sewage sludge resulted in over 10 times higher Cr, Cu, Ni and Zn content in the clay soil and 3–10 times higher metal concentrations in sandy soil; (ii) in two consecutive years grass biomass was 40% and 3.3 times higher in clay soils and 80% and 2.7 times higher in sandy soil, respectively, than in unamended soils, but in the following years turned to be lower due to depletion of

nitrogen, and required fertilization; (iii) Despite several times higher concentration of metals introduced to the soils by application of sewage sludge, the total difference in plant uptake was less than 1% for Cu and Zn for all the following trials (Matiazzo et al., 2003).

These purposely presented in detail results of a trial lead to the not very optimistic conclusion about (i) persistence and possible high level of metal contamination of soil from sewage sludge application; (ii) temporary fertilization effect; (iii) immensely long time needed to get visible effects of phytoremediation, even if more efficient specially selected plants are used. Besides, there is always a problem with a safe utilization of such metal harvesters.

As time passes following sewage sludge application, it is typical to observe a decrease of metal concentration in the plants grown on these soils that in turn indicates decrease of phytoavailability. It may not protect, though, soil microflora and organisms ingesting soil. Only singular 1-year application of the relatively uncontaminated sewage sludge in low doses (2.5–10% by weight) was reported to have no significant effect on metal concentrations in amended soils and their uptake by plants (Uri et al., 2003).

Metal transfer predictions estimated on a 1-year basis presented in the EU studies (ANDERSEN-SEDE, 2001) state that "metals brought to soil by sludge application represent a very low proportion of the amount of metals present in soil before sludge application" that differs from the data obtained from the long-term studies reported above. The same predictions vary greatly with respect to the number of years required before a limit value is reached for metal accumulation in sludge-amended soil, from 4500–34,000 years range in low accumulation scenario to 20–140 years range in the high accumulation scenario.

III.4.4.4. Organic contaminants transfer in sewage sludge-amended soils

The recent studies commissioned by EC show that limited data are available on the relative importance of contamination sources. Organic compounds applied to soil with sludge undergo various physical, chemical and biological transformation and translocation processes. Sparse data are at present available on the formation of intermediate compounds, as well as on the degradation kinetics and pathways of organic contaminants in soil (ANDERSEN-SEDE, 2001; ICON, 2001; Langenkamp et al., 2001a). Behavior of the major groups of organic substances in soil is overviewed in Table III.4.12.

The hormone steroids in soils were reported to degrade rapidly in laboratory incubations: estimated half-life of E2 was less than 0.5 days, when it was abiotically transformed into estrone (E1). E1 and EE2 were found to degrade microbially. The half-life of EE2 ranged from 3 to 7.7 days. However, the behavior and persistence of E1 in the soils are unknown (Colucci and Topp, 2001; Colucci et al., 2001). Although estrogenic steroids were reported to degrade rapidly in soils, their pathways in soils and groundwater and factors influencing their degradation remain unclear. Besides, little data are available on androgens widely used in livestock in some countries as growth promoters, which have become a recent public concern (Ying et al., 2002a). All the metabolites of widely used aromatic surfactants (alkylphenols and APE), of higher toxicity than the parent substances (nonylphenol NP, octylphenol OP, bisphenol A – PPA and AP mono- to triethoxylates NP1, NP2 and NP3) were found to demonstrate a very fast decrease within the first month, but all of them exhibited residual concentrations after 320 days (Marcomini et al., 1989;

Topp and Starratt, 2000): their persistence in Table III.4.12 is thus defined as medium. Little is known on the uptake of APEs and their degradation products both by plants and domestic animals (Ying et al., 2002b). Balance calculations showed that in Germany through the agricultural application of sewage sludge, soil is contaminated annually with 0.8 t OP, 16.5 t NP and 1 t BPA (Gehring et al., 2003).

Sorption of veterinary pharmaceuticals (tetracyclins, macrolids and sulfonamids) to soils strongly depends on the chemical itself, soil type, pH and ionic strength, e.g. sorption coefficient alteration factor due to pH is of 5–15 range. The most mobile appear to be sulfonamide compounds (Ter Laak et al., 2003). Sorption of several tested human pharmaceutical compounds also showed variability with the compound and soil type and seemed to correlate positively with the organic carbon content of the soil. Ofloxacin was reported to be strongly sorbed by soil, while clofibric was weakly bound (Drillia et al., 2003). Considering immense variety of human and veterinary pharmaceuticals of different chemical composition determining their persistence and mobility in soil and food chain, no general conclusions can be derived.

The review of the available data from literature sources performed by the EC and issued recently, which is aimed to evaluate hazard to groundwater, plants, soil organisms, animals and human from organic contaminants introduced with sludge to soils, can be summarized as follows (ANDERSEN-SEDE, 2001).

III.4.4.4.1. Hazard to ground and surface waters

The hazard of organic contaminant leaching to groundwater from the sludge-amended soil is greatly reduced, on one hand, by strong binding of persistent compounds (PCDD/F, PCB) to soil, and on the other hand, by high degradability in soil and short half-life of many organic compounds. Nevertheless, in the case of highly permeable light soils and a shallow water table, such risk cannot be neglected, in particular with respect to contaminants with longer half-life values. LAS, nonylphenols and TNT compounds show higher mobility; PAH compounds are also frequently detected in shallow aquifers. Run-off may play an important role in contaminant transfer, also with soil particulates, enriching river sediments and posing risk to the aquatic environment.

III.4.4.4.2. Hazard to microorganisms

Soil microorganisms are considered to be adaptable to organic contaminants introduced to soil with sludge, though in many cases there is no definitive evidence of lacking adverse effects on soil microflora, in particular of emerging pollutants.

III.4.4.4.3. Hazard to plants

Most organic pollutants are not uptaken by plants from the sludge-amended soil. A risk through food chain arises from spreading sewage sludge directly on plants, in particular on those to be consumed raw or semi-cooked.

III.4.4.4.4. Hazard to animals

Both soil organisms and grazing animals are exposed to the xenobiotics in sludge-amended soil through soil and sludge ingestion. These highly bioaccumulative compounds accumulate in their tissues and are transferred through the food chain.

III.4.4.4.5. Hazard to humans

Human exposure to sludge-borne contaminants occurs through the food chain, due to consumption of animal products. Quantification of organic pollutants entering the food chain through this route has not been done yet. In the case of animal products – human part of food chain, the proportion of sludge-borne xenobiotics in the total diet and accumulation is difficult to evaluate, but considered low due to limited proportion of agricultural land amended with sludge for a longer time.

III.4.4.4.6. Monitoring requirements

Though extensive efforts on harmonization of sampling and analysis methods for organic pollutants in sludge and soil have been undertaken in the last 5 years in the EU level within the works on standardization for all the major groups of pollutants, i.e. heavy metals, organic compounds and pathogens, there are still no generally accepted and validated methods for analysis of most organic pollutants and for monitoring these compounds in sewage sludge and sludge-amended soils on the regular basis. Existing databases are limited and unevenly distributed, which is revealed in Table III.4.3. To the great extent, this situation is due to the lack of limit values for organic pollutants in the Sewage Sludge Directive 86/278/EEC (1986) in force, which were set just lately by the Working document on sludge (EC DG ENV, 2000) (Table III.4.3). The formulated urgent needs comprise (Langenkamp et al., 2001a): (i) elaborating the Priority list of organic contaminants based on key substances instead of substance classes as long as there are no internationally recognized toxicity factors; (ii) conducting research on soil–plant and soil–water transfer in sites heavily amended with sewage sludge in the past to provide scientific basis for limit values for soil concentrations; (iii) elaborating standardized methods for sampling and analysis of sewage sludge and amended soil; (iv) performing a survey of organic pollutants in the EU sewage sludge to establish standardized EU databank. These needs are actually similar for every country intending to use extensively sewage sludge in agriculture.

The persistent bioaccumulative compounds of high toxicity such as PCDD/Fs, PCBs and PAHs should receive the highest attention. Though these xenobiotics are consequently declining in European soils due to restrictive source control, the situation worldwide might be different (US EPA, 2000a).

Following extensive liquid chromatography column clean-up of solvent extracts, high resolution gas chromatography–mass spectrometry (HRGC/HRMS) can be used to determine PCDD/F content in sludges and soils (Jones et al., 1995; Henkelmann et al., 1999). The HRGC/HRMS technique, though, is very expensive that might be a barrier for the survey of these compounds on a regular basis. Use of much simpler and cheaper bioassay/biomarker technique for bioanalysis offers an attractive and reliable alternative

for screening sludges and soils for dioxin and unknown dioxin-like compounds (indicated by AOX parameter) in sewage sludge and sludge-amended soils. In the last decade, a battery of *in vitro* bioassays and ligand binding assays for screening dioxins and dioxin-like compounds in complex environmental mixtures with an adequate reliability and accuracy has been developed, to be generally used in two-step process for identification of the materials and sites of interest; the identified sites are then to be analyzed by HRGC/HRMS (US EPA, 2000b; Behnisch et al., 2001). In particular, EROD and EIA(DFI) bioassays have been used to study dioxin-like compounds in sewage sludge (Schwirzer et al., 1998; Engwall et al., 1999; Engwall and Hjelm, 2000).

More detailed information on the bioanalytical tools for monitoring the effect of chemicals in the environment is given in Chapter IV.4 of this book.

III.4.4.5. Pathogens

Sludge-borne pathogens (Table III.4.6) mainly occur on the soil surface or at shallow depth when sewage sludge has been plowed into the soil. Pathogen penetration in the soil profile, in general, correlates with soil hydraulic conductivity. Survival of pathogens depends on the numerous indirect factors that comprise soil and climatic parameters, contents of pathogens in sludge and amount of sludge applied. Direct factors are related to the biological characteristics of the pathogen. Depending on these factors, survival periods may vary from a few days to several years and are generally shorter when the sludge is spread on the soil surface rather than plowed into soil.

Transfer to groundwater through infiltration and surface water through run-off is of the similar significance as for organic pollutants. Survival on the plants is generally shorter than in the soil due to better exposure to climatic factors. Transmission routes to grazing animals and humans are similar to those of organic pollutants (ANDERSEN--SEDE, 2001).

Sludges treated according to the recommended advanced methods (Table III.4.7) will not present risk to human, animals or plant health. Sludges that may contain BSE agent should not be applied to land where animals have access. If sludge is treated by conventional methods, planting, grazing or harvesting should be delayed for the time period sufficient to reduce pathogen numbers indicated by number of *E. coli* by at least a 10^2 factor. The duration of these constraints depends upon the local climatic conditions that vary significantly. Another mean of avoiding the direct contact with pathogen is incorporating sludge deep into the soil, though it increases a period of survival (Carrington, 2001).

III.4.4.6. General conclusion

To conclude, land application of sewage sludge provides an attractive sink for an unwanted waste and allows utilizing valuable nutrients and organic matter. The occurrence in sewage sludge of high concentrations of potentially dangerous inorganic and organic contaminants, persistent in the environment or of insufficiently known long-term effect, has necessitated restrictions on the quality and quantity of sludge that may be applied to land. With respect to heavy metals, the highly restrictive science-based approach is indispensable in order to prevent toxic effects on plants and soil fauna and

heavy metal accumulation in the food chain (McLaughlin et al., 2000). For heavy metals, risk assessment should consider bioavailability and its alteration over time. For these purposes, new methods and models for assessing bioavailability, which incorporate both chemical parameters influencing metal toxicity and biological response factors, and for predicting its long-term changes should be developed and adapted in regulatory programs. With respect to organic contaminants in sewage sludge, the integrated research for assessing relative importance of contaminant contribution from sludge to soil, their long-term transformations, toxic effect and transfer routes (including soil–plant and soil–water transfer) are required to provide the scientific basis for setting priority lists, limit values for sludge and soil concentrations and justified regulations for sustainable sewage sludge use in agriculture. The general monitoring and database for all kinds of pollutants of concern in sludge and sludge-amended soil based on harmonized standard methods and procedure should be established as a regulatory and validation tool.

III.4.5. Other sewage sludge applications in land

III.4.5.1. Forestry and silviculture

The term "forestry" is used with respect to the amenity forests or mature forest management, while "silviculture" refers to the intensive wood production. The purposes, agronomic benefits and environmental implications and hazards of sewage sludge use are similar to those occurring at its application in agriculture.

EC studies (ANDERSEN-SEDE, 2001) point out, besides general adverse effects connected with heavy metal, organic pollutants and pathogen enrichment on wild fauna and flora, also possibility of degradation of the upper layer of forest soil and the humus, alteration in ecosystem, disturbance of biodiversity in natural biotopes and nitrogen leaching to groundwater. For these reasons, use of sewage sludge in forestry in some countries (e.g. in France) is prohibited. A risk to humans through the food chain is considered to be low due to insignificant share of forest products in the human diet. More research on this issue was postulated.

The mass balance of nutrients and trace element fluxes for 2001/2002 period of 5-years' (1998–2003) field experiment with application of biosolids in the form of liquid and solid composted sewage sludge added at low annual rate 3 t/ha d.m. to podzol soils in 8-year-old maritime pine stands in France (Benbrahim et al., 2003) showed significant increase of nutrients in amended soil in particular Ca (by 23–240%) and N (by about 30%) but also enrichment of trace elements, in particular Zn (by 45–94%) and Cu (by 30–91%) compared to the background level. Pb and Ni increase was lower (by 2–8 and 3–18%, respectively), though for all trace elements it can be defined as high or very high (higher values were reported for composted sludge). The major part of the mineral elements was found to retain in the upper 0–20 cm humus soil layer and did not affect groundwater quality and metal concentrations in the understorey vegetation that showed 200% (liquid sludge) and 50% biomass increase and temporary growth of the species' number, while pine productivity increased by 10% at liquid sludge treatment. Liquid sludge application, though, was reported to significantly increase Pb concentrations in mushrooms and snails.

This example confirms (i) possibility of significant heavy metal enrichment in soils due to long-term application of sewage sludge (biosolids) even in low doses, similarly to that observed at prolonged use of sewage sludge in agriculture; this undermines optimistic prognosis derived on a 1-year basis regarding thousands of years required for metal accumulation in soil to reach a limit value; (ii) nonequivalence of total metal enrichment and its bioavailability (as it can be exemplified in Pb increase and no effect of high Zn and Cu enrichment in sludge-amended soil on uptake by snails, mushrooms and grass); (iii) difference in metal binding mechanisms and strength between sewage sludge and soils.

Vigorous development of understorey biomass and rather poor increase of pine productivity support the thesis about successful competition of weeds with high trees growth, especially in amenity forest. Consideration of protecting natural ecosystems and biodiversity, wild fauna and flora militates against wider use of sewage sludge, which is a remarkable harvester of all anthropogenic pollutants, in forestry and any other natural ecosystem. Sewage sludge use as soil amendment should be limited to plantations purposely cultivated for intensive wood or energy production under permanently controlled conditions. Application of sludge and wood–ash mixtures to energy forestry plantations (*Salix* sp.) has been found to be promising (Dimitrou et al., 2003).

III.4.5.2. Land reclamation and revegetation

Use of sewage sludge for land reclamation and revegetation aims to restore derelict land or protect soil from erosion through supporting humus layer and/or vegetation development. In many derelict post-industrial sites (e.g. after opencast mining, in waste dumping sites) topsoil is often absent and waste material is depleted of nutrients and is thus extremely unfriendly for purposeful plant introduction or natural plant invasion. Application of sewage sludge in such sites, often in mixture with other inexpensive or waste soil improvers has been reported to give positive results, e.g. use of sewage sludge and lime for reclamation of smelter waste pile (Stuczynski et al., 2003) or mixed biosolids for revegetation of fly ash and coal reject disposal site (Danker et al., 2003). Sewage sludge for derelict land reclamation has been already performed in Sweden, Finland, Germany and the UK (ANDERSEN-SEDE, 2001).

It is assumed that the risks in this case are lower than in the case of sewage sludge land spreading for agricultural production or in forestry, as these lands are not considered for food production, and no natural ecosystems are impacted. In the case of erosion control though, these concerns exist, in particular at sewage sludge (biosolids) application to sloping land that enhances pollutants transfer through run-off.

III.4.6. Incineration and alternative technologies

III.4.6.1. Incineration

Sewage sludge incineration with energy recovery seems to be an environmentally safer way of sewage sludge utilization provided that point ("end-of-a-pipe") emissions to air, soil and water from this process are adequately controlled. This alternative prevents the

hazard of non-point contamination of the terrestrial and aquatic environment that occurs in agricultural application of sewage sludge through spreading contaminants in vast areas, in particular that there are still wide gaps in knowledge concerning long-term pollutants routes, fate in the terrestrial and aquatic environment and toxic impact.

The rationale behind thermal waste treatment is discussed in detail in Chapter VI.3 focused on municipal waste but thoroughly applicable to sewage sludge.

Different techniques of incineration are currently in use, including sewage sludge and municipal wastes incineration in dedicated incinerators, or co-incineration, e.g. with coal in power plants for energy production. In this case, emissions into the air of chlorinated aromatics as PCDD/Fs, besides other common products of combustion, are of particular concern (Samaras et al., 1999, 2000, 2001). Modern incinerators assure environmentally safe levels of emission; recent research shows possibility of significant increase of cost efficiency of PCDD/F elimination in flue gases from co-combustion through use low-cost additives to the input. Solid waste from combustion process is another emission source that is environmentally problematic: much lesser volume of this waste product makes it easier to manage in an environmentally safe way.

III.4.6.2. Alternative technologies

Besides conventional combustion or co-combustion processes, several novel alternative technologies are being introduced onto the market, e.g. pyrolysis, gasification, wet oxidation or combination of these processes. These technologies offer advantageous solutions with respect to cost efficiency and the environmental impact. One of such lesser known but fully implemented technologies is presented in Figure III.4.4.

PYRO-KAT Technology of sludge mineralization (Rydzewski and Golos, 2002) comprises water evaporation unit (both for primary dewatered or non-dewatered sludge); water vapor sanitation unit; system for low-temperature processing of organic matter present in sludge; catalytic reactor for oxidizing organic matter to H_2O and CO_2 with 99.9% efficiency; heat exchanger system for energy utilization; filters for uptake of solid residues (including metals and metal compounds).

The advantages of the technology are: (i) lack of combustion chamber: process is conducted in temperature $\leq 500°C$ that greatly reduces energy demand; (ii) complete oxidation of organic matter to H_2O and CO_2; (iii) mineral residue accounts for 2–4% by mass of the initial input; (iv) low operational costs; installation comprises heat recovery system in catalytic reactor that is reused in the process.

Lack of hazardous emissions into the air, including PCDD/F, and low energy demands are claimed to be the most advantageous characteristics of this technology.

III.4.7. Other emerging sludge applications

III.4.7.1. Contaminated site remediation

High enrichment of heavy metals and organic pollutants in sewage sludges results from their high, though variable, sorption properties for these pollutants. CEC for 60 sludges

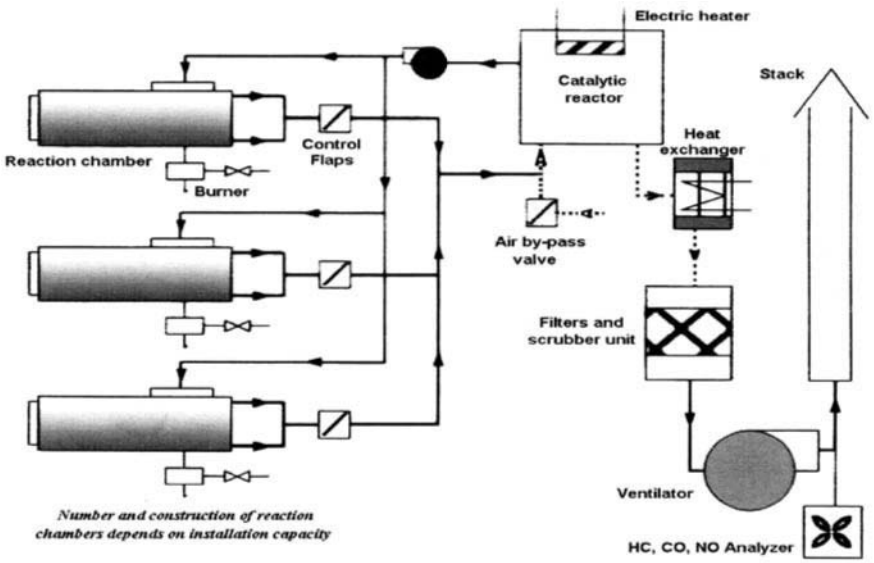


Figure III.4.4. Technological scheme of sewage sludge mineralization process (PYRO-KAT) (Hendri-Gras Chemicals B.V.).

was found to range from >10 to >100, at pH acid to neutral; the sorption capacity of sewage sludges might be up to 10 times as high as that of soils (Siebielec et al., 2003). Sorption sites in sewage sludge, in general, are not fully occupied. This has given rise to the idea of using these properties of sewage sludge for decontamination of metal contaminated sites (Brown, 1997; Li et al., 2000; Siebielec et al., 2003). The major concept is soil remediation by stabilization, i.e. by reducing the mobility of heavy metals through the addition of sewage sludge rich in organic matter. The significant difference in sorption capacity for metals has been explained by difference in humic acid (HA)/fulvic acid (FA) ratio (Shuman, 1999), though most probably it is not the only reason, and binding onto inorganic sites should be equally regarded. The affinity of metals and As to sorption onto organic-rich waste was reported to follow the order $Pb > Cd \geq Cu > Mn \geq Zn > As$, though formation of soluble metal-organic chelates partly counteracted the sorption effect (Madejon et al., 2003). This opposite effect can be used to enhance phytoremediation. Propensity to mobilization and/or immobilization of metals from sludge-amended soils is known to be strongly affected by soil factors (Brown, 1997; Miner et al., 1997), thus soil quality parameters, which are often extreme and subject to alteration over time in industrial contaminated sites, should be considered at the designing remediation program with use of sewage sludge as metal binding and mobilizing agent. For this purpose, more research is needed to explain and purposely control mechanisms of soil–sewage sludge interaction. The overall idea of using sewage sludge for decontamination of contaminated sites is attractive, cost effective and the least controversial, provided that it is properly applied.

III.4.7.2. Using as a sorbent in small commercial premises

Analysis of contaminant sources and source control status that might have influence on sewage sludge quality with respect to the environmental hazards have shown that while large industries achieved required improvement in this field, in the countries where adequate regulations and their implementation exist, small manufacturing industries (e.g. metal electroplating and vehicle related activities, laundries, etc.) still contribute significantly to the contaminant load in UWW. These enterprises usually cannot sustain economically application of advanced technologies of contaminant removal; their small scale also often reduces their feasibility.

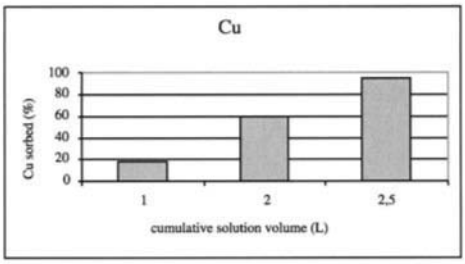
Experiments with metal sorption from electroplating effluents with use of sewage sludge in a simple batch reactor (a tank with mixing device) have shown high efficiency and feasibility of this process that can be exemplified in Figure III.4.5 (Avnimelech and Twardowska, 1997). Therefore, use of small amounts of sewage sludge as adsorbent that after use should be further directed to incineration, could greatly and practically at almost no cost improve quality of bulk sewage sludge to enable its environmentally sustainable use in agriculture. Further experiments in this promising field of application, also with the use of sewage sludge as adsorbent for organic pollutants are needed.

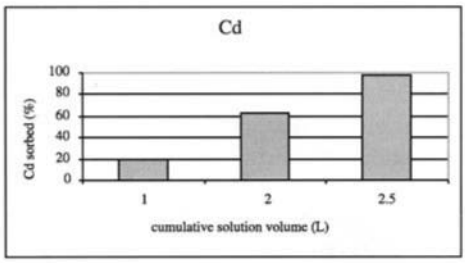
III.4.8. Landfilling

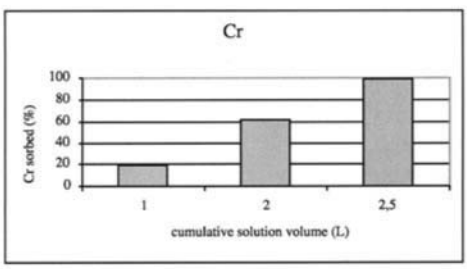
Landfilling of sewage sludge that can be performed as mono-disposal of sewage sludge only (usually at WWTP landfills) or as commonly used co-disposal with municipal wastes is the least advanced technology of utilization of this waste. The landfill construction and emissions from landfill operations are of commonly known character adequately presented in guidelines, and are not addressed in this chapter. Since landfill sites are primarily intended for dumping of municipal solid waste, much opposition exists concerning their use for the disposal of sludge.

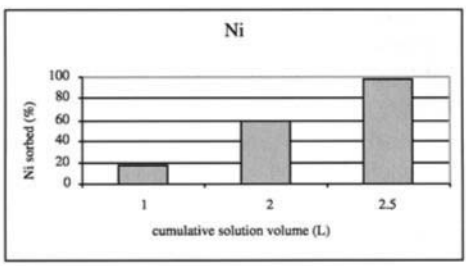
When sewage sludge is to be landfilled, its volume needs to be reduced as much as possible. To accomplish this, the sludge must be dewatered, dried, incinerated or undergo wet oxidation. Dewatering avoids the addition of a large amount of water into the landfill body and also reduces adhesion of sludge to the tires of transport vehicles and compactors. Thermal drying can increase the dry solids content by up to 90%. This reduces transportation costs and effectively meets dumping requirements. The dried sludge needs to be pelletized before being dumped, to avoid dusting. Once the pellets are dumped, there is a delay before they take up water from the landfill. When they are moist enough, the pellets will become involved in the microbiological process of the landfill body and leachability will increase with time (Van den Berg, 1993).

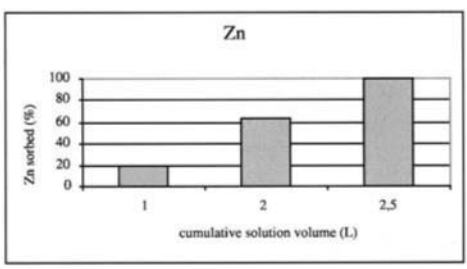
Co-disposal of domestic waste and sewage sludge increases the stabilization of the wastes. The reduction of degradable organic compounds leached from the waste is then more rapid and eventually, the quality of the leachate improves. On average, it has been found that the concentrations of heavy metals in leachates from landfills without sludge are higher than in leachates from landfill sites used for co-disposal. This finding was unexpected, as the total metal content in the co-disposal landfill site is greater than in the











Examples of removal efficiency (pilot scale, batch reactor 120 L, 1:10 ratio, single treatment cycle)

METALS	Zn	Cr	Cu	Cd	Ni
Electroplating waste I					
C_{input} mg/L	163.0	193.0	172.0	53.40	14.90
C_{output} mg/L	27.1	9.0	16.8	3.86	1.92
Reduction, %	**83.4**	**95.3**	**90.2**	**92.8**	**87.1**
Electroplating waste II					
C_{input} mg/L	121.6	10.4	19.0	4.75	3.39
C_{output} mg/L	13.9	3.6	10.0	0.30	1.30
Reduction, %	**88.6**	**65.4**	**47.4**	**93.7**	**61.7**

Figure III.4.5. Cumulative metal binding from electroplating waste onto stabilized sewage sludge in batch reactor in three subsequent sorption/desorption cycles with metals recovery (after Avnimelech and Twardowska, 1997). C_{input}, input metal concentration in treated liquid waste; C_{output}, metal concentration in outflow from the reactor. Sorption cycle: sludge:liquid waste ratio 1:10; desorption: 15% HCl; neutralization: $Ca(OH)_2$. Proven feasibility of repeated using the same sewage sludge as a sorbent. Efficiency of metal reduction: 50–95% (higher for high input concentrations, lower for low input concentrations due to lower concentration gradient between the initial content of a metal in sludge and waste).

landfill without sludge. This condition can likely be attributed to the lower pH of the moisture in the landfill without sludge (Van den Berg, 1993).

Landfill costs continue to increase as regulations have been tightening, in part due to the frequent public opposition to the siting of new landfills (Bierman and Rosen, 1994). Landfill operators demand higher solids content and suitable shear stress characteristics as conditions for tipping. These requirements have an impact on the sludge conditioning technology where sludge is disposed of in landfills.

The regulation sheet on landfills, issued by the work group "Waste" of the German Federal States, demands a minimum dry solids (DS) content of 35% for the unlimited incorporation of dewatered sludge from municipal sewage plants. The land must also be

solid, capable of being driven over, and meet esthetic, hygienic and odor emission criteria (Thomas et al., 1993).

III.4.9. Concluding remarks

In view of fast growing amount of sewage sludge generation in Europe and worldwide, its use in agriculture as a source of nutrients and valuable organic matter appears to be the most attractive and cost effective, but at the same time also the most controversial disposal outlet due to exceptional concentration of heavy metals, metalloids and hazardous organic pollutants originating from all kinds of human activity and potentially high risk of non-point persistent contamination of vast areas of a vital importance for the environment and human health. It is well known that once occurs, non-point contamination is extremely difficult to reduce and control. To avoid risks, actual status of pollutants (metals and organics) occurrence, proportion of sewage sludge (biosolids) input to soil in overall mass balance from different sources, transfer routes and fate in the environmental media and food chain, reliable science-based long-term prediction of accumulation, distribution and redistribution among pools of different bioavailability, quantitative and qualitative transformations, as well as their direct and indirect impacts on organisms should be evaluated and documented. Short- and long-term predictive models and assessments need to be validated on the basis of permanent monitoring of heavy metals and organic pollutants level in sewage sludge and sludge-amended soil in parallel with sludge and soil factors influencing pollutants availability and toxicity based on standard sampling protocol and analytical methods.

With respect to metals, new regulatory programs that incorporate chemical speciation and species-specific bioavailability and reliable methods for its assessing, supported with relevant research programs, need to be developed. With respect to organic compounds, among many needs, harmonized priority list of pollutants based on the background information on input level and transfer routes, as well as long-term observations of the fate of organic contaminants and their metabolites for evaluation of persistence and toxic effects are required to develop reliable soil protection rates and quality standards.

The current development of solid science revealed the gaps in knowledge and amount of work to be done to mend them for safe use of sewage sludge (biosolids) for land spreading. This suggests preference of the precautionary approach to intensification of sewage sludge application in agriculture until the required level of knowledge is achieved.

In this case, incineration of sewage sludge in accordance with the best available technologies or new medium-temperature treatment technologies validated with respect to safe level of emissions to air may have to be applied.

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For further information

Continuously updated additional information is available on Web sites: http://europa/eu.int/comm/environment/waste/sludge/; http://www.igpress.com/biocycle.htm.

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III.5
Dredged material

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III.5.1. Introduction

On a worldwide scale rivers transport eroded material as suspended solids to the coastal areas. Deltas, estuaries and their associated wetlands are natural sinks for this material. In the 1980s, the International Association of Ports and Harbors estimated about 350 million tons of maintenance dredging and 230 million tons of average annual new construction dredging. In the harbors around the North Sea, approximately 100 million m^3 of sediment has to be dredged annually – about 10 times the average annual sediment discharge of the Rhine river. Typical problems with these sediments are:

- increasing volumes of dredged materials and
- high concentrations of toxic substances.

These problems have been concentrated mainly at the mouth of large rivers and in coastal areas.

In Rotterdam harbor, at the mouth of the Rhine river, the volume of sediment, which has to be dredged annually, increased from less than 1 million m^3 in 1920 to more than 10 million m^3 in 1980. The possibilities of disposal of these enormous quantities of material are severely limited because of the pollutants present in the dredged material.

Due to the economic implications, there is increasing worldwide interest in the development of dredging and disposal technologies. Among the authorities particularly dealing with the subject of contaminants in dredged materials, the U.S. Army Corps of Engineers Waterways Experiment Station at Vicksburg, MS, has played a leading role. In the early eighties, the Environmental Laboratory of this institution together with United States Environmental Protection Agency (USEPA) initiated a "Decision-Making Framework for Management of Dredged Material Disposal", which includes test procedures on physical–chemical conditions, aquatic bioaccumulation, and water column effects both at the site of dredging operations and disposal of dredged materials. Further intensification of coordinated research was performed by the Assessment and Remediation of Contaminated Sediments (ARCS) Group of USEPA, which has been focusing on the Great Lakes Areas of Concern (1990–1993); an "Integrated Contaminated Sediments Assessment Approach" (Anonymous, 1994) includes six topics "sampling design and quality control", "sample collection", "chemical analysis", "toxicity testing", "benthic community structure and survey", and "tumors and abnormalities". In addition, the ARCS program was charged

with assessing and demonstrating remedial options for contaminated sediment problems in the Great Lakes; laboratory tests were conducted utilizing 13 processes, and pilot-scale (field-based) demonstration of bioremediation, particle size separation, solvent extraction and low-temperature thermal desorption were conducted.

It seems that sufficient data have been assembled by these and other organizations with respect to both risk assessment methods and remediation procedures for contaminated sediments, which should allow developing more integrative perspectives in this subject. The present geochemical approach is emphasizing on the interactive nature of chemical parameters and is focusing on the long-term effects of pollutant release from disposed sediments.

III.5.2. Geochemical concepts for contaminated sediments

Inclusion of the time factor moves beyond the civil engineering approach in waste management, which usually devotes little attention to long-term emissions from waste disposal sites. "Because we have become accustomed to considering the filling period as the most important phase in landfill operation, we have forgotten that subsequent to the active working period there is the infinitely long time in which the site has to function as a depository for all materials unwanted in the biosphere" (Stief, 1987).

Apart from the traditional approach of contaminant loss prediction, concepts are developed by biogeochemical disciplines, emphasizing the interaction of chemical cycles. This approach refers to non-linear and time-delayed responses in contaminated sediments (so-called "chemical time bomb" processes), which at present cannot be predicted, modeled or even estimated to a satisfactory extent. The underlying concepts are:

- *Chemical gradients*: long-term prognosis, in particular, of the behavior of contaminants at critical sites requires both knowledge of interactions of pollutants species in solid matter and solution, and an estimation of future borderline (particularly "worst case") conditions in a dynamically evolving medium (Förstner, 1993). In sediments, typical driving forces for intensified matrix/element-interactions are strong chemical gradients of redox conditions, pH values and organic ligand concentrations, all three factors mainly being induced by degradation of organic matter (Salomons, 1993).
- *Storage capacity controlling properties* (Stigliani, 1993) form the link between geochemical cycles comprising driving forces such as organic matter and cycles of mobilizable pollutants. They are the key aspects in the framework of chemical time bombs concept (Stigliani, 1991). It is useful to distinguish between two different mechanisms: the first is direct saturation, by which the capacity of sediment for toxic chemicals becomes exhausted. The second way to "trigger" a time bomb is through a fundamental change in a chemical property of the solid matrix that reduces its capacity to adsorb (or keep adsorbed) toxic materials. Methodologies should be designed for assessing effects related to processes of "early diagenesis", i.e. mechanisms and effects by which solids are changed in their chemical form, involving new equilibrium between solid and their dissolved species.
- *Mobility concept*: at the target site, distribution between dissolved and particle-bound micropollutants is affected by accelerating and demobilizing factors. The former, for

example, comprise the effects of pH lowering, redox changes, organic complexation, and microbially mediated species transformations such as biomethylation. Within the spectrum of "barriers", physical processes include sorption, sedimentation, and filtration; chemical barriers comprise mechanisms such as precipitation. Biological barriers are often associated with membrane processes, which can limit translocation of micropollutants such as trace metals (e.g. from plant roots to the shoots and fruits).

- *Selectivity of organic matrices*: the dominant role of organic matrices in the binding of non-polar organic pollutants and metals (as demonstrated in the multi-chamber transfer experiment for copper (Calmano et al., 1988)) is of particular relevance for the transfer of these substances into biological systems. It can be expected that even at relatively small percentages of organic matrices these materials are primarily involved in metabolic processes and thus may constitute the major carriers by which micropollutants are transferred within the food chain. Including these mechanisms of pollutant enrichment on mineral surfaces ("geoaccumulation"; Müller, 1979), organic matrices and, in particular, by organisms, the concept of coupled biogeochemical cycles as originally designed by Salomons (1993) can be extended. Biogeochemical cycles involving redox transformations usually are relatively slow compared to physical–chemical processes such as dissolution or desorption. The influence of mobilizing agents like dissolved organic carbon, salt ions or protons may be reduced by capacity-controlling properties such as cation exchange and pH buffer capacity.
- *Final storage quality* (Baccini, 1989): this approach is one way to develop and control landfills on a conceptual basis. It has been defined by the Swiss Federal Government in 1986: "Landfills with solids of final storage quality need no further treatment of emissions into air and water." Including new experience from impact evaluations related to capacity controlling properties, the mobility concept of environmental geochemistry can be implemented into waste management practice by different ways of optimizing barrier systems. As shown from the examples of large mass wastes – dredged material, mining residues and municipal solid waste – long-term immobilization of critical pollutants can be achieved by promoting less soluble chemical phases, i.e. by thermal and chemical treatment, or by providing respective milieu conditions. A common feature of geochemically designed deposits is their tendency to increase stability in time, due to the formation of more stable minerals and closure of pores, thereby reducing water permeation.
- *The biogeochemical concept* of sediment management involves integrated strategies, i.e. the analytical and experimental parameters should always be related to the potential remediation options for a specific sediment problem. In addition to the common predictive techniques for estimating contaminant losses the interactive nature of various parameters has to be recognized. This means, that particular emphasis should be posed on the evaluation of the two data sets "driving force/geochemical gradient" parameters and "capacity controlling properties". Such evaluation includes the type of dissolved/solid interactions, transfer rates of contaminants between various substrates and, in particular, processes in interstitial waters.

Remediation techniques on contaminated sediments generally are much more limited than for most other solid waste materials, since the widely diverse contamination sources in larger catchment areas usually produces a mixture of pollutants, which is more difficult

to treat than an industrial waste. Here, "geochemical engineering" (Salomons and Förstner, 1988a,b) emphasize the efforts to use natural resources and processes for reducing negative environmental effects of pollutants, e.g. by immobilizing toxic metals.

III.5.3. Risk assessment of contaminated sediments

During the last 20 years various strategies have been proposed for decision-making on contaminated sediments. One of the earlier schemes of USEPA following identification of problem areas and critical chemicals first decides on priority sources. With ongoing sources, the maximum percentage of possible source control is estimated, as well as the question, if recovery can be accomplished in an acceptable time frame. If the question on ongoing sources is denied, an evaluation takes place on combined sediment remedial action and source control. If the sources have been stopped and recovery cannot be expected in acceptable time frame, then sediment remedial action has to be evaluated.

Beside the costs of the remediation techniques, the major questions relate to the contaminant loss pathways. Contaminant loss can occur through one or more pathways. The example of a confined disposal facility indicates that the potential pathways for contaminant loss include surface runoff, effluent, seepage, leachate, dust and uptake by plants and animals. Predictive techniques for estimating contaminant losses comprise two categories (Meyer et al., 1994):

- *a priori* techniques which are suitable for planning-level assessments, and
- techniques that use pathway-specific test data provide state-of-the-art loss estimates (generally more advanced techniques).

For some remediation components there are no pathway-specific tests and *a priori* techniques for all pathways of all components available. Confidence and accuracy for *a priori* loss estimates from confined disposal facilities are low. For test-based loss estimates they vary with the stage of development of the test. Confidence is high for test-based estimates of leachate losses. Confidence and accuracy are high for estimation of test-based runoff loss.

Typical methods for measuring physical and engineering properties of contaminated sediments – *a priori* techniques – as recommended in the early seventies comprise: particle size distribution, organic content – measured as total volatile solids – solids content, liquid and plastic limit test, void ratio and density.

III.5.3.1. Sediment quality criteria

During the last 20 years, considerable experience has been assembled with pathway-specific test data, in particular with more innovative treatment procedures. However, most important progress in risk assessment of contaminated sediments has been made in the context of sediment quality criteria development, following the experience that long-term perspectives in water management need "integrated strategies", in which sediment-associated pollutants have to be considered as well. In particular, it has been evidenced, that for most cases of surface waters, the contaminant levels in the sediments have greater

impact on the survival of benthic organisms than do dissolved concentrations (e.g. BenKinney et al., 2001).

First efforts have been undertaken by the USEPA to develop standard procedures for the assessment of environmental impact of sediment-bound pollutants. Further discussions led to the differentiation of biological and chemical–numerical approaches. Biological criteria integrate sediment characteristics and pollutant loads, but they do not generally indicate the cause of effects. With respect to chemical–numerical criteria, there is no immediate indication on biological effects. Their major advantages lie in their easy application and amendment to modeling approaches.

III.5.3.1.1. Biological criteria

Biological approaches on development and application of sediment quality criteria exhibit a common basis in the study of damaging impacts from contaminated sediments on organisms. The biological parameters "bioaccumulation", "toxicity", and "mutagenity" have to be considered separately in any case. Bioassays as well as field surveys are empirical considerations, which cannot provide numerical criteria to be transferred on different situations.

Bioassays are used to estimate toxic potentials of substances. The application of bioassays for the assessment of sediment or dredged material quality is required/advised by the dredged material management guidelines of international conventions like the Oslo and Paris (OSPAR) and the Helsinki and the London convention. However, both on a national and international level the implementation of bioassays for the purpose of dredged material management is still under development. In the Netherlands, a number of bioassays are evaluated and their implementation is scheduled for 2002.

Bioassays seem a promising tool addressing explicitly two issues:

- The implementation of bioassays as additional criteria for the quality of sediments/-dredged material might cover chemicals with different modes of action, otherwise overseen relying on a limited set of chemical criteria.
- An integrated approach, combining bioassays and chemical analysis (toxicity identification evaluation, TIE) can identify harmful chemicals.

The first can complement the chemical monitoring in a cost-effective manner by investigating integrated toxic effect potentials of the "cocktail" of substances present in the aquatic environment. The latter not only detects effect potentials but also can link them to individual chemicals, which could serve as a basis for more detailed studies and subsequently enable the implementation of specific measures at the source.

Selection of the optimal methods for assessing aquatic ecosystem degradation and potential risks from contaminated sediments will depend on the study objectives, resources, and the characterization of the methods. In particular, this is valid for biological test procedures, which increasingly form the key aspect in an integrated approach, characterizing the physical–chemical conditions (including habitat and contaminant patterns), indigenous biological communities, and toxicity. The sediment quality triad (Chapman, 1986) is an integrated procedure, which uses empirical evidence that is observation, not being based on theories. Such procedures seem to be particularly

promising, since each component of the system is contributing to the interpretation of the other components.

Currently, there are not many standardized sediment toxicity tests. ASTM (1994) procedure for risk assessment is performed with use of freshwater invertebrates: insects, oligochaete and amphipods as test organisms (*Chironomus* sp., *Hexagenia* sp., *Tubifex tubifex*, *Hyalella azteca* and *Diporeia* sp.) at total duration of 28–30 days. The draft OECD TG 218 (2000) test recommends *Chironomus* sp. as an assay, with use of spiked sediments. The EU Technical Guidance Documents (TGD, 1996) based on the equilibrium partitioning method (EPM) does not provide detailed assessment procedure for sediments; besides, EPM has been found insufficient for highly sorptive or binding substances. This gave rise to the revision of TGD and to development of the newly proposed EU risk assessment concept based on whole-sediment long-term tests with bioassays that represent all possible routes of exposure. Besides benthic invertebrate species, also primary producers (rooted plant) have been considered as assays for a sediment test battery. This concept is now still under development, though already has proven to be valuable in long-term risk assessment for the river sediments (Riedhammer and Schwarz-Schulz, 2001).

Relatively simple and implementable liquid, suspended particulate and solid-phase bioassays have been carried out for assessing the short-term impact of dredging and disposal operations on aquatic organisms (Ahlf and Munawar, 1988). Standardized tests are characterized by their lack of variability, but essential information (e.g. lethality, alterations of growth rate) can only be obtained with such single species test. The influence of the main environmental variables on the interaction of suspended particulates or *in situ* sediment contaminants and organisms should also be determined under simulated field conditions. In particular, benthic bioassay procedures, due to recent developments, are important in evaluating the relationship between laboratory and field impacts (Reynoldson et al., 1987).

The concept of Ahlf et al. (1992) for the assessment of sediment-bound pollutants is mainly based on microbial toxicity tests, using bacteria and algae. An overall biological assessment scheme includes:

- field description of benthic communities,
- benthos bioassay on total sediment,
- sediment contact bioassay with luminescent bacteria,
- porewater bioassay (bacteria, Chromotest), and
- elutriate bioassay (algae, bacteria, Chromotest).

In addition, tests can be performed on fractions of the sediment, which have been extracted or treated with a co-solvent. For example, a non-polar surfactant has been applied, which is commercially used to solubilize hydrocarbons from contaminated soil. On the other hand, the concept can be modified according to users requests, in that only parts of this structure may be needed for a site-specific problem.

In practice, the following question have been posed for test procedures—in particular biotests—on contaminated dredged sediments:

- What are the most toxic sites?
- Where should remediation start?
- What technique has to be used, in accordance with the site-specific pollutant load?

- Is there a difference in the toxicity of sediments, which are resuspended into the water phase and those, which are buried in deeper layers?
- What is the minimum number of assays for non-redundant information?
- What is the relation between different assays and chemical data?

The last two questions are closely related to the costs of such investigations. At present the management of dredged materials comprises hazard assessment of the sediments. Despite the inherent difficulties of conducting risk assessments at the disposal site, it should be integrated in future approaches for decision-making frameworks. Further research is needed before implementation.

For the sake of cost-effectiveness, hazard assessment should be carried out in a multi-level approach.

- *Level I*: limited chemical criteria, limited test battery with bioassays.
- *Level II*: application of an extended battery of bioassays as well as case studies in order to identify the culprit chemicals.

Level II should only be applied for toxic or highly toxic materials where the toxicity cannot be explained by the presence of the investigated chemicals. TIE-like procedures can be used to establish links between effect potentials and causative chemicals as well as to distinguish between toxic potentials from man-made and natural compounds (e.g. phytoestrogens) (Gandrass and Salomons, 2000).

Open questions relate to the implications of anoxic sediments, mainly with respect to the effect of toxic metals. In sulfidic anoxic sediment, even if it is strongly polluted by metals, organisms are considered to be still safe due to the strong fixation of metal ions by S^{2-} or HS^- as source of acid volatile sulfide. Such polluted sediments, however, can behave as a time bomb, which is triggered by only one factor: redox increases to a critical point, i.e. by exposure to oxygen-rich overlying water or directly to air. Once this situation occurs (a possible pathway also is oxygen transfer via plant roots), toxic metals in the sediments will be released to the water phase or transformed into more bioavailable species.

III.5.3.1.2. Chemical numerical criteria

Numerical approaches for the assessment of environmental impact of sediment-associated metals are based on:

- accumulation,
- porewater concentrations,
- solid/liquid equilibrium partition (both sediment/water and organism/water), and
- elution properties of contaminants.

Background approach: compares the actual data with sites comprising natural or insignificant pollutant concentrations. Particularly useful are samples from deeper layers of the sediment sequence at a given site, for example, from drill holes, since this material is derived from the same catchment area and usually similar in its substrate composition. Nonetheless, standardization with respect to grain size distribution is indispensable.

Porewater approach: based on the experience, that the composition of interstitial waters is the most sensitive indicator of the reactions that take place between pollutants on particles and the aqueous phase, which contacts them. There is the advantage of a direct recovery and analysis of water-borne constituents. But there are several disadvantages, mainly arising from the sampling and sample preparation, which need considerable precaution, such as for exclusion of oxygen.

Equilibrium approaches: these approaches are related to the broad toxicological basis of food and water quality data – a very important advantage. On the other hand, there are the effects of sample preparation (e.g. the drying procedures) and separation techniques (e.g. filtration or centrifugation). There are also strong effects of grain size composition and the influence of suspended matter concentration in the aquatic system, which is even more important, if the kinetics of sorption and desorption are too slow for equilibrium to be achieved in a given time of interactions. Unlike non-ionic organic chemicals, K_D-values of metals are not only correlated to organic substances but also to other sorption-active surfaces. Therefore, the equilibrium partition approach exhibits strong limitations for metals.

Remobilization: short-term effects may be studied from water/sediment-suspensions, medium-term effects from experiments using tanks, and long-term effects by applying chemical extractions, either single or in sequence. Field observations often do not show clear effects, as has been demonstrated for the release of metals from anoxic sediments during oxidation. Such implications for future criteria development, particularly important for dredging and management of dredged material, will be discussed on the basis of experience from metal speciation studies on soils and sediments.

III.5.3.2. Long-term effects, particularly of redox processes

Reliability of long-term prognoses on the impact of metal-contaminated sediments is particularly restricted due to the dominance of non-linear and delayed processes in redox- and pH-controlled systems. Acidity is perhaps the most serious long-term threat from metal-bearing wastes. For decades, water seeping from mine refuse has delivered increased metal concentrations into receiving waters. The threat is especially great in waters with little buffer capacity. The acidity production can develop many years after disposal, once the neutralizing or buffering capacity in a pyrite-containing waste is exceeded.

The major processes (see Equations (III.5.1)–(III.5.3)) affecting the lowering of pH values (pH – from 3 to 2) are the exposure of pyrite (FeS_2) and other sulfidic minerals to atmospheric oxygen and moisture, whereby the sulfidic component is oxidized to sulfate. Bacterial action can assist the oxidation of $Fe^{2+}_{(aq)}$ in the presence of dissolved oxygen. Nitrification also results in proton liberation.

$$4\,FeS + 9\,O_2 + 10\,H_2O \rightarrow 4\,Fe(OH)_3 + 4\,SO_4^{2-} + 8\,H^+ \qquad \text{(III.5.1)}$$

$$4\,FeS_2 + 15\,O_2 + 14\,H_2O \rightarrow 4\,Fe(OH)_3 + 8\,SO_4^{2-} + 16\,H^+ \qquad \text{(III.5.2)}$$

$$2\,NH_4^+ + 3\,O_2 \rightarrow 2\,NO_2^- + 2\,H_2O + 4\,H^+ \qquad \text{(III.5.3)}$$

The acidification of a sediment/water system begins after hydrogen ions are generated during the oxidation (e.g. during dredging or resuspension of mainly fine-grained material containing less carbonates than needed for long-term neutralization). Primary emissions containing high metal concentration issue from waste rocks and mine tailings, while tailing ponds are primarily responsible for secondary effects on groundwater. Important and long-term sources of metals are the sediments reworked from the floodplain, mainly by repeated oxidation and reduction processes.

High concentration factors were found in inland waters affected by acidic mine effluents. The concept of acid-producing potential (APP) was initially developed in the prediction and calculation of acid mine drainage and waste tailings management (Anonymous, 1979) as summarized by Ferguson and Erickson (1988). Our findings on the effects of periodical redox processes on both APP and metal mobility in estuarine sediments (Kersten et al., 1985; Kersten and Förstner, 1991) have further enhanced research interest in this field.

Periodical redox processes can induce an increase or decrease in APP or pH in a sediment/water system. In a closed system, periodical redox processes can lead to the change or transfer between APP(s) and APP(aq) but the total APP of the system does not change. The processes are reversible. The hydrogen ions produced during oxidation will be consumed by the following reduction. Contrarily, in an open system, the total APP of the system will change depending on the properties of the system and the reaction processes. Under certain conditions total APP in the system increases, while under other conditions total APP in the system decreases. Some processes are irreversible. The components producing or consuming H^+ ions leave the system and cause the change in APP(s), APP(aq) and permanent acid neutralizing capacity (ANC).

Figure III.5.1 gives the example of "split of sulfate" (van Breemen, 1987). The first reaction is characterized by the reduction of sulfates, e.g. in tidal flats. At the same time organic matter is degraded. Most of the sulfide formed is fixed in the sediment as FeS or FeS_2. Whereas the acid producing potential APP(s) is fixed in the sediment, the ANC in the form of hydrogen carbonate is mobile and can be flushed away. After the next aeration and oxidation extreme acidification of the system can take place.

Direct assessment of the pH-changes resulting from the oxidation of anoxic sediment constituents can be performed by ventilation of sediment suspensions with air or oxygen and subsequent determination of the pH-difference between the original sample and

aerobic conditions				**anaerobic conditions**		
$4\ MeSO_4$	+	Fe_2O_3	$\xrightarrow{\text{"}CH_2O\text{"}}$	$2FeS_2$	+	$4\ Me(HCO_3)_2$
$4\ H_2SO_4$	+	Fe_2O_3	$\xleftarrow{O_2}$	acid producing potential(APP)		acid neutralization potential (ANC)
solid			——>	*dissolved*		

Figure III.5.1. "Split" of sulfate in the redox cycle (after van Breemen, 1987).

oxidized material. The greater this difference the higher is the short-term mobilization potential of metals, e.g. during dredging, resuspension and other processes, by which anoxic sediments get into contact with oxygenated water or—following land deposition of dredged material—with atmospheric oxygen. A typical example demonstrating the temporal development of redox and pH-values in a sludge suspension from Hamburg harbor is presented in Figure III.5.2.

Porewater data from dredged material from Hamburg harbor indicate typical differences in the kinetics of proton release from sulfidic and organic sources (Maaß and Miehlich, 1988). Recent deposits are characterized by low concentrations of nitrate, cadmium and zinc. When these low-buffered sediments are oxidized during a time period of a few months to years, the concentrations of ammonia and iron in the porewater typically decrease, whereas those of cadmium and zinc increase (with the result that these metals are easily transferred into agricultural crops). Of the two major release processes, the first—oxidation of sulfides—can be predicted to some extent, whereas the implications of long-term degradation of organic matter on the release of less mobile elements such as copper and lead as yet cannot be described satisfactorily. Here, as with the effects of these interactions on the cycles of anionic metal compounds such as arsenate, further research is needed.

Experimental approaches for calculating APC and ACC for sulfidic mining residues have been summarized by Ferguson and Erickson (1988). A test described by Sobek et al. (1978) involves the analysis of total pyritic sulfur. Potential acidity is then subtracted from neutralizing potential, which can be obtained by adding a known amount of HCl, heating the sample and titrating with standardized NaOH to pH 7. Bruynesteyn and Hackl (1984) calculated APC from total sulfur analysis; here, acid-producing capacity was then subtracted from acid-consuming capacity, obtained by titration with standardized sulfuric

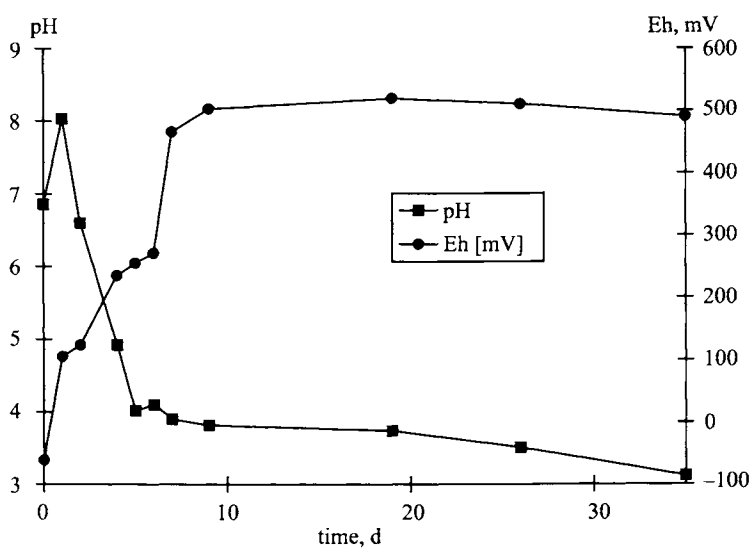


Figure III.5.2. Development of redox potential and pH during the oxidation of a low-buffered dredged mud suspension from Hamburg harbor (Calmano et al., 1992).

acid to pH 3.5. The APC relationships of sediments are more complex than that in sulfidic ores because the APC from organic matter must be considered.

The most efficient *fixation process* within anoxic sediments for trace metals is production of free sulfide during degradation of organic matter and reduction of sulfate. Study of heavy metal associations with sulfides and carbonates in anoxic sediments, therefore, provides insight into early diagenetic processes (Berner, 1981; Morse and Mackenzie, 1990).

Whereas the ability of the sediment to produce free sulfide is determined by the sulfate reduction rates, the ability to remove all produced free HS^- is given by the reactive metal—predominantly reducible Fe^{3+} concentrations—available to form sulfide minerals (available sulfide capacity (ASC): Williamson and Bella, 1980). Simultaneous application of standard sequential leaching techniques on critical trace elements and matrix components can be used for geochemical characterization of anoxic, sulfide-bearing sediments in relation to the potential mobility of critical trace metals (Kersten and Förstner, 1991). For determining the acid-producing capacity ("maximum APC") in anoxic sediments, both the FeS pool ("actual" APC) and the maximum ferrous sulfide (worst case: pyrite)-producing capacity upon disposal has to be taken into consideration.

3.3. Assessing long-term mobility of metals in sediments by titration experiments

With regard to prediction of long-term effects of sediment-bound metals, chemical extraction procedures are of limited value because they usually involve neither reaction-mechanistic nor kinetic considerations. This lack can be avoided, e.g. by an experimental approach, originally used by Patrick et al. (1973) and Herms and Brümmer (1978), where sediments can be treated in a circulation system under controlled intensification of significant release parameters such as pH-value, redox-potential, and temperature. Our experimental design (Schoer and Förstner, 1987) includes an ion-exchange system for extracting and analyzing the released metals at an adequate frequency, and compares sequential extraction results before and after treatment of the sample in the circulation apparatus. Individual metal species are released at different time intervals. Taking into account both element contents released during the 10-week experiments (equivalent to several thousand years of solid/water interaction) and those extrapolated from extraction "pools", concentrations can be calculated for different scenarios.

While these extrapolations have been made from pH 5 conditions, titration curves from investigations on a wide spectrum of metal-bearing waste materials (Obermann and Cremer, 1992) suggest, that pH 4 may be more appropriate for long-term predictions of potential metal releases from contaminated sediments. In this pragmatic approach the pH is automatically adjusted to 4 during the time period of 24 h. Apart from the release rates of metals, which can be determined from samples taken at different time intervals, the sum curve of acid consumption provides information on the potential changes of the matrix composition during acidification and the availability of buffer capacity at different time scales.

Acid consumption reflects slow long-term metal release from sediments. Because calcite dissolution is fast, the acid consumption in the first stage will increase drastically

within a short period of time. Cation release and alumosilicate dissolution are dominant factors consuming acid in the later stage. The reactions can be treated as:

$$SO{=}Me + 2\,H^+ \leftrightarrows SO{=}H_2 + Me^{2+}, \text{ and} \quad \text{(III.5.4)}$$

$$Al_2O_3 + 6\,H^+ \leftrightarrows 2\,Al^{3+} + 3\,H_2O \quad \text{(III.5.5)}$$

where SO= and Me are surface groups in solid phase and metal, respectively. The reactions of hydrogen ions with metal and alumosilicate are delayed due to the complex sediment structure and matrix. For example, special penetration of hydrogen ions is required for reaction with cations on clay minerals coated with organic matter or biofilms. Rates of reactions can be estimated by measurements of metal concentrations in solution.

In dredged material management two different target areas for combined matrix/metal criteria can be distinguished:

- sediment resuspension and
- dredged material disposal.

With respect to "resuspension of aquatic sediments", which involves more short-term effects than the disposal of dredged material, special emphasis should be posed on the factor "available metal species". Within certain categories of acid producing and consuming capacities, guideline values for individual metals should be based on elutriate data, preferentially at pH 4, for better comparison with other solid matrices (e.g. Swiss Ordinance for Waste Materials (Anonymous, 1990)). Environmental impact of sediment deposits is influenced by the internal chemical conditions rather than by the concentration and extractability of metals. Therefore, priority should be given to the optimization of long-term chemical stability (geochemical engineering).

At the moment, research on long-term effects of redox variations on metal behavior in sediments is mostly based on thermodynamic considerations. Future research should emphasize studies on the kinetics of metal species transformations, hydrogen ion production and metal release as affected by changing redox conditions. Additional important aspects involve the bridging of the gaps between numerical criteria approaches, as reflected by matrix composition and metal mobility, and biological approaches. It may well be, that for such systems, which are much less disturbed than artificial sediment elutriates, relationships between matrix conditions—as reflected, e.g. by redox indices—and metal species bioavailability may be found, which may serve as a more solid basis for the interpretation of results from bioassays, eventually with respect to chronic toxicity.

A promising tool for incorporating both bioavailability and numerical criteria approaches into generic risk assessment of metals in sediments might provide adaptation for the sediment compartment of the recently developed biotic ligand model (BLM) approach that integrates chemical (speciation, complexation) models with more biologically oriented models for predicting metal toxicity in aquatic ecosystems (Janssen and Heijerick, 2002).

III.5.3.4. Integrated process studies

Management of contaminated sediments, i.e. linking risk assessment and identification of cleanup options, requires implementing information on bioavailability and

bioaccumulation of pollutants, as well as on processes controlling their particular hydrological and biogeochemical dynamics into a comprehensive sediment assessment scheme, a set of bioassays being a powerful supplement to assess sediment quality. The final development of optimum management strategy, besides economic and social factors, involves engineering elements such as technical feasibility, contaminant reduction, permanence of remedial options like containments and capping, disposal facilities, *in situ* treatment and long-term monitoring concepts. Both for establishing sediment-related quality objectives and for developing adequate remediation procedures and technical problems solutions, a linking set of integrated process studies is needed that comprises a wide range of simulation techniques and models in different spatial and temporal scales (Fig. III.5.3).

The integrated process studies on erosion risks and pollutant mobility in river sediments have been addressed in detail in a series of review papers by Förstner (2001a,b). The major factors, which influence solution/solid equilibrium conditions and the net release of dissolved organic carbon (DOC), nutrients and pollutants from the sediments, include changes of pH and redox conditions, the competitions of dissolved ions and the complexation by organic substances. Special study targets are the formation of new surfaces for the readsorption of dissolved pollutants, or contrariwise, the potential reduction of sorption sites on minerals and the degradation of organic matter, which affects both hydrodynamic processes (erosion vs. sedimentation) and geochemical redox cycles.

For integrating the interdisciplinary study of individual processes and for transferring the results of laboratory experiments to a natural aquatic system, where the processes occur on extremely variable temporal and spatial scales, analytical and numerical models can be applied. Today's models for predicting pollutant transport in rivers are dominated by hydromechanical parameters. A first step for extending these models could involve the consideration of the above-mentioned typical ecosystem factors such as competing ions, complexing agents, redox conditions and—predominantly for metals—pH-values. The next tier would be the inclusion of binding constants, solubility products and other factors, which can describe solid/solution interactions of critical chemicals in a multi-component system. The last step, which can be seen so far, would extend the mechanical–chemical

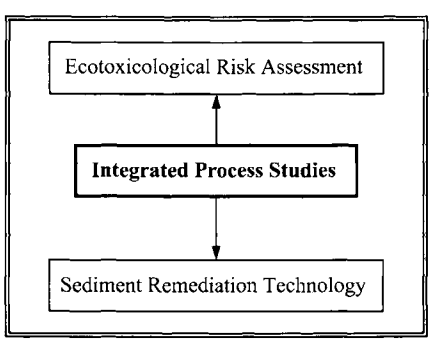


Figure III.5.3. Integrated process studies as a link between ecotoxicological risk assessment and remediation technologies in the management of aquatic sediments and dredged materials (after Förstner, 2001b).

model into biology. According to Kern (1997), such biochemical multi-component models should consider rates of growth and decay of organisms and organic matter.

The thorough characterization of processes, which influence the interaction and transfer of pollutants in sediments and suspended matter, along with development of the relevant models would greatly enhance possibility of contaminant release prevention and control from sediments and optimization of remedial measures.

III.5.4. Remediation procedures

The various types for sediment remediation can be subdivided according to the mode of handling "in place" or "excavation", or in relation to the technologies "containment" or "treatment". Important containment techniques include *in situ* capping (ISC) and "confined disposal facility". Regarding in-place-treatment, biological processes may be applied. Excavated sediments—apart from physical separation—can be treated to immobilize pollutants, mainly metals. An overview on various technology types for sediment remediation is shown in Table III.5.1.

A more general conceptual scheme related to excavated sediment material has been proposed by the TNO, the Netherlands scientific technological organization (Van Gemert et al., 1988). "A-" and "B-" techniques are distinguished: A is for large-scale concentration techniques like mechanical separation; these techniques are characterized by low costs per unit of residue, low sensitivity to variations, and they may be applied in mobile plants. B-techniques are decontamination procedures, which are especially designed for relatively small-scale operations. They involve higher operating costs per unit of residue, are more complicated, need specific experience of the operators and are usually constructed as stationary plants. B-techniques include biological treatment, acid leaching, solvent extraction, etc.

The Dutch Development Program for Treatment Processes for Contaminated Sediments (POSW), starting up in 1989 and running until 1996, was aimed at the development of ecologically sound dredging and processing techniques, to be used in the

Table III.5.1. Technology types for sediment remediation.

Technology	In place	Excavated
Containment	Capping	Beneficial use Capping/confined aquatic disposal Commercial landfills Confined disposal facility
Treatment	Bioremediation Chemical Immobilization	Chemical Biological Extraction Immobilization Physical separation Thermal

remediation and reuse of polluted sediments (Anonymous, 1997; Rulkens, 2001). Technical applicability had to be demonstrated in practice, as part of an integrated remediation chain. Attention was also paid to the economic and environmental consequences of the several types of techniques as part of entire clean-up chains.

Typical research issues of the POSW Stage II (1990–1996) program were (Anonymous, 1997; Rulkens, 2001):

- Separation of sludge into subflows (hydrocyclone separation, upstream separation, settling, flotation, dewatering of fine fractions, practical experience in pilot remediation).
- Thermal and chemical treatment methods (thermal desorption, incineration, wet oxidation, solvent extraction).
- Biological treatment (landfarming, greenhouse farming, slurry treatment in bio-reactors).
- Immobilization of pollutants in products (melting, sintering, practical experience in pilot remediation).
- Assessment of the environmental effects of processing chains (based on life-cycle analysis, LCA).
- Scenarios for large-scale processing, varying from "natural" processes in treatment plants (sedimentation, dewatering, landfarming and ripening) to maximum deployment of classifying and polishing methods.

III.5.4.1. Chemical, biological and thermal treatment of dredged sediments

In the following, typical parameters are given for important treatment procedures as well as on the costs of such methods:

Factors affecting immobilization processes: solidification/stabilization is a commonly used term to cover immobilization technologies. The former is related to physical properties, the latter suggests chemical effects. Several factors negatively interfere with the objective to solidify or stabilize: organic compounds, oil and grease, inorganic salts such as nitrates, sulfates and chlorides, small particles sizes, volatile organic compounds, and low solids content.

Factors affecting solvent extraction processes: the primary application of solvent extraction is to remove organic contaminants such as halogenated compounds and petroleum hydrocarbons. Extraction processes may also be used to extract metals, but these applications, which usually involve acid extraction, have not proven to be cost effective for contaminated sediments. Fine-grained materials are more difficult to extract, and presence of detergents adversely impacts oil/water separation. The procedure is less effective for high molecular weight compounds and very hydrophobic substances. In any case, careful selection of reagents and laboratory testing is required.

Limitations to biodegradation processes: biological treatment has been used for decades to treat domestic and industrial wastewater, and in recent years has been demonstrated as a technology for destroying some organic compounds in contaminated soils. Bioremediation or biorestoration may be applied in certain cases to organically contaminated sediments. However, since in large catchment areas contamination with only organic compounds is rare, the expectations in this technique of remediation seem to

be overestimated. Often, the request for such procedures is a simple indication of ignorance for sediment pollution problems. Even in optimal cases, there are many limitations to biodegradation processes: Temperature, nutrients, and oxygen, are the most important ones.

Factors affecting costs for treatment technologies: cost estimations for decontamination techniques cover wide range for individual examples from the fields of bioremediation, chemical dechlorination, soil washing, solvent extraction, thermal desorption and vitrification. These are mostly well-known examples from industrial waste technology. Typical cost factors for sediments include water quantity, moisture contents, physical and chemical characteristics (e.g. grain size and organic material content).

In a trial to rank the individual technologies, one can follow the proposals in the Draft Remediation Guidance Document prepared by the USEPA Oceans and Coastal Protection Division/Great Lakes National Program. Three criteria have been used:

- *State of development*: is mostly good except for non-removal and treatment alternatives. Such deficiencies should be overcome by intensified research.
- *Potential contaminant loss*: is particularly high for removal. This would favor *in situ* techniques. ISC could be the method of choice for areas, where maintenance dredging is not essential.
- *Costs*: it is already clear at this point, that the cost factor will mostly exclude treatment (in the restricted sense) of large-volume contaminated sediments. The only possibility would be the reduction of the volume by mechanical pretreatment, after that chemical–biological techniques could be used potentially.

It is quite obvious that technological options are more restricted for dredged sediments than for other waste materials in most cases. In particular, remediation techniques in the restricted sense often are economically unacceptable because of the large volume of contaminated sediments.

III.5.4.2. Geochemical engineering – application to contaminated sediments

Geochemical engineering (Salomons and Förstner, 1988a,b) applies geochemical principles (such as concentration, stabilization, solidification, and other forms of long-term, self-containing barriers) to determine the mobilization and biological availability of critical pollutants.

In modern waste management, the fields of geochemically oriented technology include:

- the study of material fluxes within and between the anthroposphere and "geospheres";
- the optimization of elemental distribution at high-temperature processes;
- the selection of favorable milieu conditions for the deposition of large-volume wastes;
- the selection of additives for the solidification and stabilization of waste materials; and
- the development of test procedures for long-term prognoses of pollutant behavior.

As shown from the examples of large-mass wastes dredged material, mining residues and municipal solid waste, long-term immobilization of critical pollutants can be achieved by promoting less soluble chemical phases, i.e. by thermal and chemical treatment, or by providing respective milieu conditions. Selection of appropriate environmental conditions

predominantly influences the geochemical gradients, whereas chemical additives are aimed to enhance capacity controlling properties in order to bind (or degrade!) micropollutants. In general, micro-scale methods, e.g. formation of mineral precipitates in the pore space of a sediment waste body, will be employed rather than using large-scale enclosure systems such as clay covers or wall constructions. A common feature of geochemically designed deposits, therefore, is their tendency to increase overall stability in time, due to the formation of more stable minerals and closure of pores, thereby reducing water permeation.

III.5.4.3. Chemical stabilization by additives/storage under permanent anoxic conditions

In general, solidification/stabilization technology is considered a last approach to the management of hazardous wastes. The aim of these techniques is a stronger fixation of contaminants to reduce the emission rate to the biosphere and to retard exchange processes. Most of the stabilization techniques aimed for the immobilization of metal-containing wastes are based on additions of cement, water glass (alkali silicate), coal fly ash, lime or gypsum (Malone et al., 1982; Wiedemann, 1982; Goumans et al., 1991).

Laboratory studies on the evaluation and efficiency of stabilization processes were performed by Calmano et al. (1986). Best results are attained with calcium carbonate, since the pH-conditions are not changed significantly upon addition of $CaCO_3$. Generally, maintenance of a pH of neutrality or slightly beyond favors adsorption or precipitation of soluble metals (Gambrell et al., 1983). On the other hand, it can be expected that both low and high pH-values will have unfavorable effects on the mobility of heavy metals.

Regarding the various containment strategies it has been argued that upland containment (e.g. on heap-like deposits) could provide a more controlled management than containment in the marine environment. However, contaminants released either gradually from an imperfect impermeable barrier (also to groundwater) or from failure of the barrier could produce substantial damage (Kester et al., 1983). On the other hand, near-shore marine containment (e.g. in capped mound deposits), offers several advantages, particularly regarding the protection of groundwater resources, since the underlying water is saline and inherent chemical processes are favorable for the immobilization or degradation of priority pollutants.

In a review of various marine disposal options, Kester et al. (1983) suggested that the best strategy for disposing of contaminated sediments is to isolate them in a permanently reducing environment. Disposal in capped mound deposits above the prevailing seafloor, disposal in sub-aqueous depressions, and capping deposits in depressions provide procedures for contaminated sediment (Bokuniewicz, 1982). In some instances, it may be worthwhile to excavate a depression for the disposal site of contaminated sediment, which can be capped with clean sediment. This type of waste deposition under stable anoxic conditions, where large masses of polluted materials are covered with inert sediment became known as "subsediment-deposit".

Under subsediment conditions there is a particular low solubility of metal sulfides, compared to the respective carbonate, phosphate, and oxide compounds. One major prerequisite is the microbial reduction of sulfate. Thus, this process is particularly important in the marine environment, whereas in anoxic freshwaters milieu there is a

tendency for enhancing metal mobility due to the formation of stable complexes with ligands from decomposing organic matter. Marine sulfidic conditions, in addition, seem to repress the formation of mono-methyl mercury, one of the most toxic substances in the aquatic environment, by a process of disproportionation into volatile dimethyl mercury and insoluble mercury sulfide (Craig and Moreton, 1984). There are indications that degradation of highly toxic chlorinated hydrocarbons is enhanced in the sulfidic environment relative to oxic conditions (Sahm et al., 1986; Kersten, 1988).

However, if a permanent advective transport through the sediment interface occurs, which may be induced by groundwater seepage, contaminant flux will reappear after a short lag-time following sub-aqueous cap installation. The application of a relatively new method of reactive permeable barriers, i.e. capping layers that consist at least partly of one or more reactive components that are capable of actively demobilizing the contaminants in percolation porewater, may significantly enhance the ISC effect from a safety measure to a full remediation technique provided that the adequately efficient reactive materials for active barrier systems are applied. Highly favorable chemical and physical properties with respect to application in sub-aqueous capping projects, as well as cost-efficiency were found to show natural microporous materials, such as natural zeolites. A field-scale investigation on use of natural zeolite in active barrier systems has been currently conducted in the framework of an Australian–German research project, funded by the German Ministry of Research and Technology (Jacobs and Förstner, 2001).

III.5.4.4. In situ sediment treatment in flood plains

Another type of sediment pollution problems that differs from managing contaminated dredged materials at harbor sites, originate from large-scale dispersion, transport and deposition of contaminants in floodplains and polder areas. In the Spittelwasser Case Study (the upper Elbe river system), a stepwise approach combining different monitoring and remediation techniques has been proposed. These techniques would include point excavations of contaminated material, promotion of plant growth as an element for stabilizing the soil and flood sediments, and the installation of sediment traps. The "diagenetic" effects of natural non-destructive attenuation processes of organic and inorganic contaminants and their temporal development in these sediments and soils will be also studied. Significant reduction of the reactivity of solid matrices due to an enhanced mechanical consolidation of soil and sediment by compaction, loss of water and mineral precipitation in pore space is anticipated there, apart from chemical processes (Förstner, 2001c).

III.5.5. Conclusions

Technological options are more restricted for dredged sediments than for other waste materials in most cases. In particular, remediation techniques in the narrow sense often are economically unacceptable because of the large volume of contaminated sediments. The widely diverse contamination sources in larger catchment areas usually produce a mixture of pollutants, which is more difficult to treat than a specific industrial waste. Even if one

has procedures at hand to reduce 9 priority pollutants below the guideline values, number 10, for example for mercury or PCB may render the whole business unrealistic. There is a long retention time for sediments in larger catchment areas. Improvement at the source may need decades to become effective in the sediments at the lower reaches and harbors close to the river mouth. For most sediments from maintenance dredging, there are more arguments in favor of "disposal" rather than "treatment". Final storage conditions would imply, that these materials should be deposited in a favorable chemical environment. At the actual state of knowledge, this could only mean "permanent" anoxic conditions". Such conditions can be made artificially by capping or be selected from natural environments. However, even for these stable geochemical conditions, which are provided, for example, in natural environments such as the Black Sea and fjords, not all potential implications for long-term pollutant release and transformations are known, and therefore, further research is needed. Capping materials usually have been clean sediments, sand or gravel. The protective function of such "non-reactive" barriers, however, is so far restricted to site-specific settings where bioaccumulation of contaminants by benthic infauna, or resuspension and transport by erosive forces, or slow diffusive transport as it may be induced by groundwater seepage are the prevalent mechanisms in contaminant release. The application of reactive barriers, i.e. capping layers that consist at least partly of one or more reactive components that are capable of actively demobilizing the contaminants in percolating porewater, extends the ISC concept in that it is not further subject to this limitation. Thus continuous contaminant loss can be long-term active as well as diffuse transport may be inhibited efficiently by employing reactive barriers.

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III.6
Mining waste

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III.6.1. Introduction

III.6.1.1. Mining waste sources and amounts

Mining waste is the high-volume material that originates from the processes of excavation, dressing and further physical and chemical processing of wide range of metalliferous and non-metalliferous minerals by opencast and deep shaft methods. It comprises overburden, run-of-mine rock as well as discard, slurry and tailings from the preparation/beneficiation or extraction plants. Wastes from mineral excavation both under US Resource Conservation and Recovery Act (RCRA, 1976 with further amendments) and EU regulations pursuant to Article 1 (a) of Council Directive 75/442/EEC (1975) on waste and article 1(4) of Directive 91/689/EEC (1991) on hazardous waste is considered non-hazardous, though many aspects related to its safe disposal and use with respect to the environmental behavior and impact are applicable also to hazardous waste. Some types of wastes from physical and chemical processing of minerals are classified as hazardous in the European list of wastes (Commission Decisions 2000/532/EC and 2001/118/EC). These wastes comprise: acid generating tailings from processing of sulfide ore (code 01 03 04*); other tailings containing dangerous substances (code 01 03 05*); other wastes containing dangerous substances from physical and chemical processing of metalliferous (code 01 03 07*) and non-metalliferous minerals (code 01 04 07*), as well as drilling muds and other drilling wastes containing oil (code 01 05 05*) and dangerous substances (code 01 05 06*). The kind of mining waste and its share in the total waste stream in the different countries highly depend on their natural resources, economic value of a mineral and market demand, and therefore ranges from almost none to the predominant proportion. Unfortunately, due to the scarce statistical data, the information on the mining waste generated and disposed is not available for countries with the highest mining output, such as China, the USA, India, Australia, Russian Federation and South Africa.

Mining activities (excluding coal) in over 130,000 of non-coal mines concentrated largely in nine western states of the USA are estimated to produce between 1000 and 2000 million tons (Mt) of mining waste annually. These activities include extraction and beneficiation of metallic ores, phosphate, uranium and oil shale, and are reported to be responsible for polluting over 3400 mile (i.e. over 5470 km) of streams and over 440,000 acre (i.e. over 178,000 km^2) of land. About 70 of these sites are on the National

Priority List for Superfund remediation (Wilmoth, 2000). The total non-coal mine waste lying in dumps was estimated in 1985 at 50,000 Mt, of this 33% being tailings, 17% dump/heap leach wastes and mine water and 50% surface and underground wastes (1985 Report to Congress, after Wilmoth, 2000).

According to published incomplete data (not including the USA and 10 other countries), among 19 of the 30 OECD member states (OECD, 1997, 1999), Canada held the dominant position in the amount of mining waste generated annually (~65.4% of the total); 23 member states of OECD – Europe produced 402.4 Mt, which was about 25%, while 15 EU member states generated 19.0% of the total OECD production covered by statistics (see Chapter I, Table I.2.1).

According to EUROSTAT (2001), 15 EU member states, 3 associated countries and 11 candidates to the EU generated in 1995–1999, a total of 420.9 Mt of mining/quarrying waste. The biggest mining waste generators were the UK (28.0%), Germany (16.1%), Sweden (15.2%), Poland (11.8%) and Romania (11.4%).

The proportion of mining waste in the total waste stream in these countries differs considerably. In Poland, waste from mineral excavation comprised 36.5 and 35.3% of the total annual waste generation, and 44.0 and 39.8% of waste lying in dumps in 2000 and 2001, respectively, that reflects a decline of coal mining activity (Central Statistical Office, 2001, 2002). Waste from physical and chemical processing of metalliferous minerals, mainly copper tailings, comprised 24.1% of the total annual waste generation and 28.2% of lying waste, which constituted 59.4% of the total annual waste generation and 68.0% of waste lying in dumps (Central Statistical Office, 2002). In Spain, mining waste accounted for about 31%, in UK 17.5% (29.8% in 1999 after EUROSTAT, 2001) and in France 12.5% (Chapter I, Table I.2.1). In some EU countries, mining activity generates a substantial part of the waste stream, e.g. in Sweden (~53.4%) (OECD, 1999). The major demerit of both OECD and EUROSTAT statistical data is their incompleteness that causes significant divergence of these sources (see e.g. data for the UK).

The character of mining waste and their share of total waste stream in different countries and regions worldwide are determined by the mineral resources and the part, which mineral excavation constitutes in their economies.

Nowadays, Western Europe (EU-15 and associated countries) in general plays a modest role in the world mineral mining, producing scarcely from 1 to 8% of metalliferous ores and 2.3% of hard coal. Of 1872 identified mining sites in the EU, only 917 are reported to be still active, of which 740 sites produce industrial minerals, 119 coal, 45 non-ferrous metals and 13 ferrous metals (BGRM, 2001). It still occupies a leading place in mercury supply (Spain) and lignite excavation (Germany), and retains an important position in salt (Germany, Finland, UK, the Netherlands, Spain), potash (Greece) and sulfur mining (Germany, France, Finland and other EU Members) (Table III.6.1) (Coakley et al., 2002; Gurmendi et al., 2002; Kuo et al., 2002a,b). Western Europe continues to be a major world processor, fabricator and consumer of minerals, whereas Central Eurasia, mainly Russian Federation, Ukraine and Kazakhstan, remains one of the major world supplier of most mineral commodities (Kuo et al., 2002a,b). The leading positions in terms of the share of world output are held by Asia and the Pacific region, in particular China and Indonesia, and America (the USA, Canada and several Latin American countries), which are endowed with a great diversity and richness of mineral resources of all kinds (Gurmendi et al., 2002; Kuo et al., 2002b). Africa ranks first or second in terms of world mining of

Table III.6.1. World mining output of principal non-metalliferous and metalliferous minerals in 2000 (after Coakley et al., 2002; Gurmendi et al., 2002; Kuo et al., 2002a,b).

Mineral	Region or country														
	Thousand tons unless otherwise specified								Percentage of world total (%)						
	EU (+associates)	Europe and Central Eurasia	China	Asia and the Pacific	USA	Latin America and Canada	Africa	Total, world	EU (+associates)	Europe and Central Eurasia	China	Asia and the Pacific	USA	Latin America and Canada	Africa
Non-metalliferous minerals															
Hard coal	83,970 (84,300)	530,854	880,000	1,620,000	896,150	136,814	228,900	3,621,000	2.3 (2.3)	15	24	45	25	3	5
Lignite	243,651 (243,651)	565,098			77,600			857,000	28 (28)	66			9		
Salt	42,056 (42,360)	57,437	31,280	61,900	45,600	36,859		214,000	20 (20)	27	15	29	21	18	
Phosphate	700 (700)	13,501			38,600	3,189 (P_2O_5)	38,000	133,000	1 (1)	10			29	7	29
Sulfur (100%)	5,970 (6,088)	16,168			10,300	12,857		57,200	10 (11)	28			18	22	
Potash, K_2O	4,852 (4,852)	12,368			1,300			25,400	19 (19)	49			5		
Metalliferous minerals and ores (mining/metal production, in terms of pure ingredient)															
Iron ore	NA	NA	224,000	474,000	63,095	287,756	48,900	1,060,000	NA	NA	21	45	6	27	5
Pig iron			131,030	278,000	47,878			567,000			23	49	8		
Bauxite	1,991 (1,991)	11,673	9,000	72,000	NA	35,340	15,500	135,000	1 (1)	9	7	53	NA	26	11
Alumina	5,050 (5,050)	11,714	4,330	22,630	4,780			49,300	10 (10)	24	9	46	10		
Chromite	–						7,480	14,400							52
Copper	189 (189)	1,912	590	2,867	1,470	6,324	465	13,300	1 (1)	14	4	22	11	48	4
Zinc	672 (672)	1,339	1,710	3,560	829	2,597	260	8,730	8 (8)	15	20	41	9	30	3
Lead	235 (235)	417	570	1,377	468	600	177	3,100	8 (8)	13	18	44	15	19	6
Nickel			51	460	–	393		1,230	NA	NA	4	37	–	32	
Tin (t)	1,203 (1,203)	6,203	97,000	171,000	–	97,000		238,000	1 (1)	3	41	72	–	41	
Tungsten W (t)	2,350 (2,350)	5,850	37,000	38,000				45,200	6 (6)	16	82	84			
Cobalt (t)							14,000	33,300							42
Silver (t)	477 (477)	3,107			1,860	8,107		18,300	3 (3)	17			10	45	
Gold (t)	0.019632 (0.019632)	285.303	178	780	353	528	605	2,550	1 (1)	11	7	31	14	21	24
Mercury (t)	545 (545)	895	200	200	NA			1,350	40	66	12	12	NA		
Diamonds (th. carats)	–	23,200					61,700	118,000	–	20					52

NA, not available; –, zero.

diamonds, chromite, cobalt, gold, manganese, phosphate rock, bauxite and uranium; the highest diversity of mineral commodities is being mined in South Africa (Coakley et al., 2002). The world mining output of principal non-metalliferous and metalliferous minerals in 2000 is summarized in Table III.6.1.

The predominant place in the world supply of minerals with respect to the mined amounts is held by coal of all grades; hard coal (bituminous coal and anthracite) comprises 81% and lignite 19% of the total world coal output. Metalliferous ore mining is dominated by iron ore and bauxite production. Other mineral commodities that comprise a wide variety of industrial minerals, and ferrous and non-ferrous metal ores are mined in substantially smaller amounts with respect to the total world balance (Table III.6.1). The scale of a mined mineral output, besides the methods of excavation and processing, to a great extent determines the amount of waste generation.

The major high-volume waste-generating mining activity in many countries worldwide is coal mining. Coal plays an integral role in the economy of many countries, and thus constitutes a substantial part of the global stream of mining waste.

III.6.1.2. Coal mining waste

Known coal reserves are spread over almost 100 countries and estimated to last over 200 years. In contrast, proven oil and gas reserves are equivalent to around 40 and 60 years, respectively, and are concentrated in the Middle East and the former Soviet Union area. The total global hard coal production has shown almost 50% growth over the past 25 years (WCI, 2002b). A further increase in coal consumption, though unevenly distributed, by an average of nearby 1.9% per year up to 2010 is expected to fulfill a substantial part of the total world energy demand (Fig. III.6.1). In OECD Europe, coal use for power generation is forecast to decrease by 0.6–0.8% per year, while in North America an annual increase by 1.6% is anticipated. Unlike the stagnating or decreasing coal market in OECD Europe, for ASEAN countries the growth of coal use for power generation is expected to increase most dramatically by over 9% a year, and 2.8% for the rest of the developing economies including India and China. The growth of hard coal consumption in some developed economies, such as the USA, Australia and Japan, where increasingly competitive electricity markets favor low-cost power, is also projected. The expanding Asian coal market brings extensive opportunities for exporters of thermal coal, in particular for China, Australia, Indonesia and Latin America. The annual growth rate of Chinese thermal coal exports by 2010 is anticipated to be the highest (6.4–11.4%), while the largest coal exporter Australia, and emerging coal suppliers Indonesia and Latin America are likely to reach annual growth rates in the range 1.1–3.6%. The growth in the global consumption of coking coal by 2010 is estimated at 1.1% per year that is linked to increases in iron and steel production in Asia (WCI, 2002a).

Currently, the top three major coal producers are China, USA and India, which in 2001 covered 66.7% of the world's supply. Other 10 countries mined from 6.7 to 0.21% of world total hard coal output. Germany is the world's largest brown coal/lignite producing country (Table III.6.2). In OECD Europe, the biggest hard coal producer is Poland, where underground mining is concentrated in the Upper Silesia coal basin (USCB). In 1980–1985, the total coal output was 192–193 Mt (Central Statistical Office, 1996), falling down by 2001 to 104 Mt/a (WCI, 2002b). Further decrease of coal production below

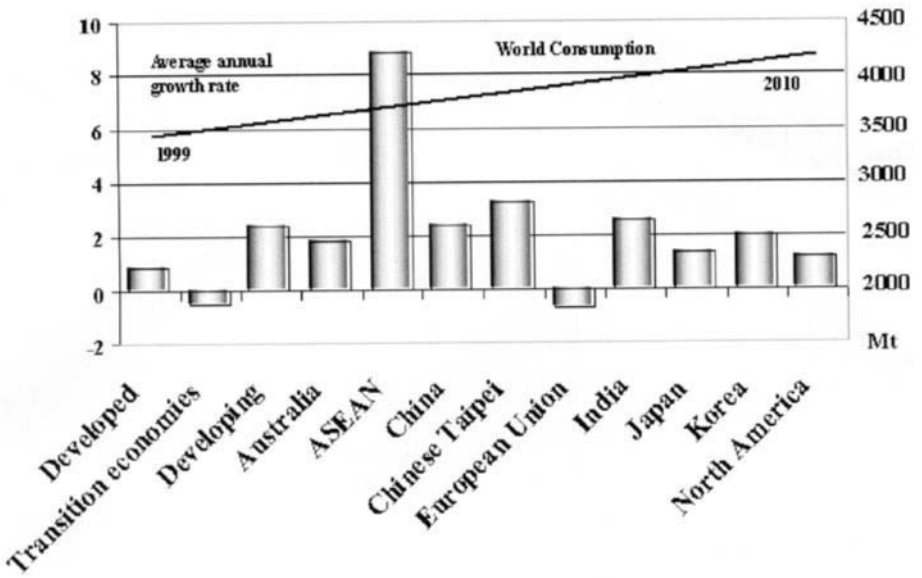


Figure III.6.1. Prospects for world hard coal consumption to 2010 (after WCI, 2002a; ABARE, 2002).

100 Mt/a will occur in 2003, reflecting general trends in coal consumption in OECD Europe that showed a dramatic decline of 95% (from 19.5 to 10% of global hard coal consumption) in two decades, 1981–2001. Coal consumption in North America remained stable (22–25%), while Asia-Pacific region showed continuous dynamic growth (from 34 to 52.5%). In 2000, 39.1% of total world electricity generation and almost 70% of total global steel production was dependent on coal, which confirms the importance of coal in total world primary energy consumption (WCI, 2002b).

The amount and characteristics of coal mining waste highly depends upon the local geological conditions and the methods of mining. As a result of mechanization of the mining, as well as of coal preparation process, the proportion of waste rock compared to the saleable coal produced accounts for some 30–50% (Glover, 1978). Annual world generation of hard coal mining wastes can be estimated roughly to be 1200–1400 Mt in 1995, and approximate amounts of wastes already lying in dumps throughout the coalfields of different countries account for 3000 Mt in the USA, 2000 Mt in the UK, 1200 Mt in China, 1000 Mt in South Africa, 600 Mt in Japan and 200 Mt in France (Skarżyńska, 1995a). In Poland, the waste/saleable coal ratio in 2001 was as high as 0.39; total hard coal mining waste generation accounted for 38.4 Mt, while 668.5 Mt were deposited in dumps in the USCB area (Central Statistical Office, 2002).

Considerable amount of coal mining waste deposited at the big central dumping sites or smaller colliery tips has been reused, predominantly in civil engineering. To underline beneficial properties of coal mining wastes and the commercial applicability in civil engineering, the term "minestone" for this material has been introduced by British Coal's Minestone Services, and since 1990 has been increasingly used by civil engineers involved in its reuse. By far, the biggest application for mining waste is as

Table III.6.2. Coal production and major producers in 1998, 2000 and 2001 (after Gurmendi et al., 2002; Kuo et al., 2000a; WCI, 1999, 2001, 2002b).

Producer	Hard coal						Producer	Lignite					
	Mt			% of total				Mt			% of total		
	1998	2000	2001	1998	2000	2001		1998	2000[a]	2001	1998	2000[a]	2001
World total	3,656	3,639	3,834	100			World total	895	857	903	100		
China	1,236	1,171	1,294	33.8	32.2	33.8	Germany		168		~20.0	19.6	
USA	936	899	945	25.6	24.7	24.6	Russia		84			9.8	
India[b]	303	310	312.5	8.3	8.5	8.2	USA		78			9.1	
Australia	219	238	257	5.6	6.5	6.7	Greece		62			7.2	
S. Africa	223	225	224.5	6.1	6.2	5.9	Poland		59			6.9	
Russia	149	169	168	4.1	4.6	4.4	Czech R.		51			6.0	
Poland	117	102	104	3.2	2.8	2.7							
Indonesia[b]	61.2	79	92.5	1.7	2.2								
Ukraine	74	81	82	2.0	2.2	2.2							
Kazakhstan	67	71	73	1.8	2.0	1.9							
Canada		69[c]			1.9								
Columbia[b]	33.8	38.1[c]		0.92	1.04								
Venezuela[b]	6.8	7.8[c]		0.18	0.21								

[a]Data for lignite production after Kuo et al., 2000a.
[b]Countries showing significant growth of coal production since the early 1980s.
[c]Data for coal, all grades after Gurmendi et al., 2002.

fill and earthworks material: (i) for restoration of mining subsidence areas in close proximity to mines and filling disused open pits and quarries, land leveling and elimination of surface irregularities on building sites; (ii) filling of disused canals and docks; (iii) mine backfilling; (iv) reclamation of municipal waste disposal sites (landfills). Another vast area of coal mining waste utilization is application as construction material in hydraulic and road engineering structures: river, road and railway embankments, dams, harbor constructions, quays, etc. Minor amounts of mining waste is used as raw material for manufacturing construction materials and mineral recovery (British Coal; Skarżyńska, 1995b).

In Poland, the reuse of carboniferous waste rock in 2001 accounted for 91% of its annual generation (Central Statistical Office, 2002). In 1995–1996, it was applied mainly at the surface for reclamation of land disturbed by mining (87.9%) with the remaining 12.1% being disposed off underground (State Inspectorate of Environment Protection, 1997). In 2000–2002, considerable amount of coal mining waste was used for road engineering and construction of river embankments. Application at the surface, besides undisputable economical and technical benefits, results in an extension of exposure to atmospheric conditions and development of the exposed surface of material, vulnerable to interaction with the environment, generally known as weathering processes. This leads to the considerable transformations of waste properties and chemical composition of pore solutions within the waste layer.

Coal mining waste is thus an abundant, high-volume waste worldwide, usually concentrated in the relatively small, but thickly populated coal mining areas, which brings about complex environmental problems, not always adequately recognized and managed.

Since coal mining is a source of the bulk amount of mine waste in Poland and also in the world as a whole, this chapter focuses on characterization of this waste with regard to its environmental impact. Environmental behavior of this material has been exemplified in the evaluation of pollution potential of coal mining waste generated and disposed in the USCB (Poland), on the background of the environmental issues in other coalfields of the world.

Simultaneously, it addresses the general aspects of leaching behavior of other groups of sulfidic wastes from metal ore mining that despite different origins, display a substantial similarity in geochemistry, major mechanisms of pollutant loads generation, release and transport to ground and surface waters (Lawrence, 1994; Ritchoe, 1994; Munroe and McLemore, 1999; Munroe et al., 2000).

III.6.2. Waste composition and properties

III.6.2.1. Waste sources and kinds

In general, coal mining waste comprise: (i) run-of-mine waste (usually dry rocks discharged directly from the mine workings, of particle size 0–500 mm); (ii) coarse-grained washery discard (wet solids of 10–250 mm discharged from dense medium separation); (iii) fine-grained discard (wet solids of 0.5–30 mm discarded from jigs); (iv) slurry, reject, tailings (solids < 1 mm from flotation process).

III.6.2.2. Lithological characteristics

Petrographically, coal mining waste consists of argillaceous and arenaceous rocks, represented mainly by mudstone, siltstone and sandstone with admixture of coal and coal shale.

The properties of freshly wrought waste largely depend on the regional variability and stratigraphic position of mined coal seams. In the USCB, they belong to the Westphalian A–D and the Namurian A–C series of the carboniferous formation. The proportion of run-of-mine and different kinds of washery discards in waste is also of considerable importance. In coal mining waste (known also as "spoil" or "minestone"), the predominant lithological type of rock is usually mudstone, which ranges from <50 to $>80\%$ of the total. Due to changeable petrographical composition of carboniferous strata, run-of-mine waste has a variable petrographical, mineralogical and chemical composition. The characteristic feature of run-of-mine is the frequent occurrence of just one type of rock, i.e. mudstone, siltstone or sandstone in the subsequent portions of output. The material is usually resistant to particle size degradation due to wetting and a low content of coal shale. Washery discards display much higher stability of composition, increasing with the decrease of the particle size. Along with the decrease of particle size of spoil, sandstone and siltstone contents also decrease, while the proportion of coal shale substantially grows. Average lithological/petrographical characteristics of waste disposed is a resultant of the lithology of mined seams determined by their location within the carboniferous sequence and the proportion of different waste kinds in the discarded output.

III.6.2.3. Mineralogical composition

Mineralogical composition of the waste material is determined by the presence or dominance of the particular lithological types of carboniferous rocks, which is, in most cases, mudstone. The major components of waste are thus clay minerals, quartz and coal. Clay minerals are predominantly those with non-swelling lattices: kaolinite/illite and minor amounts of chlorite. In rare cases, mixed swelling illite/montmorillonite structures also occur. Abundant component of mudstone is quartz (up to about 20%) and coal (up to several percent). In siltstone, quartz content is higher (up to 30%), while clay and coal proportions are distinctly lower than in mudstone; coarse-grained quartz is the major component of sandstone. Minor, but common components of coal mining wastes are feldspar, mica and plagioclase. All lithological rock types contain minor amounts of iron disulfide FeS_2 (mainly pyrite, more rarely marcasite) and carbonate minerals: calcite $CaCO_3$, dolomite $Ca,Mg(CO_3)_2$, siderite $FeCO_3$ and anchorite $Ca(Mg,Fe)(CO_3)_2$ in different proportions and concentrations. The lowest pyrite content is contained in sandstone, the highest in coal shale, as the main pyrite carrier in carboniferous rocks is coal. Sulfides of other metals also occur in trace amounts, e.g. chalcopyrite $CuFeS_2$ (in shale), sphalerite ZnS and galena PbS_2 (in shale and sandstone). Different trace metals are also ubiquitous admixtures in iron sulfide (Twardowska, 1981; Twardowska et al., 1988).

These minerals are commonly occurring in all mining waste, while presence, proportions and kinds of sulfide and carbonate minerals determine its pollution potential.

III.6.2.4. Chemical composition

The chemical composition of coal mining waste is a resultant of its lithological and mineralogical composition (Table III.6.3). Broad constituents' lithological/mineralogical composition and concentration range in the fresh wrought spoil reflect heterogeneity of rocks, both spatial and vertical, along the carboniferous profile, as well as the generic structure of waste. At the same time, comparison of data from different coalfields and countries, presented in the comprehensive overview by Skarżyńska (1995a,b), displays similarity of the component contents, though their overlapping within a wide range does not show the specificity of the particular materials with respect to critical factors and their interrelations, controlling the environmental behavior. In general, the trace element contents in coal and coal mining waste are within the range of mean, up to maximum concentrations occurring in the surface soils (Kabata-Pendias, 2001) (Table III.6.4). These elements are being released during the pyrite decomposition; therefore their migration to the groundwater with infiltration water determines the risk to the environment. In sulfidic metal ores, concentrations of metals in waste rock are determined by the metals and accessory elements extracted, and the efficiency of metal extraction.

Leaching of trace elements from coal mining waste was reported by different authors in late 1970s/early 1980s (Wewerka et al., 1976a,b; Palmer, 1978; Krothe et al., 1980; Twardowska, 1981), and registered directly by authors in pore solutions, leachate and groundwater in lysimetric and field studies, as will be presented further.

III.6.2.5. Environmental impact

The environmental burden of coal mining dumps, caused by obvious factors, such as development of an anthropogenic landscape, land deformation, problems with establishment of vegetation, self-ignitability and atmospheric pollution, has been known for a long time. Spontaneous combustion of waste dumps is being now effectively controlled by substantial reduction of coal content in spoil and air permeability of disposed material due to improvement of coal preparation, dump reshaping and compaction of waste in thin layers. At the same time, the pollution potential of coal mining wastes to the aquatic environment, though already recognized by specialists, is still not thoroughly understood by decision-makers and civil engineers dealing with waste management, since, hidden from view as it is, few realize how seriously the water resources can be compromised. Despite the knowledge of pollution potential formation processes and controlling factors suggesting a specific approach to the evaluation of coal mining waste pollution potential (e.g. Caruccio, 1975, 1978; Palmer, 1978; Twardowska, 1981; Twardowska et al., 1988, 1990; Hutchinson and Ellison, 1992), as well as a general evidence on the time-delayed, long-term adverse environmental impact of coal mining waste (e.g. Glover, 1978; Nutting, 1987; Szczepańska and Twardowska, 1987; Sleeman, 1990; Twardowska and Szczepańska, 1990; Hutchinson and Ellison, 1992), there is still a common practice of evaluation of the pollution potential of these wastes on the basis of a simplified batch leach testing of fresh wrought material (e.g. Cañibano et al., 1990), while the long-term environmental impact of sulfide-bearing non-coal mining wastes has been recognized and considered since a long time (Durkin and Hermann, 1996).

Table III.6.3. Chemical composition of coal mining wastes from the USCB, Poland (%, dry weight).

Constituent	Run-of-mine waste 0–500 mm	Washery discards from		Slurry, tailings (<2 mm)
		DLS[a] (20–200 mm)	Jigs (20–0 mm)	
Min–max concentration range				
LOI	2.40–42.47	8.13–52.88	17.04–68.02	23.24–62.51
SiO_2	32.81–89.36	22.08–61.07	25.79–58.39	11.30–37.79
$Al_2O_3 + TiO_2$	3.46–28.97	12.79–28.09	12.98–26.50	5.80–21.85
Fe_2O_3	1.18–9.77	1.40–13.88	2.19–11.80	3.10–28.64
CaO	0.00–3.75	0.00–4.48	0.38–4.40	0.78–11.95
MgO	0.00–3.32	0.11–5.70	0.47–3.30	1.17–4.96
$Na_2O + K_2O$	1.26–5.14	0.05–3.62	0.37–3.23	0.77–2.55
MnO	0.01–0.21	0.65[b]	0.03–0.19	
S_t	0.03–2.93	– 3.91 (5.29[c])	0.22–4.17	0.32–7.71 (21.60[b])
CO_2	0.00–5.26	0.00–7.16	5.84[b]	1.66–12.70
C	0.48–25.65	0.38–31.69	8.09–43.47	7.98–50.65
Mean concentration range				
LOI	6.89–18.16	11.31–35.54	22.93–37.18	29.36–45.60
SiO_2	51.19–74.84	42.13–56.94	31.61–56.77	21.83–33.10
$Al_2O_3 + TiO_2$	10.16–26.26	18.00–25.32	13.09–25.80	9.92–18.00
Fe_2O_3	2.07–6.65	2.94–9.49	2.19–11.80	4.54–19.41
CaO	0.32–1.16	0.50–3.31	0.38–2.89	1.35–9.38
MgO	0.68–1.88	1.09–3.60	0.83–3.09	1.58–4.79
$Na_2O + K_2O$	1.57–4.05	0.42–3.70	0.85–3.38	1.44–2.09
MnO	0.05–0.10	0.03–0.29	0.05–0.13	
S_t	0.16–0.71	3.00[b]	0.33–3.09	0.48–5.58 (12.98[c])
CO_2	0.31–1.64	0.24–4.60	0.17–5.52	1.68–11.00
C	3.84–9.80	3.93–18.88	10.58–26.94	11.49–35.42

[a]DLS – dense liquid separator.
[b]Single available value.
[c]Single outlier value.

Table III.6.4. Concentrations of trace elements in coal and coal mining waste (mg/kg).

Trace element (mg kg^{-1})	USCB, Poland		The Netherlands	Soils of the world[a]	
	Coal mining waste, seams 100–700	Pyrites, coal seams 618–625	Coal[b]	Min–max	Average
As	3.5–4.3	0.02–0.63	3.7	<0.1–66.5	4.4–8.5
B			43	<1–210	22–45
Ba			158	10–1,500	330–520
Be	<0.10–0.40		3.3		
Br			5.4		
Cd			0.10	0.01–2.7	0.37–0.62
Ce			17		
Co	4.2–115	0.01–0.21 (10.18[b])	5.8	0.1–70	5.5–12
Cr	12–21		14.4	1–1,100	47–83
Cs			1.0		
Cu	4.6–190.5	0.10–0.24	16.6	1–140	13–24
Eu			0.4		
F	11–75		80	<10–1,194	130–550
Ga	8–9				
Ge	<5		2.0		
Hf			1.2		
Hg			0.16	0.008–1.11	0.05–0.1
I			2.2	<0.1–10.8	1.7–3.4
La			7.6		
Mn	14–42		4	7–9,200	270–525
Mo	<2	0.88–1.12	3.0	0.1–7.4	1.3–2.8
Ni	7–60	0.00–0.16	11	0.2–450	13–34
Pb	11–44.7		8.5	1.5–176	22–28
Rb			9.2		
Sb			0.8		
Sc			3.3	0.8–30	5–10
Se		0.00–0.17	2.2	0.005–1.9	0.25–0.38
Sm			1.8		
Sr			107	5–1,000	87–210
Th			2.9		
Tl			1.0		
U			1.5		
V	52–60		29	6.3–500	67–115
W			1.0		
Zn	17.6–525		24	3.5–770	45–100
Zr	6–8				

[a]Kabata-Pendias (2001).
[b]Meij and Schaftenaar (1994).

III.6.3. Pollution potential of mining waste to the aquatic environment

III.6.3.1. Factors determining leaching behavior of waste

Pollution potential to the aquatic environment from coal mining and other mine waste disposed in tips or used in civil engineering works is determined by several basic factors: (i) content of soluble compounds (chlorides and sulfates) in fresh wrought rock material; (ii) content and reactivity of iron disulfide FeS_2 (pyrite, marcasite) and other sulfides, chemically unstable under atmospheric conditions; (iii) buffering capacity of Ca, Mn-carbonates and aluminosilicates; (iv) occurrence and availability of trace elements in the waste matrix and the vadose zone beneath a waste layer; (v) water balance, hydraulic conductivity and air penetration to the waste layer.

While soluble compounds in fresh wrought waste (chlorides and sulfates) determine the initial pollution potential of the material, the total life cycle pollution potential of waste, its extent, duration and character are dictated by the dynamics of generation, release and migration of qualitatively and quantitatively new loads of pollutants generated from the decomposition of geochemically unstable constituents, of which iron disulfide FeS_2 is a critical one. Complex physical and biogeochemical transformations in time that mining waste rocks undergo as a result of exposure to the atmospheric conditions, are known as weathering processes and comprise: (i) physical particle size degradation in rock material due to cyclic wetting–drying, freezing–thawing; (ii) chemical or biochemical decomposition of sulfide minerals with consecutive interaction of reaction products with other constituents of wastes, formation of secondary minerals, release, migration and transport of newly formed constituents within the waste layer and in to the dump bedrock, and interaction of leachate with the compounds of the vadose zone.

III.6.3.2. Pollution potential of fresh wrought waste

Soluble compounds in the fresh wrought waste discharged from the USCB occur in relatively low concentrations, usually from 0.1 to 0.5% wt, rarely >1% wt, and comprise mainly chlorides ranging from 0.001 to about 0.1% wt balanced by sodium ions, and minor amounts of sulfates. Chlorides occur predominantly in pore solution. Their content in mining waste is a function of chloride salinity of mine water and porosity of the rock material, which confirms that chloride content in carboniferous strata is a consequence of filling pore voids with water occurring in the strata. In the USCB, the chloride salinity of mine water of the carboniferous sequence is highly variable and shows both regional and vertical hydrogeochemical zonality (general increase with depth), while chloride concentration in rock material (C_{Cl}, mg/100 g) can be derived from an equation (Herzig et al., 1986; Twardowska et al., 1988; Szczepańska and Twardowska, 1999) showing good conformity with the direct measurements:

$$C_{Cl} = 3.6889 c_{Cl}^{0.621} W \qquad \text{(III.6.1)}$$

where c_{Cl} is the chloride salinity of ambient mine water, g/l and W the natural moisture content of a rock, %.

Beside chlorides, soluble compounds in fresh wrought material comprise sulfates. Their concentration in rock is generally low (from 0 to 3–5% of the total sulfur content S_t), while the pH is neutral up to weakly or moderately alkaline, within the stability field of the majority of trace elements. Therefore, the pollution potential of fresh wrought waste is relatively low, though it cannot be neglected due to specificity of constituents' migration in the anthropogenic and natural vadose zone under the conditions of waste disposal in dumps or use for civil engineering constructions (that will be discussed further).

III.6.3.3. Long-term pollution potential of mining waste

III.6.3.3.1. Acid generation potential

III.6.3.3.1.1. Mechanism and kinetics of acid generation

Long-term pollution potential of mining waste results from the oxidation of the thermodynamically instable sulfide minerals (predominantly iron disulphide FeS_2: pyrite, occasionally marcasite and minor amounts of other sulfides) in waste rocks extracted from underground anoxic environment and exposed to air and water on the surface. This process may result in the formation of an acidic and sulfate-rich solution that has the potential to mobilize toxic trace metals both from waste and any material or the vadose zone matrix of the bedrock. The mechanism of iron sulfide oxidation is generally recognized as a multi-stage process involving direct abiotic pyrite oxidation from the reaction with oxygen and water, indirect reaction with ferric iron and biochemical oxidation by bacteria *Thiobacillus ferrooxidans*. The mechanism of reaction as a three-stage process proceeding both abiotically and by direct bacterial oxidation was presented by Kleinmann et al. (1981):

1. $2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$ (III.6.2)

2. $4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^+$ (III.6.3)

3. $2Fe^{2+} + O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O$ (III.6.4)

4. $FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$ (III.6.5)

Stage I: Reaction 1 – both mechanisms, Reaction 2 – abiotic; gradually slowing down. Chemical conditions: pH > 4.5; high SO_4^{2-}, low Fe^{2+} and acidity.

Stage II: Reaction 1 – both mechanisms, Reaction 2 – bacterial oxidation. Chemical conditions: pH 2.5–4.5, high SO_4^{2-} and acidity, increasing Fe_t, low Fe^{3+}/Fe^{2+}.

Stage III: Reaction 3 – totally bacterial oxidation, Reaction 4 – rate determined by Reaction 3. Chemical conditions: pH < 2.5, high SO_4^{2-}, acidity, high Fe_t and Fe^{3+}/Fe^{2+}.

Various aspects of the process have been discussed in a vast number of publications. A comprehensive review of the state of the art concerning acid-forming processes in sulfide-bearing rocks is presented by Hutchinson and Ellison (1992). The intensity of sulfide decomposition, which is typically a surface process, and the resultant acid and sulfate generation capacity depends on the pyrite content, specific surface of pyrite grains and availability of reagents, i.e. oxygen and water that also plays the role of transport means for the generated reaction products.

It has been shown by Caruccio (1978), Caruccio and Geidel (1981) and Caruccio et al. (1983) that the sulfide oxidation and acid generation is a direct function of the

mineralogical and textural mode of the sulfide, which determines the specific exposed surface area. Low-crystalline metacolloidal and framboidal forms show particularly high reactivity.

Physical weathering or mechanical crushing of the rock material also facilitates sulfide oxidation due to the increase of physical accessibility. In turn, the secondary mineral formation in the reactions (gypsum, jarosite, melanterite, copiapite, etc.) may cause coating of mineral surface and thus decrease its availability to reagents.

It should be added that the extensive sulfide oxidation occurs predominantly under the vadose zone conditions, while in a water-logged material the intensity of the process is very low due to the lack of oxygen accessibility.

In general, duration and extent of sulfide oxidation is determined by the reaction kinetics (sulfide reactivity) that can be expressed in terms of half-life of sulfide ($t_{1/2}$ days) or intensity of acidity or sulfate generation vs sulfide content in rock material expressed as a first-order kinetic equation (Caruccio, 1975):

$$(C_S)_t = (C_S)_0 \exp(-kt) \tag{III.6.6}$$

where $(C_S)_t$ is the residual sulfide content in waste (mg/100 g) after a period of time t (days), $(C_S)_0$ the initial sulfide content in waste material (mg/100 g) and $k = \ln 2 \cdot t_{1/2}^{-1}$ the kinetic constant (days^{-1}).

III.6.3.3.2. Acid generation potential of coal mining waste

III.6.3.3.2.1. Sulfide abundance

Total sulfur content S_t of coal mining waste from the USCB ranges from 0.01 to above 10% wt, the mean value being as low as about 1% wt. The dominating form is sulfide sulfur, mainly pyritic S_p, comprising 85–95% S_t. In the carboniferous strata of USCB, the organic sulfur content is negligible (in some world coalfields and mining areas, e.g. in the majority of those in India, organic sulfur is abundant or prevails). The main sulfur-bearing rock is coal. In the USCB, sulfur concentrations in coal display spatial zonality, and generally increase in SW to NE direction, showing the highest concentrations in the shallow seams of 100 and 200 group (Westphalian C, D series), while the mean S_t content in coals from two-thirds of all mines is below 1% (Szczepańska and Twardowska, 1999). A similar tendency is shown in the wrought waste material also. In conformity with coal content, the highest sulfur concentrations occur in coal shale, lesser in mudstone. Distinctly, the poorest in sulfide is sandstone. During the coal preparation process, due to the difference of the specific gravity of coal and pyrite, considerable amounts of FeS_2 pass to waste, enriching particularly the finer-grained material (Table III.6.3). In general, though, sulfur content in the averaged waste material does not exceed 1%, occurring most frequently in the form of pyrite, occasionally marcasite.

III.6.3.3.2.2. Textural forms of sulfides in waste rock from the USCB

Grain size of crystals ranges from micrometers to several millimeters, present separately or in aggregates of size ranging from several tens of μm (mainly in shale) to about 3 mm. Practically in all rock material, the advanced process of sulfide crystallization or re-crystallization is observed. The crystallization of sulfides is the most advanced in

sandstone, weaker in coal, the weakest in shale, where the finest microcrystalline aggregates were preponderant.

With respect to the primary and secondary sulfide deposits, three major FeS_2 generations were identified.

- Syndiagenetic: the oldest one, represented by ball, framboidal, more seldom striped, impregnating, metacolloidal and microcrystalline textures.
- Anadiagenetic: younger generation represented mainly by organogenic, but also stripe/lenticular and pseudo-vein forms.
- Catadiagenetic: the youngest generation, where sulfide grains occur in pocket or vein forms and crystal aggregates.

Generally, in the older stratigraphic rock formations, the proportion of crystalline forms increases, while metacolloidal and framboidal sulfides decrease, though no distinct spatial regularities were found. Sulfide abundance, availability to water and air and the extent of the specific surface development are the critical factors for the acid generation potential of waste material.

Taking into account substantial differentiation of textural modes of sulfides in different types of waste and rock position along the carboniferous sequence, different ranges of pyrite reactivity of wastes from different seams could also have been anticipated.

III.6.3.3.2.3. Sulfide reactivity

The half-life of sulfide in rock along the Upper Silesia carboniferous sequence, $t_{1/2}$, was found to range within the wide limits: from 29.11 to 10,502 days, following a log-normal distribution. The mean half-period was estimated to be $t_{1/2} = 588.2$ days, and the sulfate generation rate per mass unit of rock R_{SO4} was 20.8 g/t d (Fig. III.6.2A and B) at full accessibility of oxygen and moisture to the pyrite surface (Witczak and Postawa, 1993). Under natural conditions, though, in coarse-grained and compacted material disposed at the dumps, the process is substantially slower.

Sulfide reactivity shows clear dependence on the rock lithostratigraphic position (Fig. III.6.3). Observations confirmed the highest reactivity of syndiagenetic framboidal, microcrystalline and organogenic forms and resistance of catadiagenetic vein and aggregate forms. Sulfides occurring in coal and mudstone display the highest decomposition rate, while sulfides present in sandstones are the most resistant to decomposition. Corrosion of sulfides is being developed in microfissures and along the borders of aggregates. The factors stimulating reactivity appeared to be the occurrence of microfissures, textural type of sulfides and structural type of sulfide mineralization.

III.6.3.3.3. Buffering capacity of coal mining waste

III.6.3.3.3.1. Principal components of buffering

The pollution potential of coal mining waste and other mining waste, besides acid generation due to sulfide oxidation, depends also on the buffering capacity of the material. The principal acid-consuming processes are: (I) reaction with calcium and magnesium carbonate minerals: calcite $CaCO_3$, dolomite $CaMg(CO_3)_2$ (siderite $FeCO_3$ has no neutralizing properties) and (II) reaction with aluminosilicates, involving two mechanisms: (i) cation exchange capacity of clay minerals (most abundant in waste kaolinite,

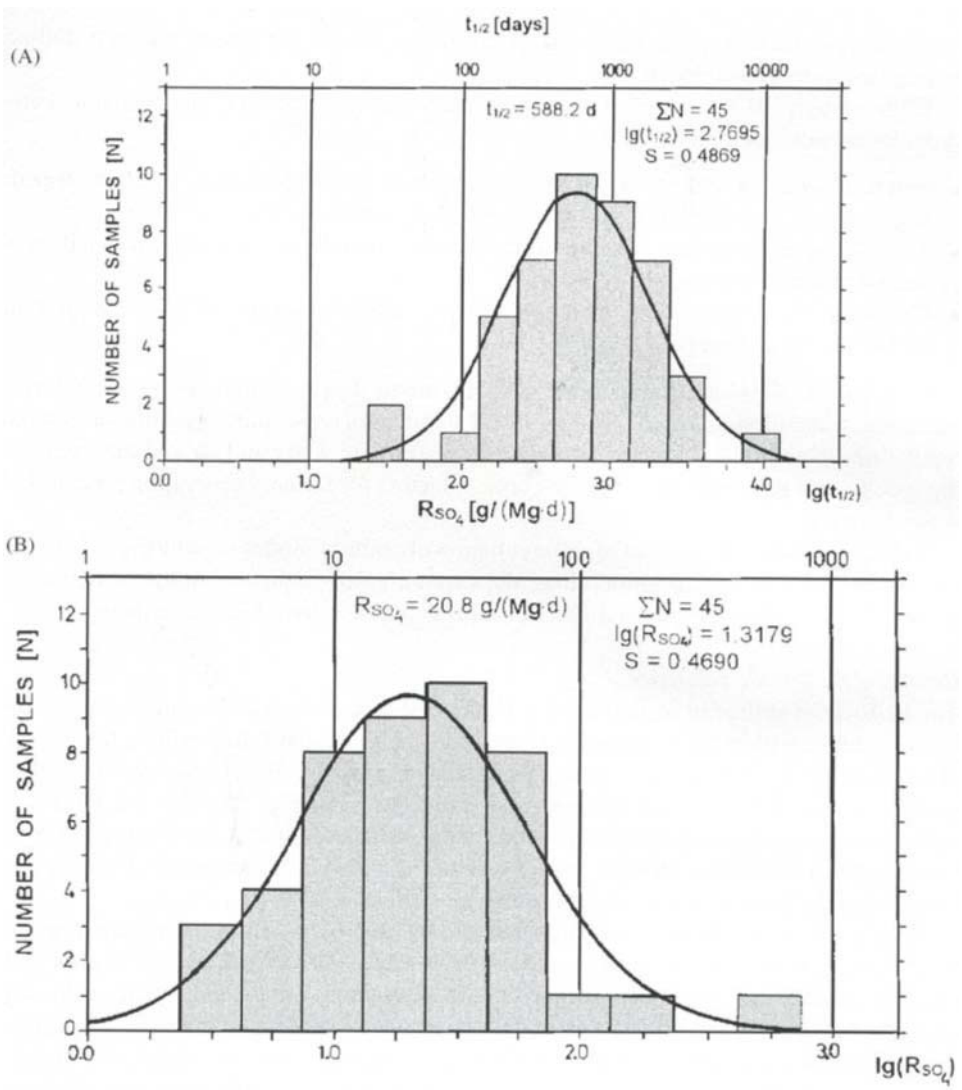


Figure III.6.2. (A) Distribution of sulfide half-life values for rocks of the Upper Silesia carboniferous sequence (Poland). (B) Distribution of sulfate generation rates in the rocks of the Upper Silesia carboniferous sequence (Poland).

illite, chlorite) and mica; (ii) dissolution of aluminosilicates and silicates (e.g. feldspars) with formation of Al-rich clay minerals or hydrolysis in solution of aluminum ion released from the lattice of clay minerals, congruently limited by dissolution of kaolinite (Palmer, 1978; Hutchinson and Ellison, 1992).

Just Ca^{2+}- and Mg^{2+}-carbonate buffering and the cation exchange in clay minerals have the neutralizing effect (pH $\approx$ 7.0, dependent on the pCO_2). Coal mining waste is rather poorly buffered in the range pH 5.0–3.5, while high acid consumption at

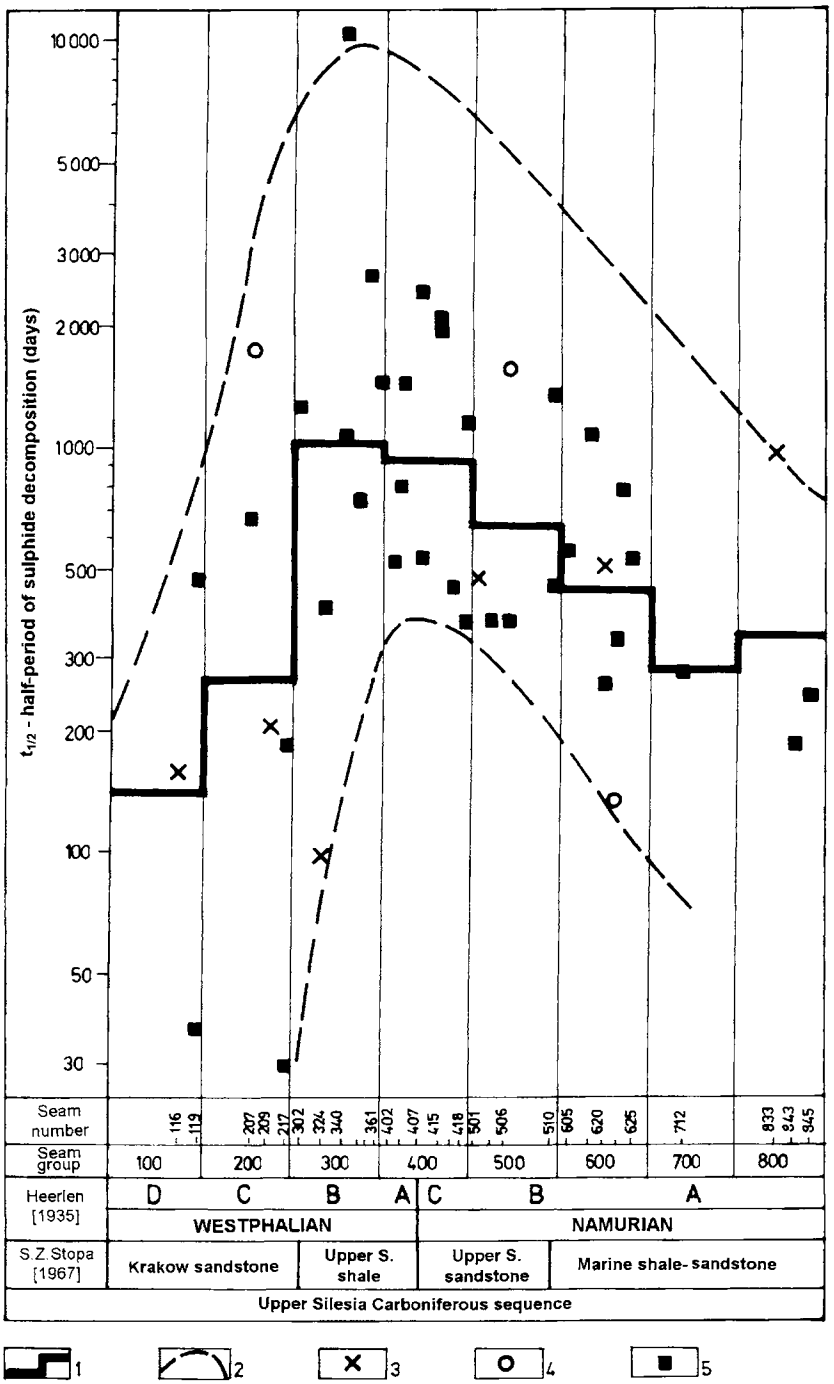


Figure III.6.3. Variability of sulfide half-life values along the Upper Silesia carboniferous sequence. 1, Estimated values of $t_{1/2}$ for seams of Upper Silesia carboniferous sequence; 2, range of $t_{1/2}$ variance; 3, mudstone; 4, sandstone; 5, coal.

the dissolution of aluminosilicates occurs at low pH range 2.5–2.8 (Palmer, 1978; Hutchinson and Ellison, 1992). From the environmental safety reasons, buffering at pH values close to neutral, which are within the stability fields of trace elements, is of particular importance.

III.6.3.3.3.2. Buffering capacity and mechanism

The main part of buffering capacity comprises calcium and magnesium carbonates (calcite and dolomite). Exchangeable ions are also of considerable importance.

Though clay minerals are abundant compounds of coal mining waste, the preponderance of minerals with non-expanding lattices in the carboniferous sequence of the USCB (kaolinite, illite, accessory chlorite) results in the relatively low cation exchange capacity of fresh wrought rock material ($CEC_t = 47-113$ eq/Mg) ranging within the mean values specific for kaolinite. Composition of exchangeable ions distinctly depends upon the chloride salinity of ambient mine waters. Downwards in the carboniferous profile, the proportion of Na^+ ion in sorption sites grows (up to 43–72%) in parallel with the increase of mine water and rock salinity. This leads to the conclusion that sodium ions were introduced onto the exchange surfaces through cation exchange with mine waters. The rest of the exchangeable places are occupied by Ca^{2+} and Mg^{2+} ions. The proportion of exchangeable ions in the total buffering capacity (C_{buf}) ranges from 7 to 40%.

In general, in buffered Ca,Mg-carbonate-rich material of low NaCl salinity, the role of cation exchange capacity of the material in acid buffering is minor (Figs. III.6.4I and III.6.5I), while in Na-saline and low-buffered rocks, cation exchange processes are of considerable importance. In buffered material, the effect of buffering through ion exchange results in displacing alkali in exchange surfaces for Ca^{2+} and Mg^{2+} ions, and thus in mainly qualitative changes of CEC_t (Figs. III.6.4II and III.6.5II). In low-buffered rock, further decrease of Ca^{2+} displaced by H_3O^+ ions, increase of the Mg^{2+} proportion and decline of the total sorption capacity CEC_t occurs (Figs. III.6.4III, III.6.5III and III.6.6). In deeper layers of the dump, these processes are time-delayed with respect to the surface layer (Figs. III.6.4–III.6.6). The H_3O^+ ions in low-buffered rock may further displace Al^{3+} ions from the lattice, enriching pore solution. The pH of a solution is then determined by the hydrolysis reaction of aluminum ions (at the level $\leq$pH 5), limited by the dissolution of kaolinite and reaction with aluminosilicate minerals (feldspar) at low pH <3.5, affecting the composition of the pore solution.

Buffering of acidification potential by Ca^{2+}- and Mg^{2+}-carbonates in the coal mining waste dumps occurs by two different mechanisms, dictated by the heterogeneity of the rock material. This buffering of acidification results from the occurrence of acid-generating and buffering minerals in different microenvironments and makes their direct interaction difficult. (i) The acid generation and equilibrium-limited process of carbonate dissolution occur independently in pore solutions of separate microenvironments; protons and carbonate ions migrate to water infiltrating through voids of the dump where neutralization of acidity occurs. (ii) Decomposition of carbonates results from its direct interaction with acid loads and transfer of Ca^{2+} and Mg^{2+} ions to infiltrating solution.

The process of carbonate dissolution is determined by the equilibria constraints, mineralogical form, extent of crystallization and abundance in the rock matrix. Carbonate minerals are ubiquitous components in the seams of the Upper Silesia carboniferous sequence and occur in the form of a binder or a component of the binding agent in

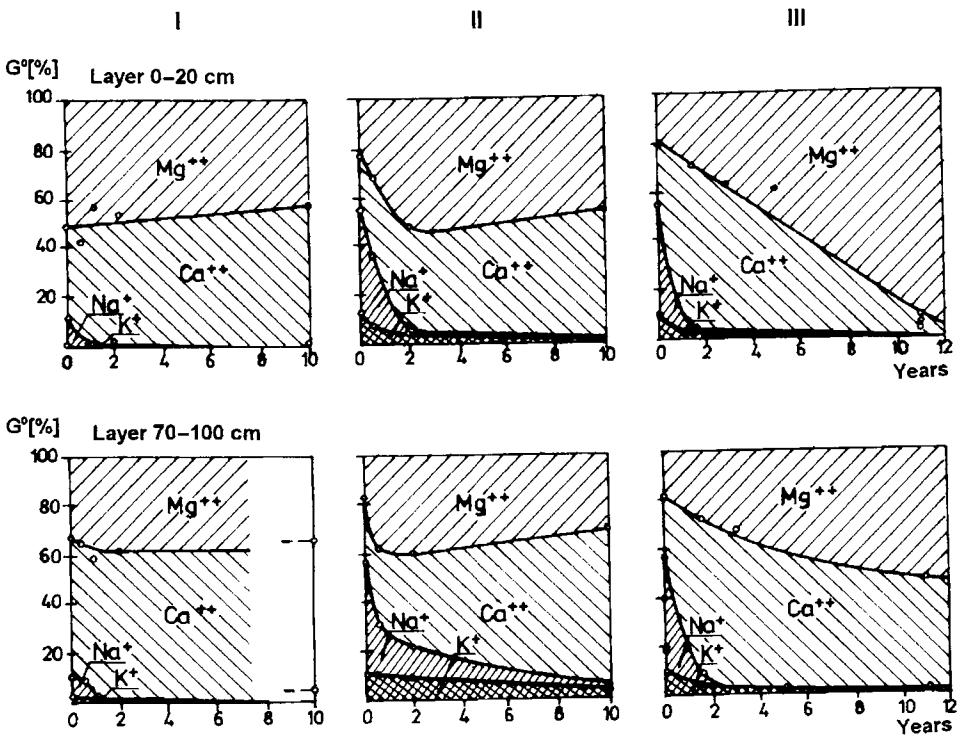


Figure III.6.4. Qualitative transformations of exchangeable ion composition in disposed coal mining waste of different buffering capacity and chloride salinity vs period of dumping. (I) Buffered waste from Siersza mine ($\xi = 2.5$) of a low chloride salinity (0.95–1.96 eq Cl/t), Siersza-Misiury dump; (II) buffered waste from Pawlowice mine ($\xi = 3.3$) of a high chloride salinity (28 eq Cl/t), Przezchlebie dump; (III) low-buffered waste from Szczyglowice mine ($\xi = 0.60$–0.70) of a mean chloride salinity (15.0 eq Cl/t), Smolnica dump.

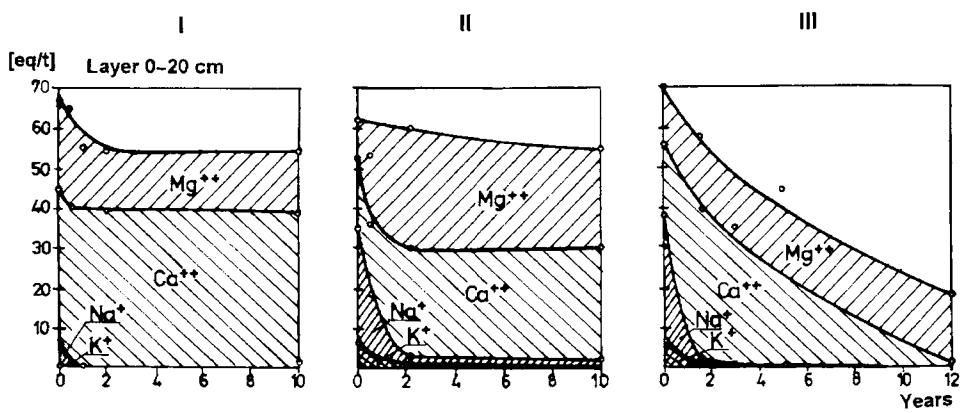


Figure III.6.5. Quantitative and qualitative changes of cation exchange capacity of disposed coal mining waste of different buffering capacity and chloride salinity vs period of dumping. Descriptions as in Figure III.6.4.

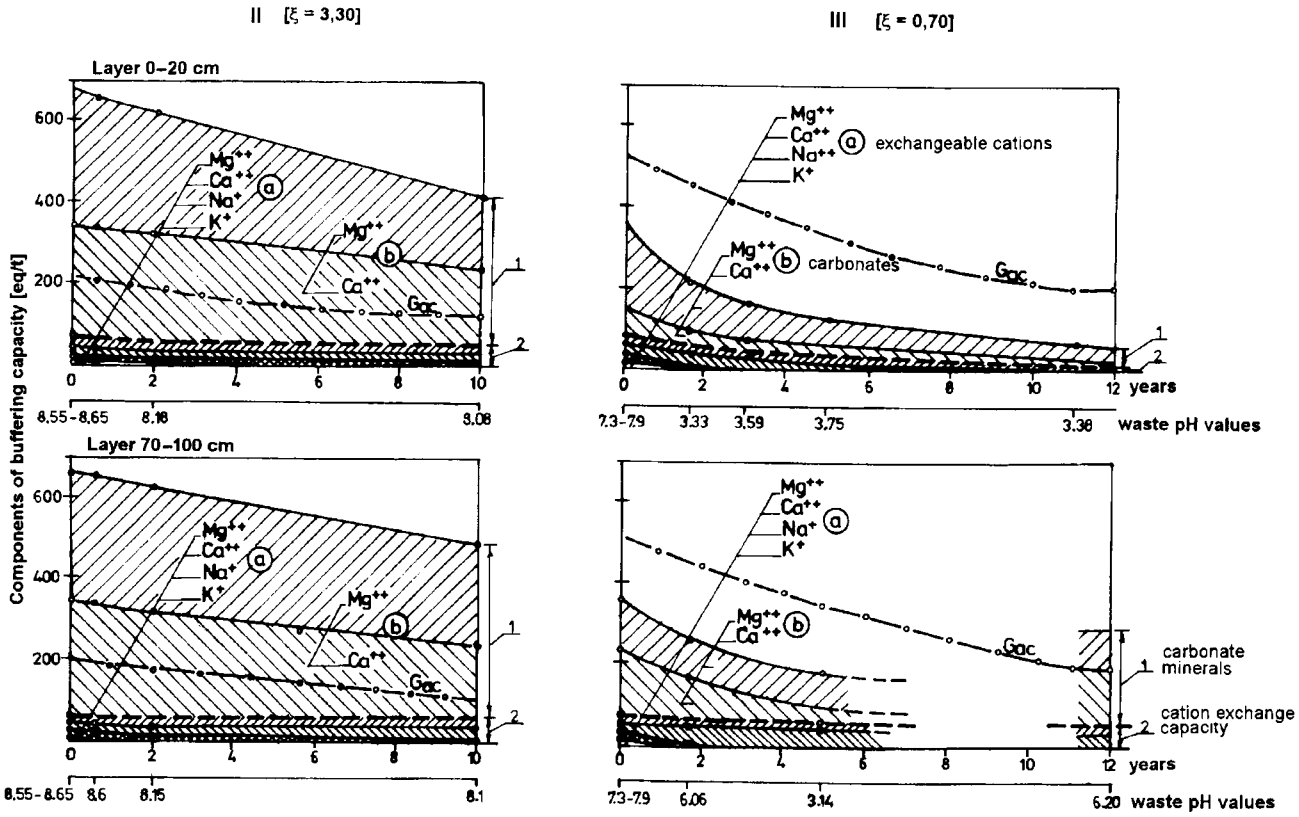


Figure III.6.6. Changes of buffering capacity of buffered (II) and low-buffered (III) coal mining waste disposed at a dump vs period of dumping. Descriptions as in Figure III.6.4.

sandstone, aggregates in mudstones and coal, as well as veins, impregnations and pockets in coal seams. In some parts of a seam, carbonates occur in a disseminated, fine- or microcrystalline form. As both the direct and indirect buffering by carbonates is a surface process, the specific surface of carbonates is an important factor in the process efficiency. No clear regularity in abundance and mineralogical forms of carbonate occurrence along the profile of the USCB carboniferous series has been observed. This hinders the accurate prognosis of the buffering capacity of the waste rock material on the basis of the stratigraphic position of a mined seam.

Due to the domination of the indirect buffering mechanism by means of the dissolution of the carbonate minerals, the acidification of low-buffered material deposited at the dump depends on the length of a dry period. Maximum acid load in the rock occurs at the end of a dry period, when acid generation proceeds, but is not released due to the declining infiltration or lack of flushing. The total load of the generated acid is therefore proportional to the duration of the dry periods, while dissolution of buffering carbonates is limited by equilibria constrains (Garrels and Christ, 1965; Pačes, 1983; Brookins, 1988). This statement has been thoroughly confirmed by field results (Vimmerstedt and Struthers, 1968; Morth et al., 1972; Twardowska, 1981; Twardowska et al., 1988; Olyphant et al., 1991) and column studies (Geidel and Caruccio, 1977; Geidel, 1979; Twardowska, 1981), when maximum acidification of rock and leachate from the coal mining waste dump was observed after long dry periods. In case of the permanent leaching/flushing, the acidification often does not occur even in low-buffered material. A particular vulnerability of a rock material to acidification in the top layer of the dump (Neumann-Malkau, 1993), besides other factors such as permeability to air, is due to the more frequent water deficiency than in deeper layers. This results in lower availability of dissolved carbonates at the same acid generation rate.

The secondary products forming as a result of buffering reactions within the matrix are mainly gypsum appearing commonly as precipitate on the rock particles in the mining waste dumps of USCB and iron hydroxide (Twardowska, 1981, 1986). Other identified secondary minerals are jarosite, melanterite, copiapite, halotrichite (Caruccio, 1978; Hutchinson and Ellison, 1992). Possible coating effect of precipitates is assumed to have stronger effect on shielding buffering minerals than on acid generating process (Hutchinson and Ellison, 1992).

Taking into consideration that the pollution potential of mining wastes largely depends on susceptibility to acidification, which commonly is a time-delayed process, the evaluation of acid generation potential of wastes is of particular importance. Due to inconsistency of stoichiometric proportions and actual interaction of minerals in a heterogeneous matrix, buffering potential $\xi = C_{buf}/C_{ac\text{-}t}$ of rock material and resistance to acidification has been evaluated as the ratio of total buffering capacity C_{buf} (or neutralization potential (NP)), assessed as the total cation exchange capacity and calcium/magnesium carbonates content, to the total acid-generation potential $C_{ac\text{-}t}$ (or acidification potential (AP)) in terms of the total sulfur in real systems under field conditions, both values converted to common equivalent units (Twardowska, 1981, 1990; Twardowska et al., 1988) (Fig. III.6.5). Use of total sulfur content instead of the more exact sulfide sulfur assures more conservative estimation of the potential for acidification. Acidification of the material does not require the consumption of all carbonate minerals, which are usually still present in substantial amounts in the acid rock. The prerequisite of

a satisfactory buffering effect is the balanced dissolution of carbonates, able to neutralize generated acid loads. Due to the different kinetics of these two processes and heterogeneity of the material, buffering minerals should occur in the matrix much in excess compared to sulfides, and their specific surface at the solid–liquid interface should be adequately high. On the basis of the long-term observations and generalization of a large number of cases, mining waste has been defined by the authors with respect to the buffering potential within three-range limits (Twardowska et al., 1988; Twardowska, 1990).

(I) $\xi = C_{buf}/C_{ac\text{-}t} \geq 2.4$: buffered waste, no acidification will occur in the life-cycle of a dump;
(II) $\xi = C_{buf}/C_{ac\text{-}t} \leq 1.5$: low-buffered waste, susceptible to acidification; threshold of acidification to start was evaluated for $\xi \leq 0.6$;
(III) $\xi = C_{buf}/C_{ac\text{-}t} > 1.5 < 2.4$: weakly buffered waste, acidification may occur (possibly acid generating waste).

Very close to the evaluation proposed earlier by authors is the method by Smith and Barton-Bridges (1991). In general, it consists of a three-stage procedure; the first stage is the same, but with a higher degree of conservatism with respect to the estimation of potential for acidification.

(I) $\xi = C_{buf}/C_{ac\text{-}t} \geq 3.0$: buffered, non-acid generating waste. If $\xi = C_{buf}/C_{ac\text{-}t} < 3.0$, then the material should be tested with respect to $C_{ac\text{-}s}$ (sulfide sulfur). If
(II) $\xi = C_{buf}/C_{ac\text{-}s} \geq 3.0$: buffered, non-acid generating waste. If $\xi = C_{buf}/C_{ac\text{-}s} < 3.0$:
(III) Perform a kinetic test using the humidity cell or column/lysimeter and a leach test. Determine all mobile/mobilizable species (leachable plus potential products of acid generation).

Hutchinson and Ellison (1992) present several short static test techniques for evaluation of AP (or C_{ac}) and NP (or C_{buf}), along with their summary evaluation. The tests include the BC research initial test, the Sobek test, the modified Sobek test, the alkaline production method, the hydrogen peroxide test and net acid production. All of them except the last two are based on the total sulfur and sulfur-bearing forms' analysis for AP evaluation, and acid titration of sample to evaluate NP (the same approach has also been used independently by the authors) and give comparable results. Hydrogen peroxide tests were not recommended as non-reliable. Reliability of acid rock drainage (ARD) testing, besides proper selection of test methods, require careful sampling and representative sample preparation techniques (Broughton and Robertson, 1992; US EPA, 1994).

III.6.3.4. Geophysical parameters critical for the pollution potential from mining waste dumps

III.6.3.4.1. Air penetration

Intensive sulfide oxidation can occur entirely under the vadose zone conditions, which are predominant within mining waste dumps. Inundation of the waste layer causes inhibition of the reaction due to the decrease of oxygen in water at pyrite surfaces by more than an order of magnitude; diffusion or convection transport in water-saturated pores cannot supply enough oxygen, while less than 10% of air content in pore atmosphere is sufficient

for sulfide oxidation to proceed (Good, 1970; Morth et al., 1972; Frost, 1979; Twardowska, 1981; Twardowska et al., 1988). Due to the lack of analytical data, some authors previously assumed that in a well-compacted waste, the permeability to air is effectively nil and evaluated air penetration depth for the range 0.1–0.25 m to a maximum of about 4 m (Good, 1970; Glover, 1978). The contemporary approach considers air penetration measurements as an essential factor in evaluation of environmental behavior of sulfidic waste rock dumps (Helgen et al., 2000; Hockley et al., 2000).

Results of our own studies conducted at compacted coal mining dumps of different ages (7–15 years old) displayed the presence of oxygen in the full profiles 10–12 m thick of the vadose zone of both high and low hydraulic conductivity ($k = 10^{-2}$–10^{-6} cm/s, i.e. 10^{2}–10^{-2} m/d). The gas composition of the pore atmosphere is typical for an oxic environment in the full profile ($O_2 = 12.78$–20.54% vol, lack of CO and H_2S) and proves active oxidation of sulfide and coal (consistency of O_2 diminution and CO_2 increase, relatively high CO_2 values, up to 1.7–4.48 vol%, occurrence of CH_4 and C_2H_6, mode of respiration index distribution). Distinct corrosion of all textural forms of sulfides, in particular framboidal, metacolloidal, micro- and fine-crystalline forms and the occurrence of secondary products of sulfide decomposition (gypsum, goethite and iron oxyhydroxides) confirmed the occurrence of oxidation processes and water infiltration in the whole profile of the investigated dumps. The most susceptible to oxidation appeared to be sulfides in coal shale and coal; the most resistant are sulfides in carbonatic rocks.

III.6.3.4.2. Conditions determining water flow in the waste dump and transport of the released contaminants to groundwater and surface waters

III.6.3.4.2.1. Hydraulic conductivity

Hydraulic conductivity of coal mining wastes deposited in dumps or used in civil engineering constructions depends on a number of factors, the most essential are particle size distribution, susceptibility and character of weathering decomposition (effect of drying–wetting, freezing–thawing, chemical processes of salt leaching, pyrite oxidation and secondary reactions) and technical conditions of waste dump construction (layer formation and compaction).

In general, as results from the waste generic structure, more than 75% of coal mining waste in the USCB represents coarse, massive granular material of grain size ranging from 30 to 500 mm. Rock material from marine shale/sandstone and brackish sandstone series of Namurian A–C is resistant to the physical weathering breakdown. Upwards the carboniferous sequence susceptibility to weathering grows, up to the maximum values in the youngest sandstone Westphalian C–D formations.

Hydraulic conductivity for surface layer of the tips where the typical coarse-grained coal mining wastes are disposed ranged from 10^{-7} to 10^{-1} cm/s (10^{-3}–10^{3} m/d), reflecting the effect of lithological type and position in the carboniferous sequence, which determine rock susceptibility to weathering. Physical weathering disintegration of waste rock material is the strongest in the first months or year of exposure to atmospheric conditions, while further disintegration proceeds very slowly. The conditions of water infiltration through the dump thus undergo fast stabilization. In the majority of profiles, the decrease of hydraulic conductivity in the top layer of several tens of cm, up to 1.0 m thick

is observed. This confirms a limited thickness of the physical weathering zone as proven by other authors (Sullivan and Sobek, 1982).

Mechanical compaction causes reduction of hydraulic conductivity up to four orders of magnitude compared to a fresh wrought waste in a layer of about 20 cm thick, but never less than $k = 10^{-7}$ cm/s (10^{-3} m/d), in many cases not less than 10^{-3} cm/s, i.e. 10^{-1} m/d (rocks from the oldest strata). Therefore, compacted dumps in the USCB are either fairly permeable or at least semi-permeable to water. The pattern of hydraulic conductivity in two characteristic coal mining waste dumps in the USCB of different susceptibilities of the rock material to self-sealing is presented in Figure III.6.7A and B.

The relevant values for loose and compacted mining waste from the various coalfields of the world (Czech Republic, Germany, Spain, UK and the USA) quoted by Skarżyńska (1995a) showed similar permeability range as rocks from the USCB, i.e. from 10^{-1} to 10^{-4} cm/s ($10^{3}-10^{-1}$ m/d) for loose coarse material and $10^{-3}-10^{-5}$ cm/s ($10-10^{-1}$ m/d) for the compacted layer, with the exception of some mining waste from UK coalfields, which are generally less permeable both in the loose ($10^{-2}-10^{-6}$ cm/s, i.e. $10^{2}-10^{-2}$ m/d) and compacted state ($10^{-2}-10^{-9}$ cm/s, i.e. $10^{2}-10^{-5}$ m/d).

III.6.3.4.2.2. Moisture content in the vadose zone of the dump

Water occurring in granular waste material in a dump represents several categories. The total volume of voids in rock and spaces between rock particles delimits the maximum amount of water in material in a saturated state (w_t). Part of it is physically bound by molecular forces (sorption water w_m), and held by capillary forces or suspended on the local interlayers of low permeability (retention capacity w_r). Water ($w_n - w_r$) determined by the natural moisture content w_n in excess with respect to w_r forms an infiltration stream w_i, which percolates downward through the waste layer under the vadose zone conditions due to gravitational forces and transports contaminants released from solid rock matrix out of the dump. In the initial stage, part of the infiltrating stream fills up the retention capacity of the consecutive waste layers, provided a dry or semi-dry material is disposed. Retained water, being a function of the specific surface of the rock, forms an environment for equilibria–non-equilibria processes at the liquid–solid phase interface, controlling the released contaminant load. An amount of free water percolating through the waste layer depends on the waste properties determining a hydraulic conductivity, atmospheric conditions (precipitation), and water balance of the dump.

III.6.3.4.2.3. Total moisture content of the vadose zone in the coal mining waste dump

A sufficiently thick waste layer forming the anthropogenic vadose and saturated zones, can be divided into three specific parts with different conditions of water flow and moisture content (Fig. III.6.8):

- upper surface zone, up to about 1.0 m thick, of unsteady water flow, depending upon the atmospheric conditions (precipitation, evaporation and evapotranspiration);
- dump body, of a relatively stable moisture content, proportional to average infiltration rate;
- bottom part at the border of the vadose and saturated zones, where moisture content increases up to the complete saturation (w_t) in the capillary suction zone or at the water table border.

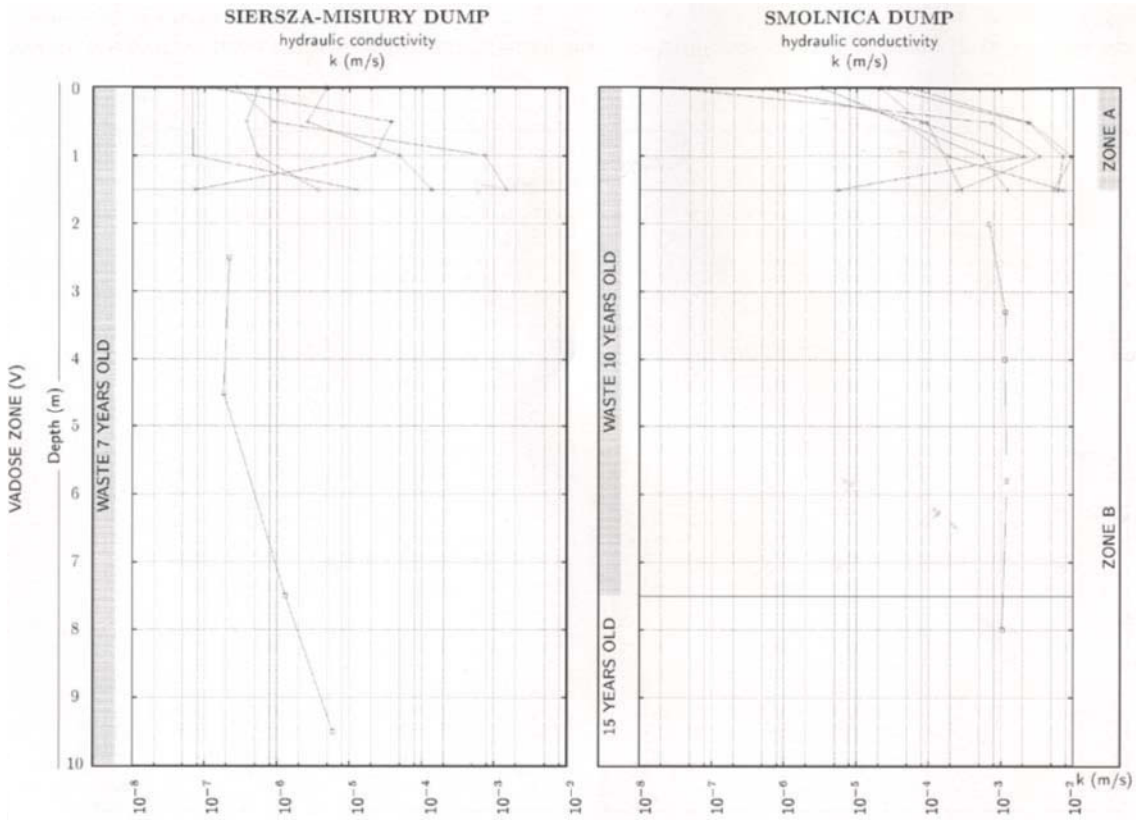


Figure III.6.7. Hydraulic conductivity of waste rock material in the coal mining dump (Siersza-Misiury and Smolnica sites). A, Surface vadose zone of unsteady hydraulic conductivity; B, vadose zone of a stable hydraulic conductivity.

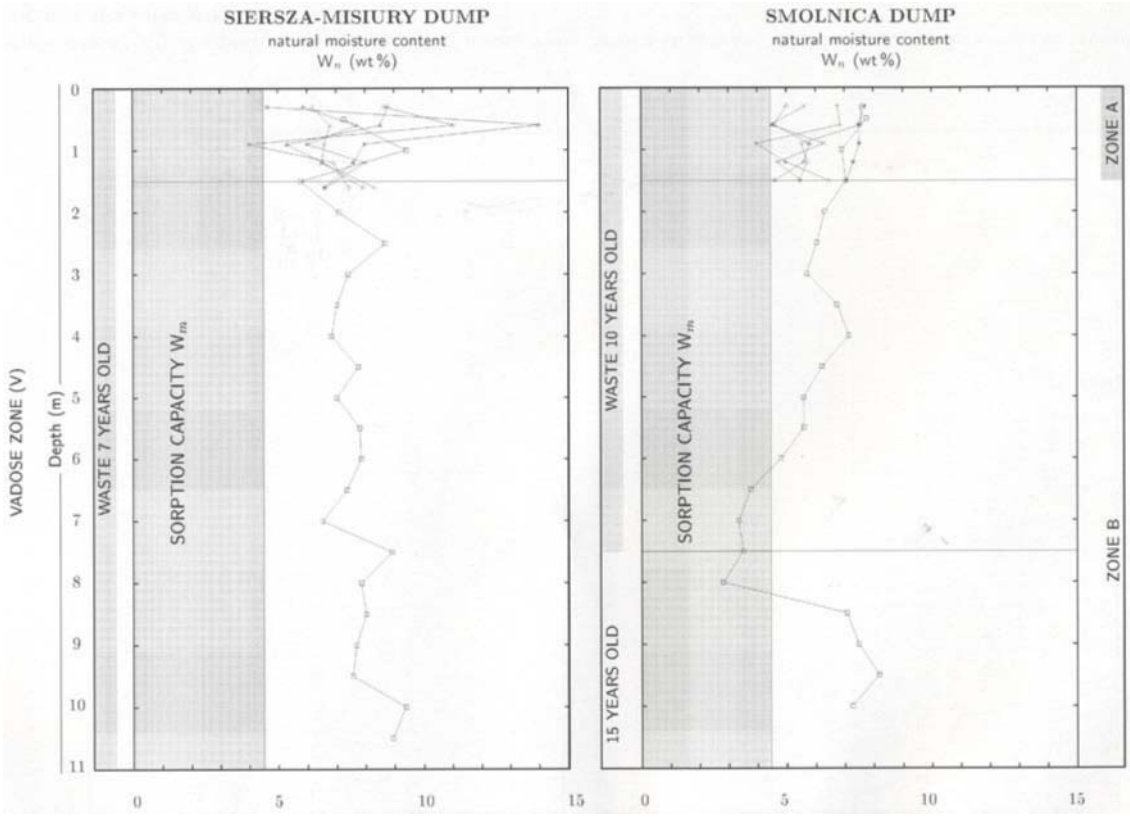


Figure III.6.8. Distribution of natural moisture content values along the coal mining dump profiles (Siersza-Misiury and Smolnica sites). A, Surface vadose zone of unsteady moisture content; B, vadose zone of a stable water flow.

The total free water not bound by molecular forces ($w_n - w_m$) takes part in water percolation through the dump. Also the retained, looser bound water is gradually exchanged.

The stability of moisture content in the dump body largely depends upon the uniformity of grain size distribution. In coarse, granular shales from the Namurian C series (e.g. Smolnica site, Fig. III.6.8A), the decrease of moisture content with the increase of grain size vs depth was observed, while in easily disintegrating rock material from the Westphalian C–D series (e.g. Siersza-Misiury site, Fig. III.6.8B) the natural moisture content in dump body was uniform.

The moisture content profiles for different dumps fills pore spaces in the mean range from 25 to 50%. Moisture content values range from several to more than 10% wt, and are considerably above the w_m values estimated for 2.29 to 4.64% wt. The difference determines the proportion of infiltration water stream in the dump.

The available data on moisture content in the coal mining dumps in the different coalfields worldwide are very close to those evaluated for the USCB and range from 2 to 15% wt; only for coalfields of the UK, the reported moisture content values are higher, up to 28% wt (Skarżyńska, 1995a).

III.6.3.4.3. Water balance of coal mining waste dumps

III.6.3.4.3.1. Elements of a waste dump water balance

The basic elements of water balance that is one of the decisive factors in the assessment of pollution potential from a dump are: (i) surface runoff; (ii) evapotranspiration; (iii) infiltration. The infiltration rate is crucial for transport of contaminants from the dump. Runoff waters also participate in contaminants leaching and transport to receiving waters, but to a considerably lower extent (Swift, 1982; Vipulanandan and Krizek, 1983; Trouart and Knight, 1985).

For evaluation of the water balance of typical coal mining waste dumps, experimental studies on two typical dumps (Smolnica and Siersza-Misiury sites) were conducted. Surface runoff (in the 5 cm thick surface layer) was evaluated by simulating precipitation of different intensities in experimental plots on the top and slopes of a bare and a grassed dump surface, using F method of sprinkling (Ven Te Chow, 1964).

Infiltration and evaporation assessment was based on lysimetric studies (Fig. III.6.9). Lysimeters of an effective height (1.5 m), adequate to the thickness of the surface active zone, were filled with representative coal mining waste from the USCB of different ages and exposed to natural atmospheric conditions (experiment began at the end of 1984 and was continued for more than a decade) (Fig. III.6.10).

III.6.3.4.3.2. Surface runoff

The rate of the surface runoff depends on a number of factors, the most essential being ground slope, hydraulic conductivity of the material and its change due to weathering, intensity and duration of the rainfall, the antecedent moisture content in the surface layer, extent of a surface retention (dumps) and subsurface flow (Atkinson, 1977), as well as vegetative cover.

At the flat surface of the dumps having small ground slopes, in particular of those constructed of permeable waste, at a low precipitation intensity (such as 0.026 mm/min,

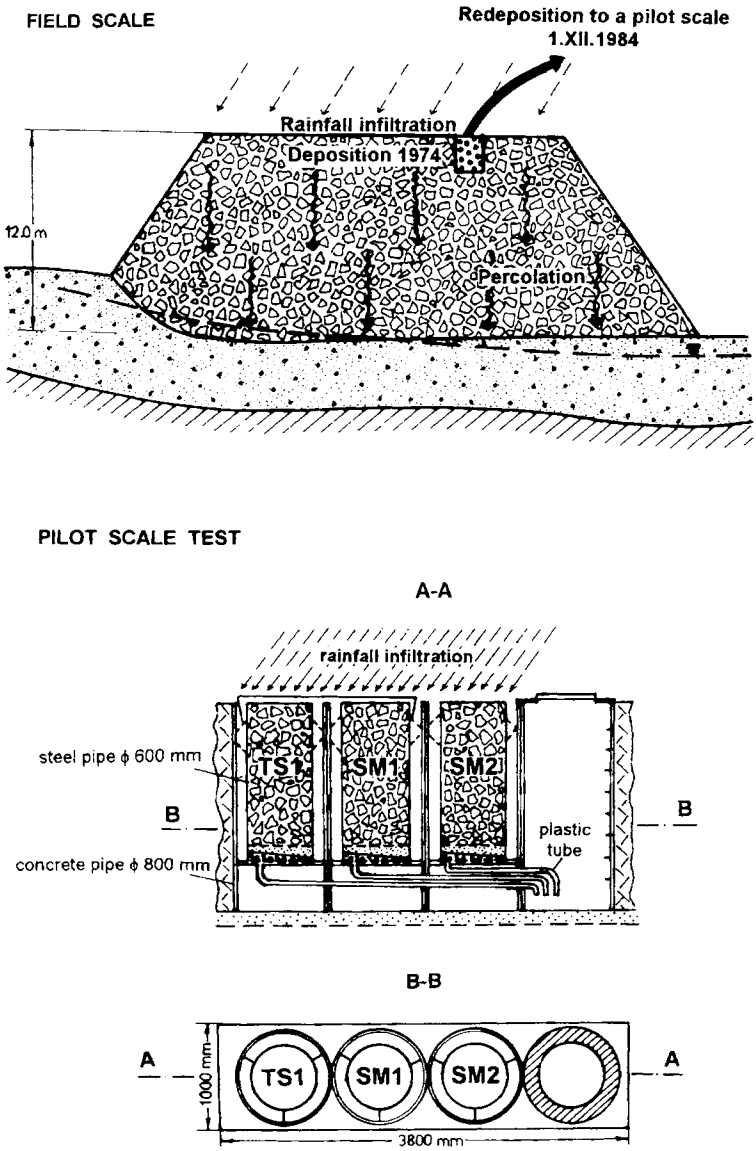


Figure III.6.9. Scheme of the long-term lysimetric studies (1984–1996) of water balance, kinetics of sulfide decomposition and contaminant leaching in the surface vadose zone layer 1.5 m thick of coal mining waste dumps. Lysimeter fill: TS1, 7 year old waste of w_n = 7.5% wt from Siersza-Misiury dump; SM1, fresh wrought waste; SM2, 10 year old waste from the Smolnica dump.

a mean annual intensity in the Upper Silesia area) surface runoff is effectively nil. During storms, runoff comprises 50–60% of the total precipitation. Following the nomogram to determine storm runoff coefficients (NCB, 1982), a similar one was constructed for the approximate evaluation of a mean annual runoff for permeable and low-permeable mining

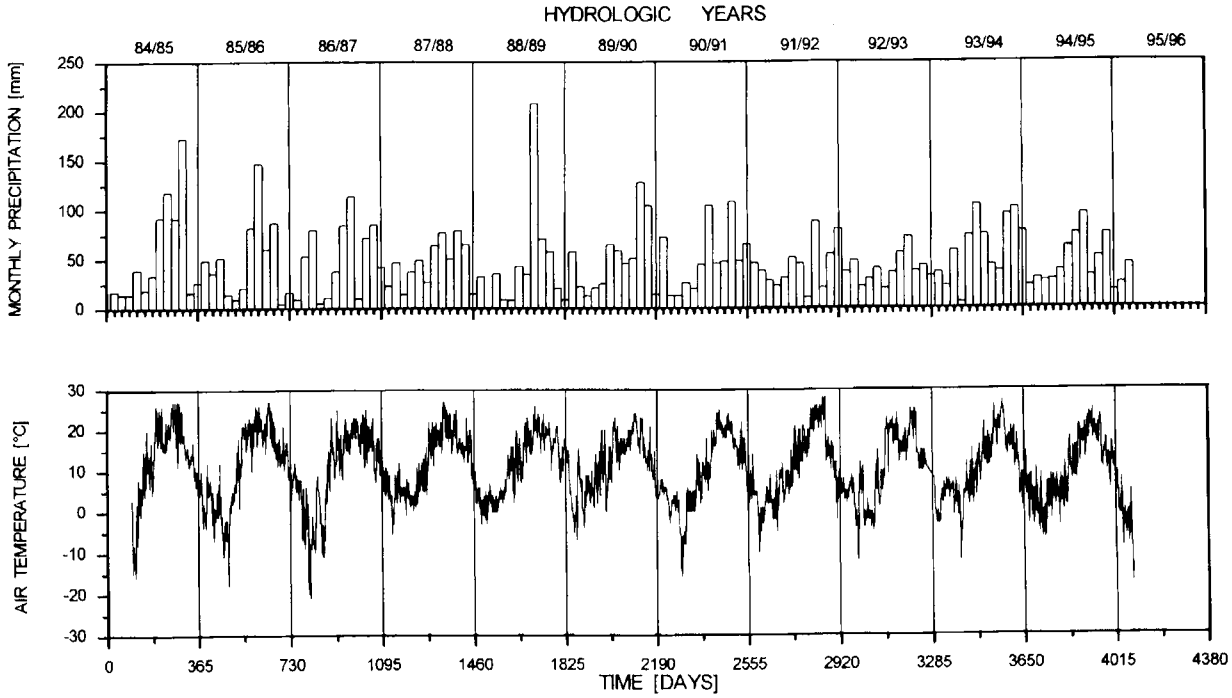


Figure III.6.10. Atmospheric precipitation and air temperatures at the lysimetric site during study (hydrologic years 1984–1996).

waste (Fig. III.6.11). The obtained values account for 5–15% of the mean annual precipitation, i.e. much less than for storms. In case of environmental impact assessment, the safety coefficient should be, though negative, greater than used for the design of the drainage system. Field observations also confirm low values of runoff in the coal mining waste dumps.

Hutchinson and Ellison (1992), following the Soil Conservation Service methodology (USDA, 1972), constructed a more detailed approximate rainfall–runoff relationship, though it was not validated experimentally.

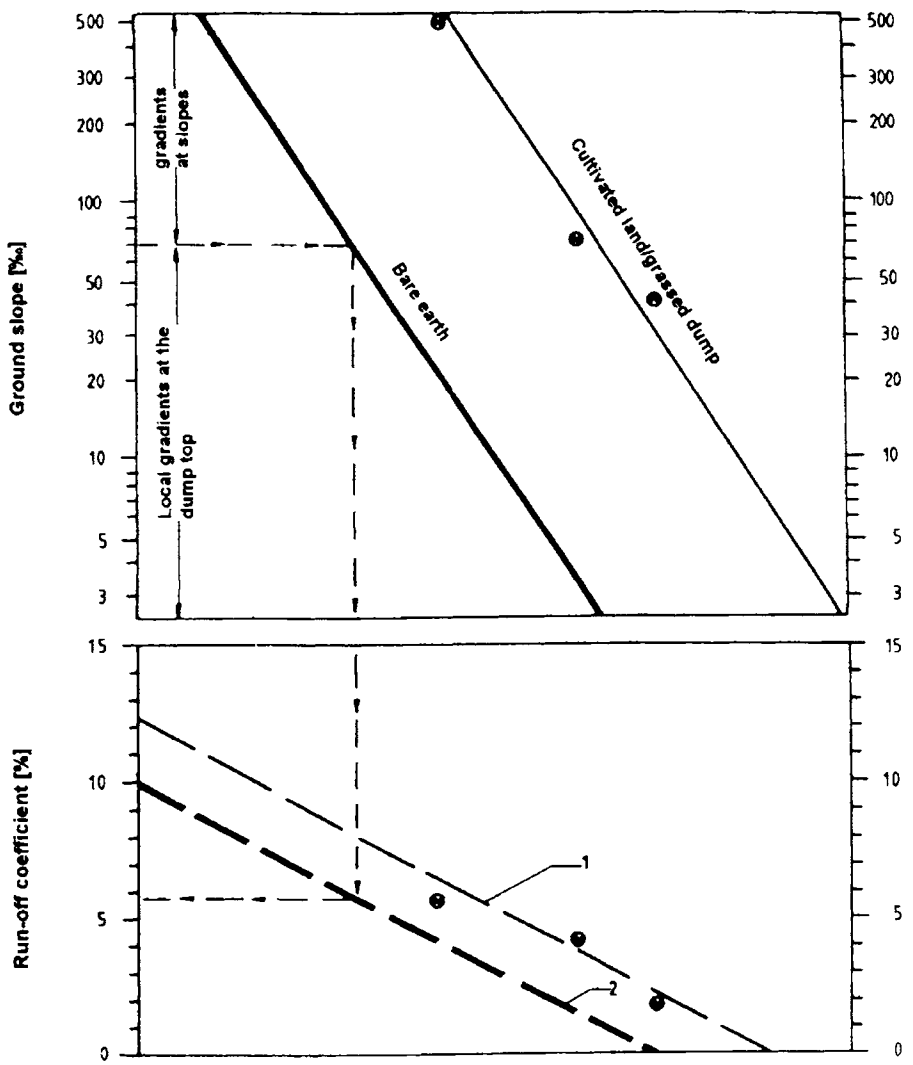


Figure III.6.11. Nomogram to estimate mean annual runoff coefficients for coal mining waste dumps (percent of the annual precipitation sum) for: (1) a revegetated dump; (2) the bare dump surface.

III.6.3.4.3.3. Infiltration and evaporation

Water balance derived from lysimetric studies shows a high rate of infiltration with respect to evaporation from the bare non-compacted surface. The rate of evaporation for both permeable and low-permeable materials was as high as 39–45% of precipitation in the case of a low runoff, or of precipitation of less runoff. The infiltration rate for flat top surfaces of the waste dump, simulated by lysimetric studies, comprise 55–61% of the total precipitation (Fig. III.6.12).

III.6.3.4.3.4. Water exchange rate in a dump

Due to the heterogeneity and granularity of rock material, as well as to physiochemical changes in the properties of waste resulting from weathering processes, conditions of water flow within the dump are complex. During the vertical flow of percolating water, both retardation of flow resulting from either retention capacity (capillary bound water) or formation of zones with low permeability, or voids of privileged flow within the dump can occur.

Water exchange rate and liquid/solid (L/S) ratio during water percolation under the vadose zone conditions are crucial for a correct evaluation of contaminant loads and concentrations in leachate. The common practice of using very high proportions of water in leach laboratory tests (L/S ratio) leads to deriving too optimistic conclusions concerning leaching behavior of coal mining waste. Actually, under the vadose zone conditions, the amount of percolating water is low compared to the mass of deposited rock. At a mean moisture content ranging from several to $>10\%$ wt, and average natural moisture content accounting for about 6% wt, the stream of percolating water will account for 6% wt, i.e. about 9.5% vol. This is equivalent to a column of water about 1.9 m high in a waste layer 20 m high. At the mean annual precipitation in the USCB area accounting for 700 mm/a and infiltration rate for the Upper Silesia coalfield area of 420 mm/a (0.42 m), a single water exchange in the waste dump 20 m high will last for about 5 years. This rough estimation shows that the process of contaminant leaching and transport to groundwater can be a long-term process, in addition retarded by a number of factors, e.g. filling up the retention capacity of a dump.

In the environmental evaluation and monitoring of coal mining dumps and engineering constructions built of mining waste, their long-term effects should be therefore strongly considered.

III.6.4. Environmental behavior of disposed mining waste

III.6.4.1. Testing methods

The above conclusion, along with the double nature of the pollution potential of sulfidic mining waste rock, suggests the necessity of applying testing methods specific for this kind of material and its exposure to environmental conditions. As most of the processes determining the loads and concentrations of pollutants occur within the mining dump, which forms an anthropogenic vadose zone, the testing methods were focused on either direct observation of the processes of contaminants' generation, release and transport along the profiles of the existing dumps and engineering constructions (Twardowska, 1981; Twardowska et al., 1988; Szczepańska and Twardowska, 1999; Helgen et al., 2000;

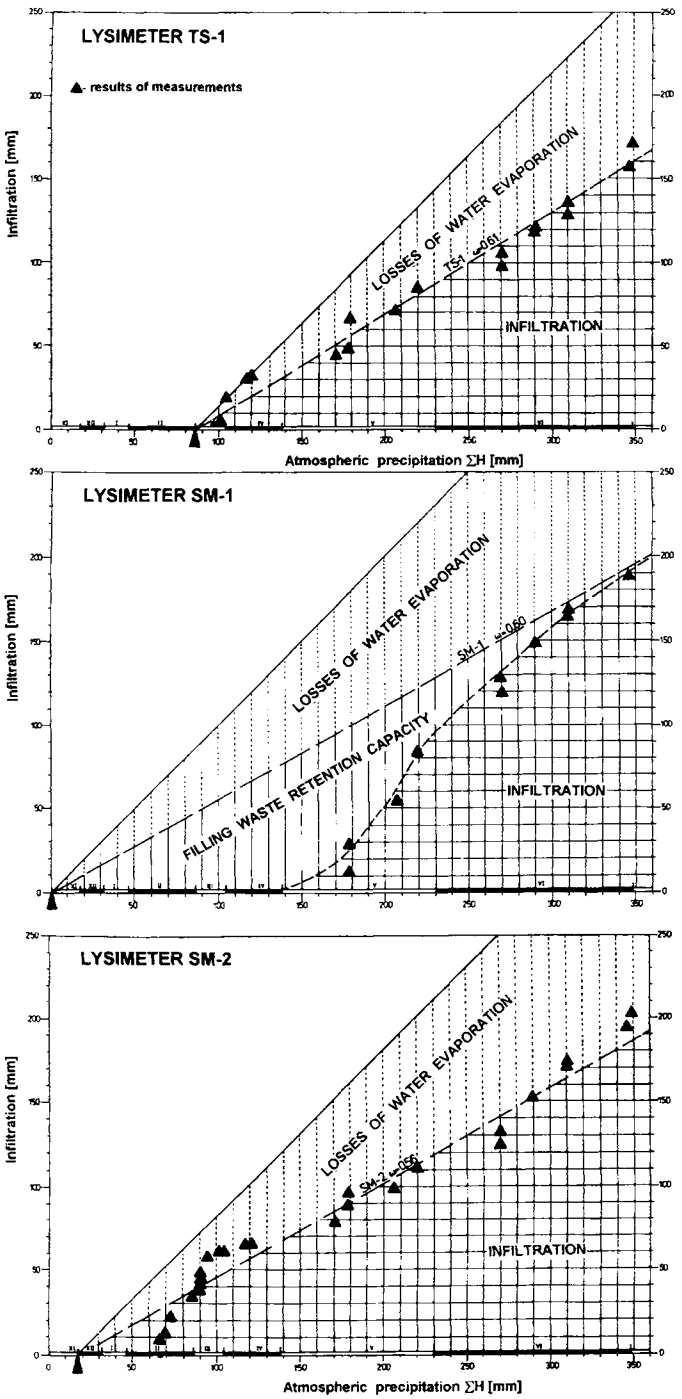


Figure III.6.12. Infiltration vs evaporation in the surface coal mining waste layer 1.5 m thick in 12 years' hydrologic cycle (lysimetric studies).

Hockley et al., 2000) or simulation of the real conditions in the geochemical kinetic tests. The concept behind the development of kinetic tests or anthropogenic vadose zone monitoring is to elucidate the mechanisms and kinetics of formation of contaminant loads in order to correctly predict, and subsequently attenuate, the chemical constituents leached from the rock matrix or the bedrock before the recoverable groundwater resources become degraded. The tasks of geochemical kinetic tests are to provide data on the oxidation rate, retardation period for onset of acidification (lag time), metal release and loading in the leachate from waste. A comprehensive review of geochemical kinetic tests and vadose zone monitoring methods with respect to mining wastes are presented in a fundamental publication by Hutchinson and Ellison (1992). The columns and humidity cells reported by Environment Australia (1997) are those most frequently used laboratory-based techniques; column tests being considered more representative for simulating field conditions. Humidity cells have been developed by the mining industry for testing overburden materials in opencast mines. The duration of a standard testing procedure for this technique is 8–10 weeks or more, which is considered to be enough for evaluation of a lag period for an overburden (Environment Australia, 1997). The lag period for the mining waste from the USCB lasts for several years. Therefore, this technique cannot be used directly for acid generation assessment. The authors modified it successfully for assessment of kinetics of sulfide oxidation measured as sulfate production and release.

The further development of the testing methods based on the simulation of time-dependent changes that occur in waste, leads to the integrated and unified, and at the same time waste-, use- and site-specific "tailor-made" approach to evaluation of leaching behavior of various solid waste materials (Eighmy and van der Sloot, 1994; Quevauviller et al., 1996). Apart from the variety of methods and protocols, the basic scheme used by the authors, which comprises characterization of waste materials and long-term tests that can be conducted for a period of months or even years, are discussed below.

For obtaining correct qualitative and quantitative information, the applied geochemical kinetic testing methods were focused on providing procedures close to the actual conditions of the environmental exposure. In particular:

(i) For evaluation of the dynamics of soluble constituents' leaching occurring in a fresh wrought material, a sequence of 10 columns ϕ 0.4 m, $H_{ef} = 2.0$ m, filled with fresh wrought coal mining waste of a natural grain size was used. Distilled water of pH 6.5, equivalent to the pH value of rain water in the area, was added to the first column in portions corresponding to the mean annual daily precipitation in rainy periods, and the leachate was consecutively directed to the subsequent columns, simulating the total actual dump thickness of 20 m.

(ii) Sulfide decomposition kinetics, generation and release of contaminants, along with the water balance of the surface vadose zone layer of the typical coal mining wastes deposited in dumps were studied in the lysimetric investigation described above (Fig. III.6.9) for 12 years.

(iii) The role of *T. ferrooxidans* in pyrite decomposition at the colliery dumps was estimated on the basis of active cell number in the surface layers of different dumps up to a depth of 100 cm below the surface.

(iv) Transformations of chemical composition of pore solution along the dump vadose/saturated zone profile vs water exchange rate have been studied on core

samples of a natural moisture content taken along the dump profiles of the age defined from the dump construction scheme. Pore solution has been extracted from the rock by a pressure method under nitrogen and analyzed for metals using ICP-OES. The method is routinely used by the authors in different cases and environmental impact assessment studies, from which come examples of different situations, presented in the chapter.

(v) Transformations of groundwater chemical composition in the saturated zone in the vicinity of a coal mining dump have been studied during the routine local monitoring programs and exemplified by the data from 1994–2002 for the network of 28 monitoring wells in the Smolnica site.

III.6.4.2. Time-dependent transformations of chemical composition of pore solution and leachate from mining waste

Environmental behavior of sulfidic mining waste disposed in dumps displays two major phases of macro- and trace elements leaching of different dynamics dictated by the constituents leached and controlling factors specific for the process.

- *Phase I*: Leaching of soluble constituents available in the fresh wrought mining waste, mainly chlorides and sulfates. The process is controlled by the hydrology of the dump, and availability and vertical redistribution of soluble constituents.
- *Phase II*: Leaching of soluble constituents generated from the sulfide decomposition. The controlling factors are kinetics of sulfide decomposition and buffering capacity of the material.

III.6.4.2.1. Phase I: leaching of primary soluble constituents from fresh wrought mining waste

In this phase, the major constituents leached from the dump are macro-compounds, such as chlorides predominantly balanced by Na^+ ions and sulfate, generally occurring in fresh wrought rock in amounts not exceeding some 5% of the total sulfur content, and balanced by Ca^{2+}, Mg^{2+} and Na^+. In general, disposed material shows a deficiency of moisture content with respect to the retention capacity, while the amount of percolating water depends on the water balance of a dump under the vadose zone conditions. In the leaching of soluble constituents during the gravitational flow of percolating water from atmospheric precipitation through a mining waste layer, two stages can be distinguished.

1. Initial stage of unstable flow, when the deficient retention capacity of the material is gradually filled up by the subsequent portions of percolating water.
2. Phase of a stable flow, when water percolates through the whole waste layer; the beginning of this stage is indicated by the appearance of leachate from the dump toe.

Chlorides and the sodium ions balancing them, occurring predominantly in the primary pore solution of the rock and unconstrained by equilibria limitations, readily migrate with infiltration water filling up deficient retention capacity of consecutive dump layers by subsequent portions of infiltrating precipitation water. It results in the vertical redistribution

of chloride content along the dump profile, showing a decrease in the upper part of the profile, and higher concentrations in consecutive layers, increasing downwards proportionally to the deficiency of the retention capacity (Fig. III.6.13). Due to high dynamics of chloride migration, a single water exchange in a particular layer is generally enough to reduce chloride content to the permissible level (MCL), therefore the time required to reach this level is controlled by the single water exchange rate within the dump. Considering the time required for thorough exchange in a dump several meters thick, in a short time after waste disposal the chloride content in pore water will be negligible in the uppermost layers of a dump, whereas the concentrations of this ion in leachate at the dump toe within several years after its appearance will be many times higher than in the original pore solution of mined rock. Its concentration in leachate will be proportional to the thickness of the layer and the retention capacity deficit and water exchange rate in the layer.

Chloride concentrations in actual pore solutions of dumps constructed of mining waste of elevated chloride salinity show the specific pattern described above, which reflects the shifting of maximum concentrations from the top in a freshly constructed layer downward in older dumps and a gradual decrease up to a uniform low residual concentration in dumps, in which the thorough pore water exchange has already been completed (Fig. III.6.14).

The pattern of a vertical redistribution of sulfate in the pore solution of the vadose zone of a dump in the initial stage, when primary sulfate load in rock matrix exceeds sulfate generation, strongly depends upon the balancing cation. In the rock of a moderate up to high NaCl salinity, where the bulk of the cation exchange capacity of clay minerals is occupied by Na^+ ions balancing released sulfate, the leaching behavior is similar to that of chlorides. To summarize, for chloride-bearing waste, the leachate quality will be controlled by the released primary load of sodium chlorides and sulfates. In materials of low chloride salinity, the sulfate concentration along the vertical profile of the waste layer is controlled by the geochemical constraints (equilibrium with gypsum and carbonate

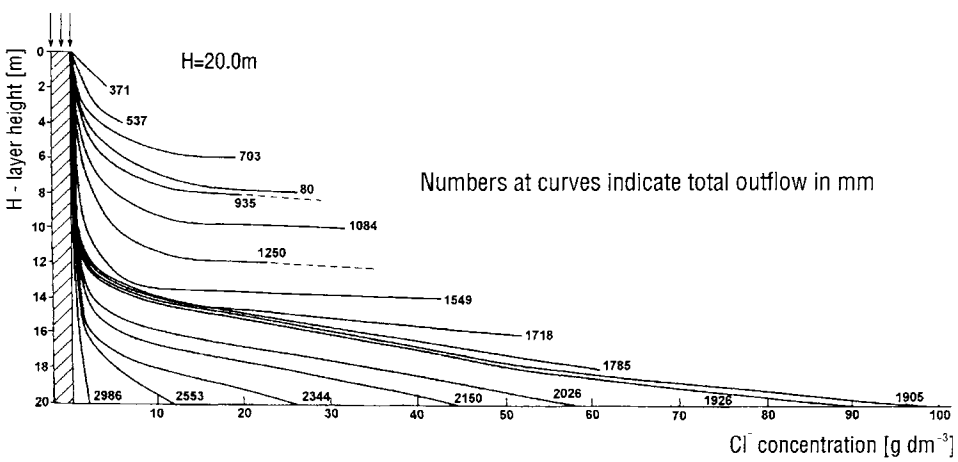


Figure III.6.13. Chloride redistribution along the vertical profile of fresh wrought minestone layer 20 m thick. Column leach experiments.

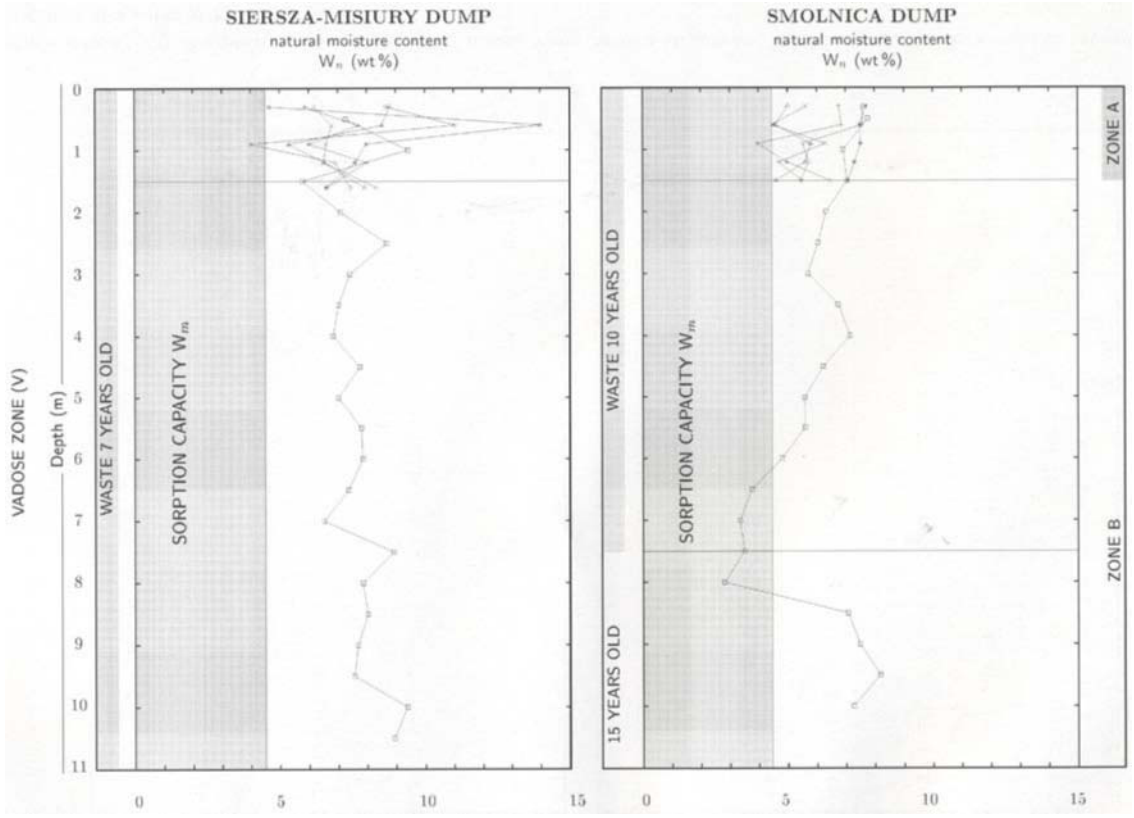


Figure III.6.8. Distribution of natural moisture content values along the coal mining dump profiles (Siersza-Misiury and Smolnica sites). A, Surface vadose zone of unsteady moisture content; B, vadose zone of a stable water flow.

equilibria). The time of a single water exchange in a waste layer 1.5 m thick, estimated for the mean natural humidity of a surface waste layer (7% wt) and infiltration rate of 400 l/m^2 a, is 157–183 days, i.e. about a half-year period after the filling is required to satisfy the water retention capacity.

At the initial stage of leaching, the buffering capacity of carboniferous rock material is sufficient for neutralization of relatively low loads of acidity: the pH value of leachate is generally neutral or slightly or even moderately alkaline within the stability field of trace elements occurring in the matrix of carboniferous rock or the bedrock of a dump. Therefore, no elevated release of toxic trace elements occurs. Nevertheless, due to the concentration of high volumes of this waste in a relatively limited area, and the leaching pattern of macro-constituents showing downward vertical redistribution, the deep deterioration of groundwater quality in the vicinity of a coal mining dump by the extensive release of macro-components already occurs in the initial stage of the dump construction.

III.6.4.2.2. Phase II: leaching of soluble constituents generated from sulfide decomposition

III.6.4.2.2.1. Controlling factors

The environmental behavior of coal mine wastes at this stage is controlled mainly by the sulfide decomposition and is a resultant of two opposite processes: acid load generation being a function of sulfide content and its reactivity and the buffering of acid loads at pH $\approx$ 7.0 determined by the content and availability of calcium and magnesium carbonates. The long-term lysimetric experiments (Fig. III.6.9, Table III.6.5), along with results of the direct field studies in mining waste dumping sites confirmed sulfide decomposition to be a first-order process described by Equation (III.6.6). In the changeable hydrological and temperature conditions in subsequent years, the half-period of sulfate decomposition was invariably stable for each of the three kinds of waste and ranged from 328 days (about 1 year) for a buffered 7 year old material from Westphalian C series TS1 to 1440 days (about 4 years) and 1037 days (about 3 years) for non-buffered fresh wrought material from Namurian C series SM1 (Fig. III.6.15, Table III.6.5).

The comparative analysis of laboratory and long-term lysimetric experiments leads to several conclusions, the most important of them are: (i) The kinetics of sulfide decomposition appeared to be stable for a particular rock material, but are distinctly higher for 10–12 years old acidic material than 0–12 years old alkaline rock from the same site. This suggests changes in the prevailing mechanisms of pyritic sulfide oxidation, e.g. from the stage I slower abiotic process at pH $>$ 4.5 to the stage II reactions at pH 2.5–4.5 with much faster process catalyzed primarily by the activity of *T. ferrooxidans* (Kleinmann et al., 1981); the growth of *T. ferrooxidans* in the surface layer up to a depth of 100 cm in different coal mining dumps proved that the number of bacteria in waste (maximum 10^5 cells/g) is not large enough to significantly affect pyrite oxidation (Fig. III.6.16), though its catalytic effect in Reaction 2 according to Kleinmann et al. (1981) should not be neglected (Twardowska, 1986, 1987). In carbonate-depleted rock, bacterial activity can play a more important role (Environment Australia, 1997). (ii) Sulfide reactivity is determined by the location of the rock in the lithological profile of the carboniferous sequence (and thus mainly by the textural types of sulfides) (Fig. III.6.2); data obtained

Table III.6.5. Long-term lysimetric studies on water balance, kinetics of sulfide oxidation and constituent leaching in the natural 12 years' hydrologic cycle (1984–1996).

Lysimeter	Series	Waste age t_0 (years)	Initial sulfur content S[a] in waste (%)			Concentration range of major hydrochemical parameters			Reactive sulfide half-life $t_{1/2}$ (days)	Reactive sulfide 99% decomposition time t_{99} (years)
			S_t	S_S	$S_{S(r)}$	pH	γ_{25} (μS/cm)	SO_4 mg/l		
TS1	Westphalian C	7	1.72	1.48	0.062	6.8–8.5	900–55,000	372–3,461	328	6
SM1	Namurian C	0	0.90	0.81	0.087	6.4–9.1	770–22,500	332–7,967	1,440	26
SM2		10			0.140	2.6–6.3	530–6,400	298–6,153	1,037	19

[a] S_t, total sulfur; S_S, sulfide sulfur; $S_{S(r)}$, reactive sulfide sulfur.

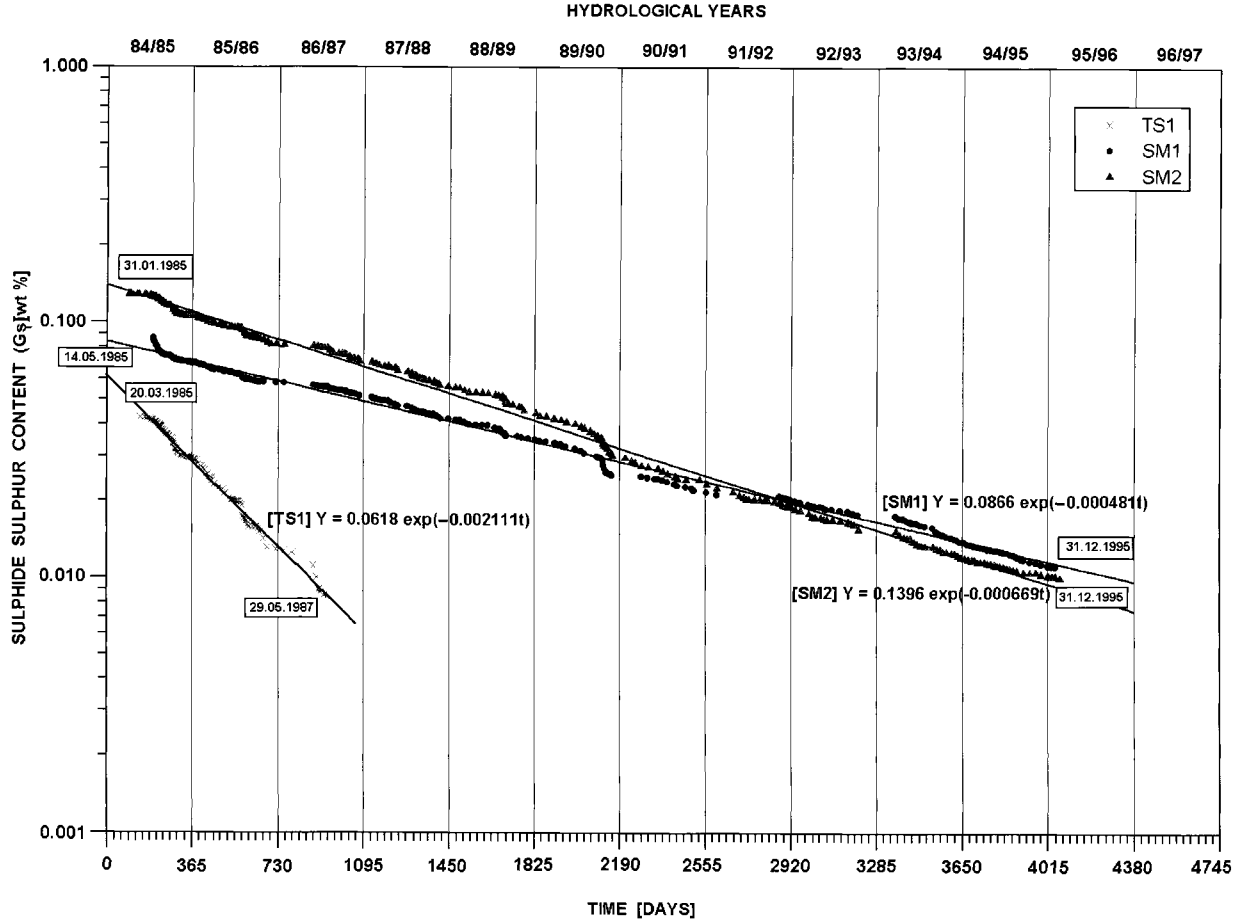


Figure III.6.15. Kinetics of sulfide decomposition in surface coal mining waste layer 1.5 m thick. Long-term lysimetric studies in the 12 years' natural hydrologic cycle (1994–1996). Description as in Figure III.6.9.

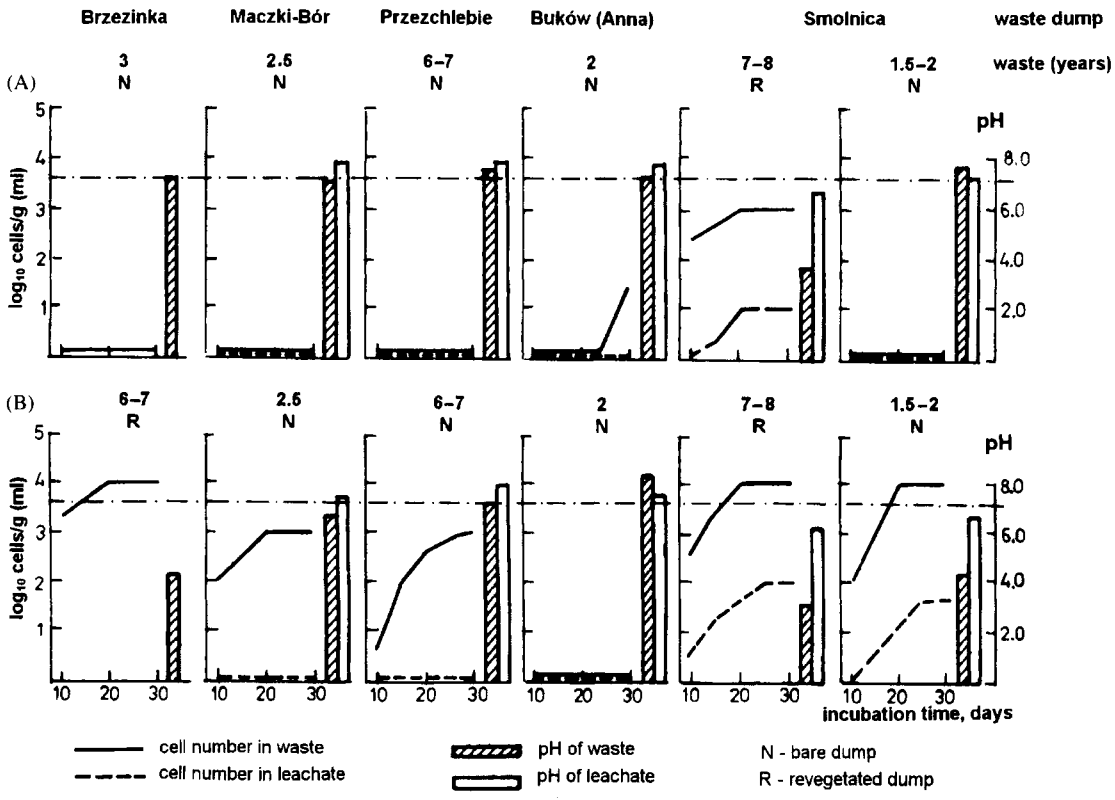


Figure III.6.16. Growth of *T. ferrooxidans* in the surface vadose zone layer of coal mining dumps. (A) Summer period; (B) autumn period.

from the lysimetric studies show good qualitative correlation with the laboratory experiments. The half-period of pyritic sulfide decomposition, estimated from laboratory kinetic tests, is though distinctly shorter than in the lysimetric studies; for the fresh wrought rock SM, it appeared to be 45–52%, for TS, even 80% shorter than that obtained from the lysimetric experiments due to optimum exposure of pyrite to air and moisture. (iii) Values of the initial load of sulfide undergoing oxidation, derived from the results of the long-term dynamic experiments and described by the first-order Reaction (6), appeared to be much lower than the total load of sulfides in the fresh wrought material and comprised: 11.0% (SM1), 17.7% (SM2) and 4.2% (TS1) of S_s (Table III.6.5). It results from the surface character of sulfide oxidation and proves that just part of the pyrite is available to the oxidation and release processes.

III.6.4.2.2.2. Macro-components release and chemical transformations of pore solutions

The composition of leachate from waste rock material in this stage follows the pattern defined by the dynamics of sulfide oxidation generating acidity and sulfates, as well as by the buffering capacity of rock. The beginning of the phase II of leaching starts after a single water exchange in the waste layer. After this period, primary soluble compounds (chlorides and sodium-balanced sulfates) are practically removed from the rock matrix. The macro-components' leaching is controlled by the sulfide decomposition – sulfate/acidity generation and release process. Therefore major anions in the leachate become sulfates (Fig. III.6.17) and balancing cations, mainly Ca^{2+} (Fig. III.6.18) and Mg^{2+} ions are in proportion, showing that the buffering mineral is dolomite. The succession of the dry periods when the acidity/sulfate loads are generated and stored within the material, and wet periods when the leaching of generated loads from the material by the percolating infiltration water prevails, result in observed fluctuations of sulfate concentrations in leachate from the surface layer, which reflect the fluctuations of precipitation (Fig. III.6.10).

The alkaline reaction of leachate reflects the heterogeneity of the disposed rock, which causes the acidification of low-buffered waste SM to start after different periods of exposure, generally after about 10–12 years of disposal. This moment illustrates leachate from 10 year old waste (SM2). In 10 year old waste (SM2), the depletion of buffering capacity below the critical level resulted in a sharp drop of pH from 6.5 to <3.0 and acidification of material to a deep level (Fig. III.6.19), with a simultaneous increase of sulfate concentrations in leachate from about 500 to above 6000 mg SO_4/l due to intensification of pyritic sulfide oxidation and dissolution of gypsum under conditions of the lack of equilibria limitations. In the next 10 years of exposure, the concentrations of sulfates in leachate had more than a twofold increase in concentration as a result of leaching from the fresh wrought rock, and just in the last 2 years was the concentration brought close to that in the input water due to the gradual depletion of sulfides (Fig. III.6.17). The general pattern of sulfate release shows a gradually declining tendency in 12 years period, due to the depletion of the exposed sulfide load (Fig. III.6.17, Table III.6.5). In the acidic conditions (SM2), an increase of pH during the long-term leaching cycle was observed (Fig. III.6.19), in parallel with an increase of Ca^{2+} (Fig. III.6.18) and an elevated occurrence of Al^{3+} and SiO_2 in leachate, which is specific for the transformations that were proceeding. In this stage, the major buffering compounds are aluminosilicates: kaolinite

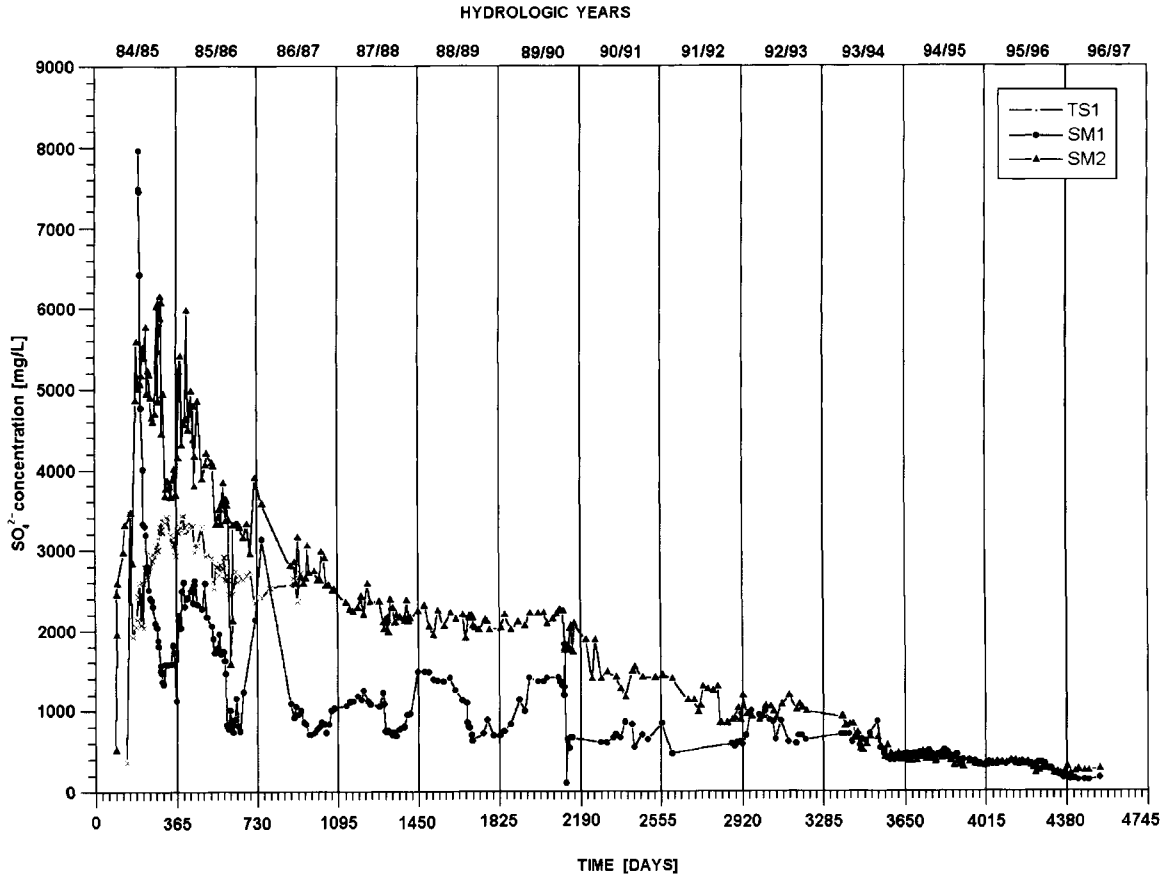
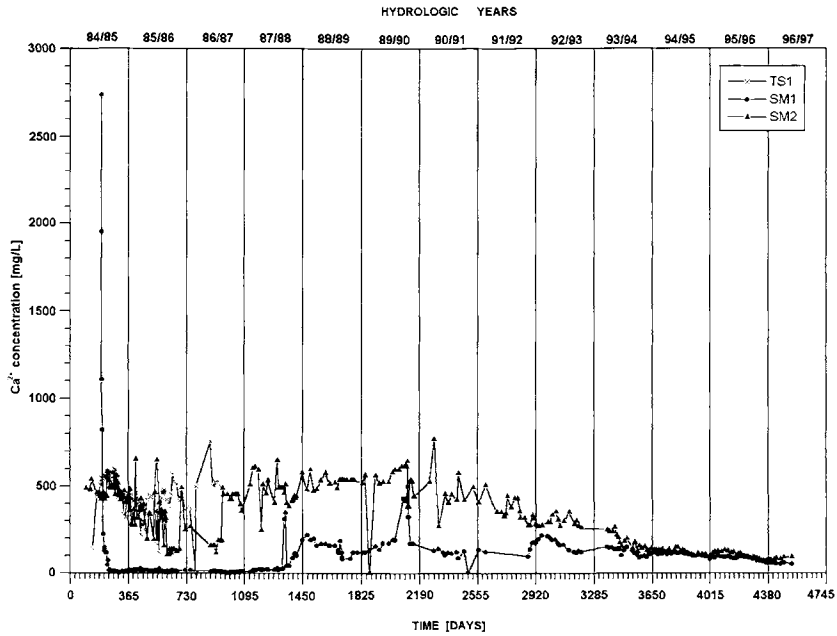


Figure III.6.17. Sulfate leaching from the surface coal mining waste layer 1.5 m thick of different buffering capacity. Long-term lysimetric studies in the 12 years' natural hydrologic cycle (1984–1996).

(a)



(b)

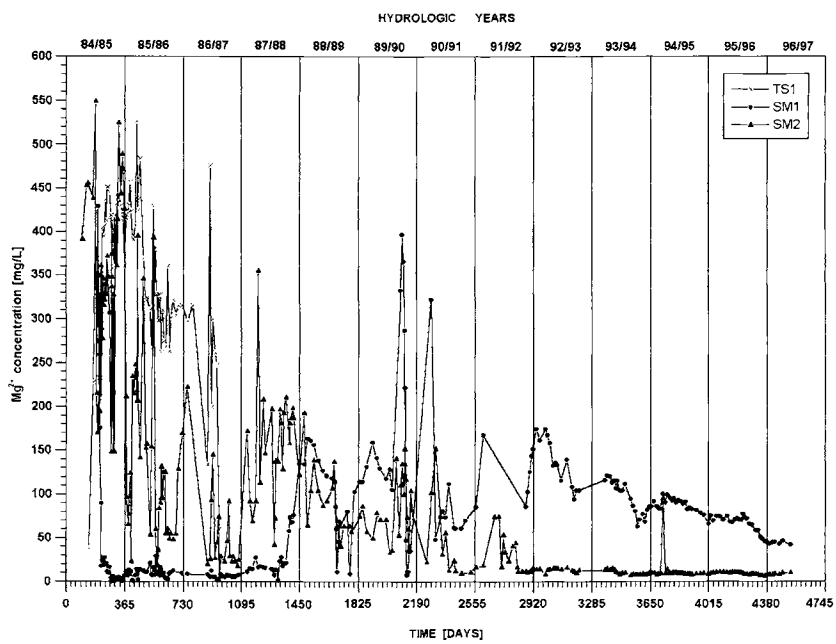


Figure III.6.18. (a) Calcium and (b) magnesium leaching from the surface coal mining waste layer 1.5 m thick of different buffering capacity. Long-term lysimetric studies in the 12 years' natural hydrologic cycle (1984–1996).

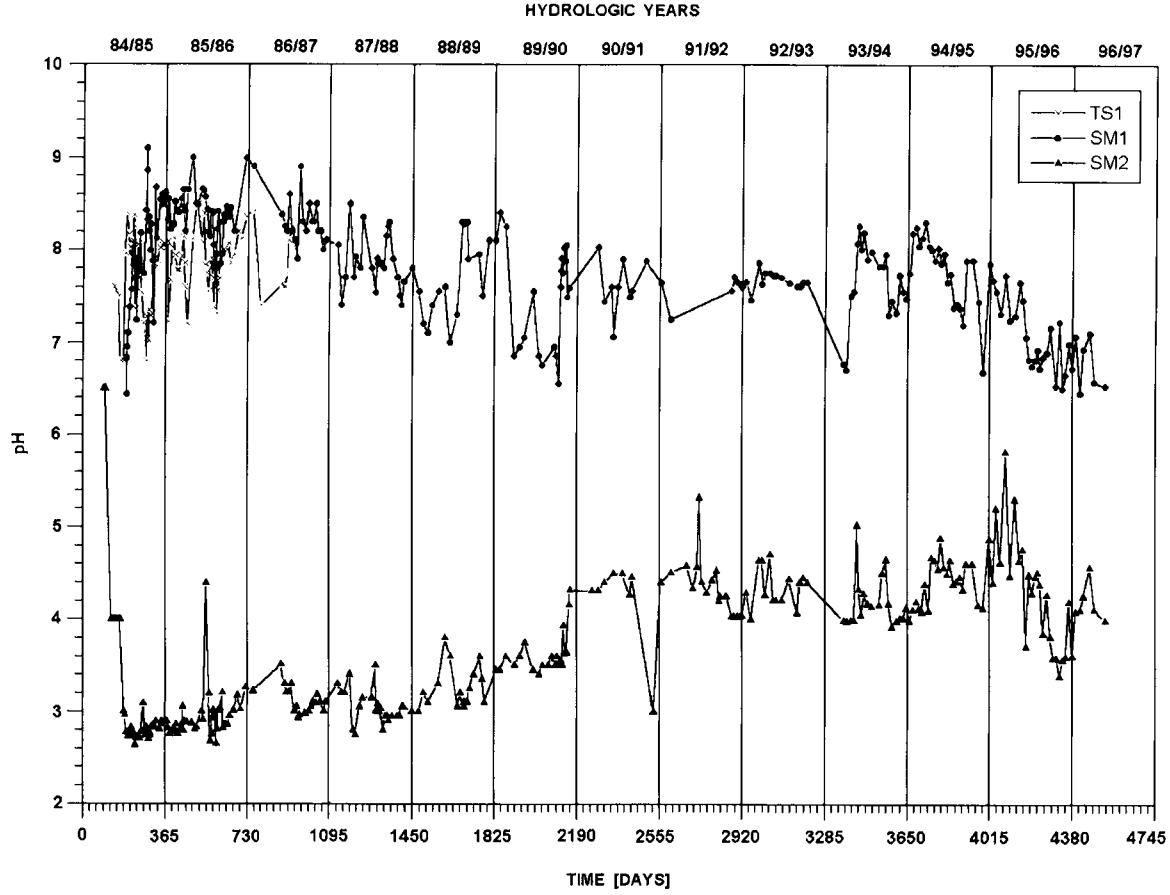


Figure III.6.19. pH values in the leachate from the surface layer of coal mining waste 1.5 m thick of different buffering capacity. Long-term lysimetric studies in the 12 years' natural hydrologic cycle (1984–1996).

and calcic (potassic, sodium) feldspar. Hydrogen ions displace Al^{3+} ions from their position in the lattice of clay minerals, dissolve kaolinite and react with feldspars, forming alumino-rich clay minerals, while Ca^{2+} is released into solution according to the reactions (Palmer, 1978; Lapakko, 1987):

$$(Al{\cdot}6H_2O)^{3+} + H_2O \rightarrow (AlOH{\cdot}5H_2O)^{2+} + H_3O \quad \text{(III.6.7)}$$

$$Al_2Si_2O_5(OH)_4 + 6H^+ \rightarrow 2Al^{3+} + 2H_4SiO_4 + H_2O \quad \text{(III.6.8)}$$

$$CaAl_2Si_2O_8 + 2H^+ + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} \quad \text{(III.6.9)}$$

These reactions seem to be major acid consuming ones at the stage of deep acidification of the material SM2. Temporary growth of chloride and sodium concentrations proves the decapsulating effect of preceding physical decomposition of particle size.

In addition in the younger non-acidified material (SM1), weathering decomposition of rock grains rendered available new loads of dolomite formerly encapsulated in rock particles that somewhat extended the decreasing buffering capacity of the material, which was reported by other authors also (Toran, 1987).

Both sulfate concentrations and chemical composition of leachate from the 7 year old material TS1 from the top youngest Westphalian C series buffered by Ca^{2+} and Mg^{2+} carbonate minerals (mainly dolomite), which are uniformly disseminated in the rock matrix, displayed a considerable stability at the level controlled by the carbonate and gypsum equilibria in the system Ca–Mg–C–O–H–S (Garrels and Christ, 1965; Brookins, 1988).

III.6.4.2.2.3. Trace elements leaching

The water balance that has been presented and the mechanisms of acid generation are common for most mining wastes. Since pH and Eh are critical factors controlling the release and leaching of trace elements, the acidification of pore solution in oxic conditions in the anthropogenic vadose zone of mining waste dumps should cause mobilization of heavy metals. Particularly susceptible to release are trace elements occurring directly in the centers of acidification, i.e. those being the major or accessory components of sulfides. Of different mining rejects, coal mining waste is the most abundant, but the least hazardous material also in terms of trace element concentrations, which do not exceed the range of average values for soil (Table III.6.4). In buffered material, as well as in low-buffered mine wastes in the phase I, and in the initial stage of the phase II, when buffering capacity is above the critical level and acidification has not yet developed, no release of trace elements in elevated concentrations is observed.

Acidification of the low-buffered material and simultaneously about a twofold increase of Eh results in a release into leachate of almost all analyzed elements, of which SiO_2, Zn and Mn are in amounts more than an order of magnitude higher than from the same material in the buffered phase. Metals appeared in the acidic leachate from 10–22 years old waste in a descending concentration order: $(Fe^{2+}) > Zn > Al > Mn > Sr > Li > Ni > B > Co > (Fe^{3+}) > Cu > Cd$ (Fig. III.6.20). Iron plays a different role in the various stages of leaching under acidic conditions. In the initial stage of a deep acidification when pH drops below 3 and Eh $\approx$ 0.3, iron can appear in pore solution in

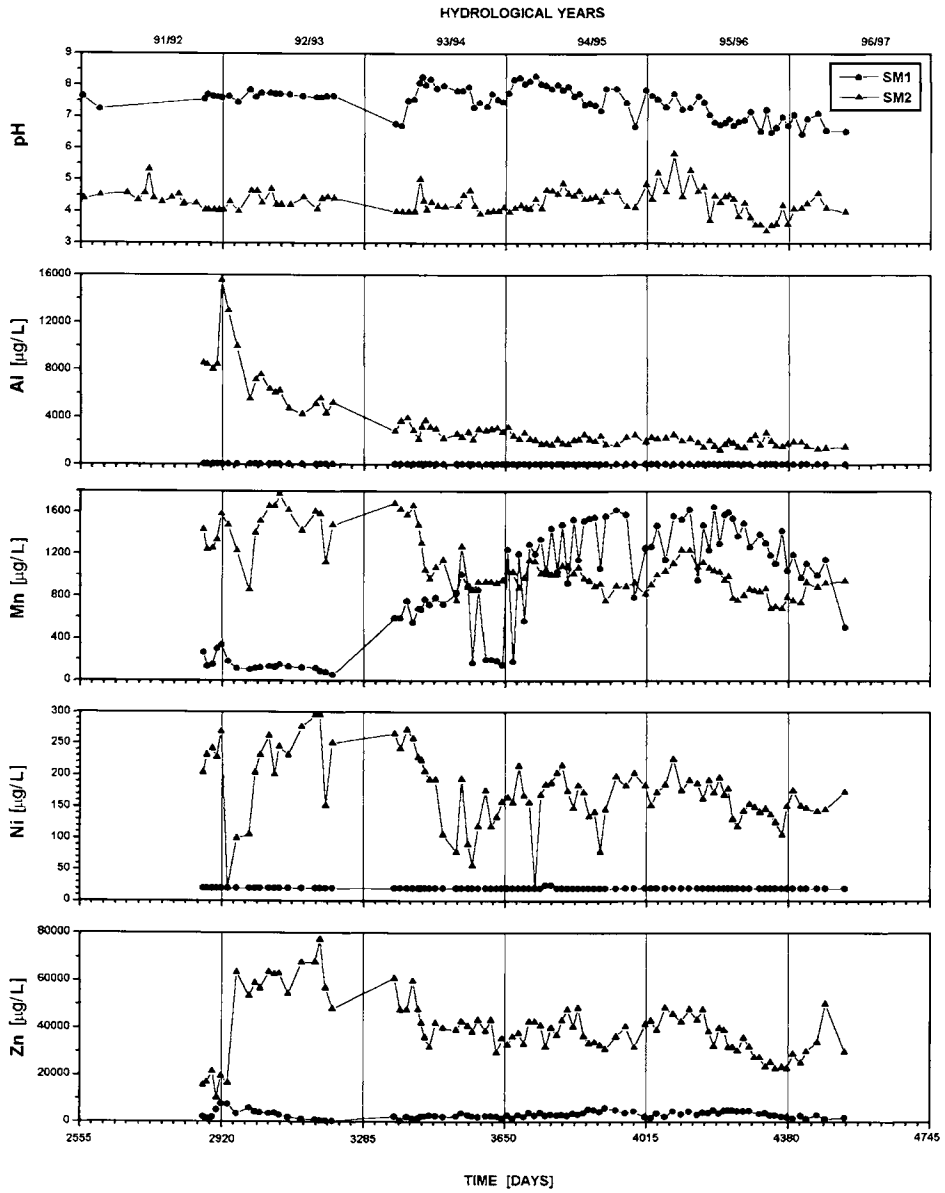


Figure III.6.20. Aluminum, manganese, nickel and zinc leaching from the surface layer of coal mining waste 1.5 m thick of different buffering capacity exemplified in the results of the hydrologic years 1992–1996. Long-term lysimetric studies in the 12 years' natural hydrologic cycle (1984–1996).

fairly high concentrations, from several to >100 mg Fe dm^{-3} (waste 10–12 years old), mainly as Fe^{2+} and $FeSO_{4aq}$ species. Along with gradually increasing pH to ≈ 4 at Eh ≈ 0.45, iron readily precipitates forming goethite and crystals of secondary sulfate minerals (melanterite, copiapite, halotrichite), abundant as coatings in disposed rock

material 18–22 years old. Concentrations of such elements as Zn, Al, Mn, Cd, Ni exceed more than tenfold the MCL for drinking water, according to SDWA, WHO and Polish national standards. Geochemical speciation with the use of computer programs WATEQ4F, Visual MINTEQ v. 2.01 and PHREEQC 2.7 shows that trace metals are present in leachate most frequently as Me^{+} and $MeSO_{4aq}$ species.

Taking into consideration the volume of acidic leachate and its long-term impact, heavy metals released from mining dumps, also from coal mining waste, may pose a serious risk to the aquatic environment, while the most problematic metal contaminants are dependent on the mined mineral (Table III.6.6).

III.6.4.3. Formation of pore solutions along the profile of a waste dump

Presented examples of long-term lysimetric studies show that even a layer of coal mining waste 1.5 m thick can be a serious source for vadose zone and groundwater contamination lasting for decades, while maximum contaminant release may have non-linear, time-delayed character. Chemical composition of pore solutions along the profile of coal mining waste dump that may be some scores of meters thick is controlled by the same factors as a surface layer i.e. by acid generation potential/buffering capacity and water exchange rate in the waste layers downward in the profile. Formation of pore solutions in a waste dump has been exemplified in the hydrogeochemical profiles of the anthropogenic vadose/saturated zone of the coal mine dumps about 11 m thick, constructed of the material analyzed above. This is shown for the Smolnica dump (SM) in Figure III.6.21 and for the Siersza-Misiury dump (TS) in Figure III.6.22.

In the hydrogeochemical profile of the Smolnica dump constructed of low-buffered material disposed in two layers, 3.5 and 7.5 m thick, which are 15 and 10 years old, respectively, both acidification and distinct differentiation of chemical composition of pore solutions have been observed (Fig. III.6.21). Concentrations of the major species in the pore solution in the waste layer show a typical vertical redistribution pattern, specific for the vadose zone in the conditions of the lack of equilibria constraints, and reflect decreasing water exchange rate in the subsequent waste layers downward the profile. Pore solution is the sulfate type, SO_4–Mg–Fe in the top layer 0–1.5 m and SO_4–Na–Mg in deeper layers of the profile. Low chloride concentrations (mean from 100 to 500 mg Cl/l) prove high water exchange rate (leachate from the fresh wrought waste contains several thousands mg Cl/l). Along the whole profile of the vadose zone, advanced oxidation of all textural forms of sulfides and precipitation of gypsum was observed. The chemical composition of the pore solution showed acidification up to pH 4.0 and extensive sulfate release (Table III.6.6). Sulfate mineralization in the pore solution along the whole profile of the vadose zone many times exceeded the MCL for drinking water according to Polish regulations (Directive of the Minister of Health, 2000), i.e. TDS up to 30 times and SO_4 up to 82 times, and according to WHO guidelines, up to 66 times (Galal-Gorchev, 1993); concentrations of SO_4 in pore solutions and leachate were also up to 10–16 times higher than MCL for liquid waste discharged to waters or soil (Directive of the Minister of Environment, 2002a). The chemical composition of water in the saturated toe layer is a resultant of mixing leachate from the overlaying vadose zone with groundwater of the saturated zone. Despite significant dilution, the concentrations of both TDS and SO_4 still

Table III.6.6. Examples of drainage, pore solution and leachate quality at several mining waste disposal sites.

Parameter, constituent (mg/l)	Coal mining waste, USCB, Poland						Ore mining waste, Canada[a] and N. Guinea[b]			
	Leachate from waste layer 1.5 m thick (lysimeters)		Pore solution along the dump profile				Tailing pond in uranium mine[a]-seepage	Silver mine waste dump[a] seepage	Under-ground copper mine[a] water	Copper mines waste dumps-leachate[b]
	SM1[1] 1.5 m	SM2[1] 1.5 m	SM[1] 0–10 m	TS[2] 0–10 m	PS[3] 0–3 m	P[4] 0–10 m				
Waste age (years)	9–10	19–20	10–15	7	6–8	5–13	Abandoned	Active	Active	Active
pH (–)	6.70–8.24	3.92–4.64	4.0–5.2	5.8–8.5	4.04–7.62	3.39–7.35	2.0	2.8	3.5	4.0–9.2
Na	7.58–84.22	9.12–88.50			2,044–12,492	638.6–3,236.4				20–38
TDS	900.2–1,966.3	653.2–1,826.6	4,162–24,287	4,030–5,234	4,071–32,541	3,004–14,603				
Cl	4.28–335.2	20.21–198.3	84.8–1,276.2	123.4–493.6	50.0–12,131	52.9–3,164.6				
SO_4	384.6–997.6	377.4–1,188.8	2,829–16,511	2,541–3,711	1,521–5,010	1,762–8,187	7,440	7,650	1,500	
Al	<0.06–0.06	2.11–15.54			<0.06–0.166	<0.06–11.63	588.0	359		2–25
As						<0.05– < 0.05	0.74	25.0	0.05	
Cd	<0.005–0.005	<0.005–0.035			<0.005	0.005–0.173				<0.001–0.028
Cu	<0.01–0.02	0.018–0.100			0.047–1.936	0.098–0.970	3.6	89.8	16.5	0.001–235
Fe	<0.01–0.03	<0.01–0.07			0.31–14.28	<0.01–90.78	3,200	1,190	10.6	0.13–0.2
Mn	0.057–1.246	0.76–1.77			0.229–4.785	0.070–2.508	5.6	78.3	6.4	12–32
Ni	<0.02– < 0.02	0.077–0.295			<0.02–0.411	<0.025–0.501	3.5	8.0	0.06	
Pb	<0.05– < 0.05	<0.05–0.05			<0.05– < 0.05	<0.050–0.428				<0.001–0.003
Zn	0.383–7.402	10.05–77.25			0.458–4.698	0.149–320.52				0.001–3.0

Coal mining waste dumps in Poland (own data): [1]SM–Smolnica waste dump, low-buffered waste; [2]TS–Siersza waste dump, buffered waste; [3]PS–Piast waste dump; [4]Przezchlebie waste dump.

[a]After Hutchinson and Ellison (1992) (Reference: Paine, 1987).

[b]After Jeffery et al. (1988).

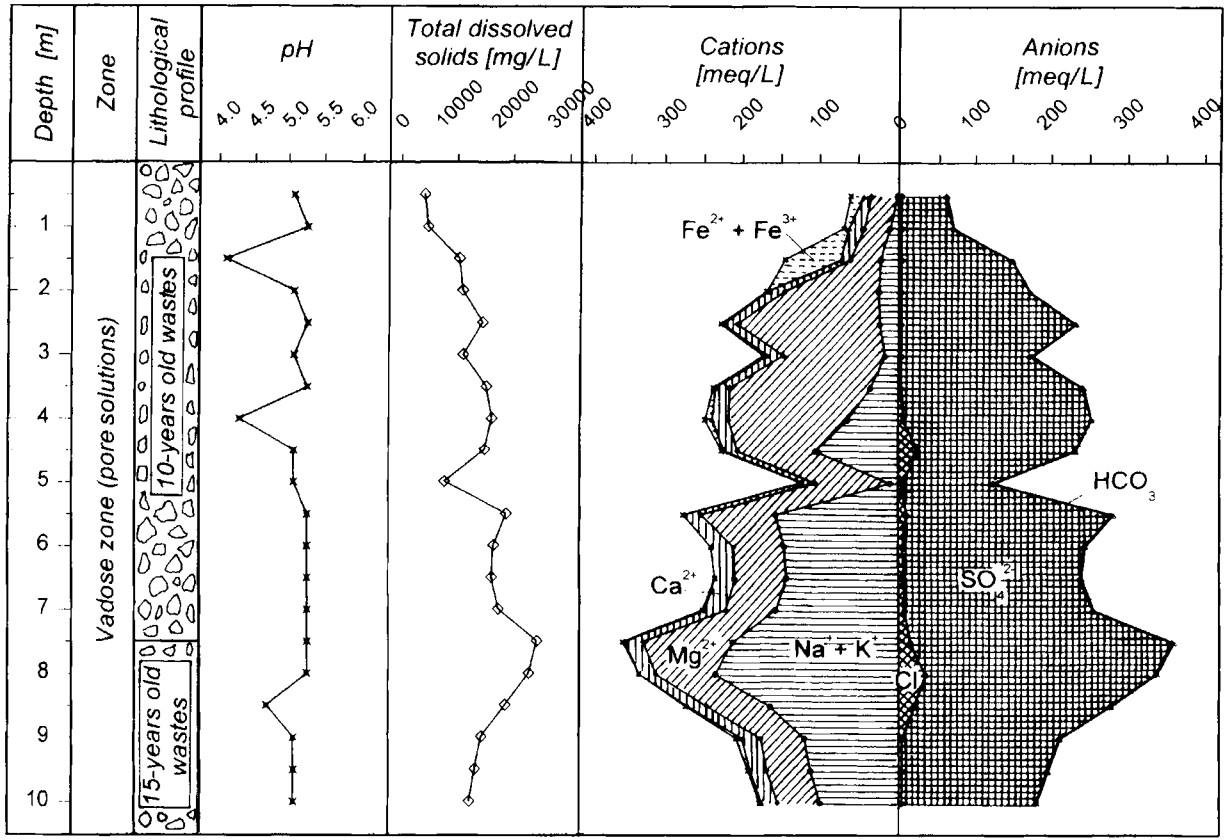


Figure III.6.21. Hydrogeochemical profile of pore solution within the low-buffered, acid generating waste SM (Smolnica dump).

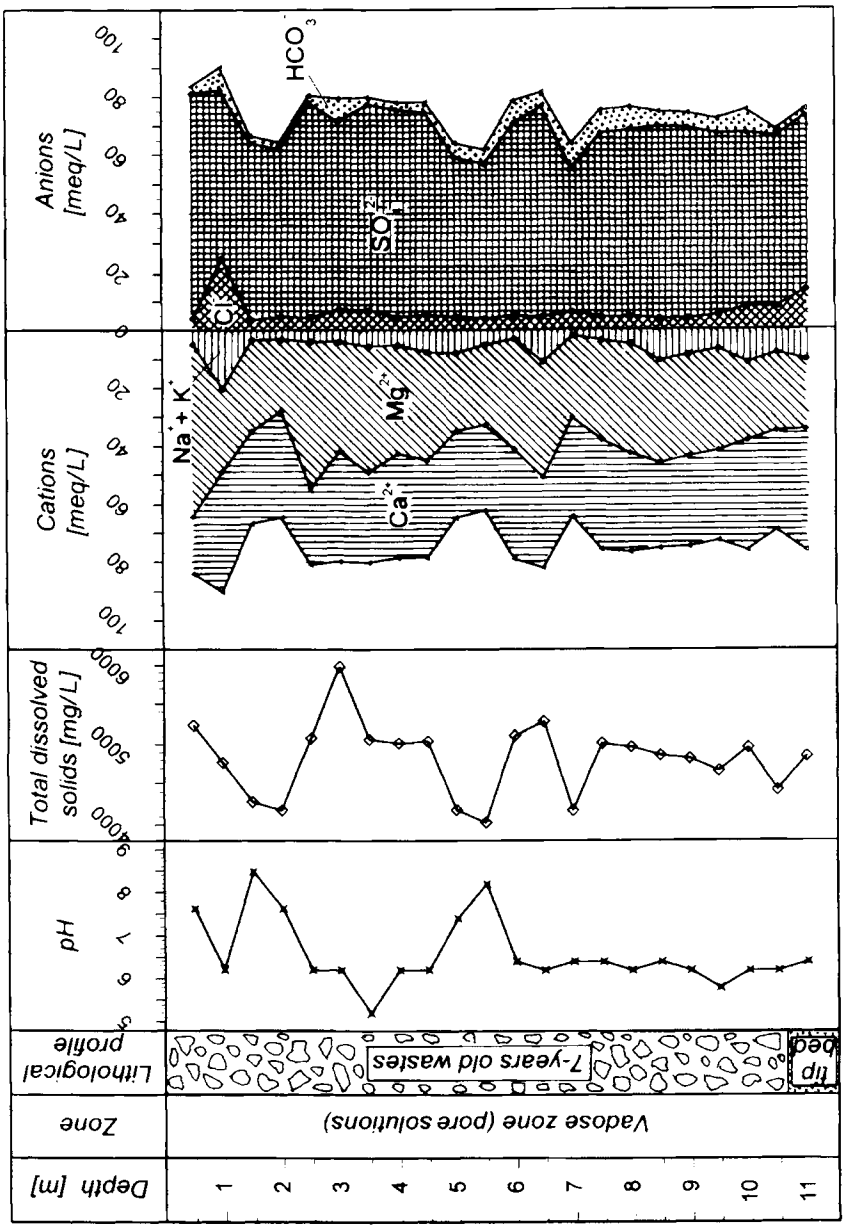


Figure III.6.22. Hydrogeochemical profile of pore solution within the buffered, non-acid generating waste TS (Siersza dump).

exceeded MCL by about an order of magnitude, causing serious deterioration of the groundwater quality.

In the profile of low chloride, buffered waste 7 years old (TS), the chemical composition along the profile is controlled by the equilibrium with gypsum and carbonate, and differs substantially from the pattern in the non-buffered material. Due to equilibria limitations, the concentrations of constituents along the whole profile are practically uniform (Fig. III.6.22). Pore solutions are of SO_4–Mg–Ca type, Mg:Ca ratio (in equivalent units) is close to 1, pH close to neutral, and gypsum precipitation is abundant along the whole dump profile. Due to the equilibrium constrains, the concentrations of both TDS and SO_4 are determined by the gypsum solubility (Table III.6.6). They are therefore significantly lower than the unconstrained concentrations in non-buffered wastes, though still 10–20 times higher than MCL for SO_4 in drinking water (Galal-Gorchev, 1993; Directive of the Minister of Health, 2000) and also several times exceeds MCL in liquid wastes discharged to water and soil (Directive of the Minister of Environment, 2002b).

The chemical composition of pore solution along the profile of another coal mining waste dump of the USCB, which consists of 3 layers of 1–13 years old material, also illustrates the time course of long-term environmental transformations of waste properties, from the buffered stage in the uppermost and youngest layer, through the acid generating stage in the middle layer and severe acidification of waste to pH 3.4 in the oldest layer. Elevated SiO_2 concentrations originate from the dissolution of kaolinite. High trace element release follows the sequence: Zn >> B > Fe > Ba > Sr > Al > P ≈ Ni > Mn > Cu > Se ≈ Mo ≈ Cd. The pollution potential of the oldest material appears to be the highest one (Fig. III.6.23, Table III.6.6).

This example also shows non-linear increase of the pollution potential of coal mining waste, resulting from the time-delayed depletion of the buffering capacity and acidification of the material. The data on leachate from acid coal mining and metal ore mining waste (Table III.6.6) prove the necessity of a careful evaluation and prediction of mining waste susceptibility to acidification and to adjust adequately the groundwater protection measures to the long-term leaching behavior of waste and to site-specific hydrogeological conditions.

III.6.4.4. Impact of mining waste dumps on the groundwater quality

Approximately 40–50% of dumping sites of high-volume waste all over the world, including mining waste, have been located in areas of unprotected aquifers used as a source of drinking water. The range and extent of the environmental impact of a mining waste dump, besides its short- and long-term pollution potential, largely depends on the hydrogeological conditions of the site, i.e. hydraulic conductivity and buffering properties of the bedrock and the dilution capacity of groundwater stream. The construction of a dump usually lasts for years; therefore, different layers and spatial parts of the dump display different pore solution exchange rate and its related chemical composition is dependent on the duration and mode of exposure to the atmospheric conditions. Hydrogeochemical profiles of the dumps illustrate this diversity (Figs. III.6.21–III.6.23). The construction period of the dump and its pattern, along with the heterogeneity of the disposed material,

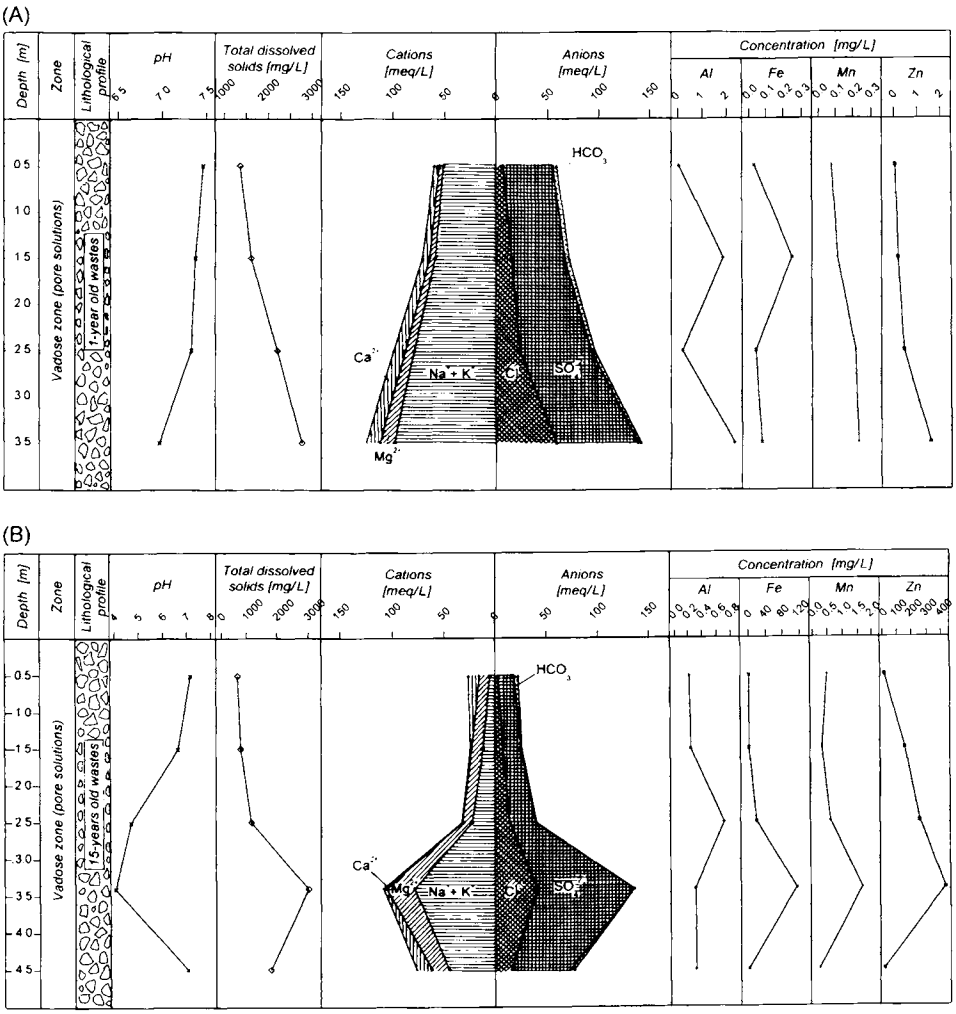


Figure III.6.23. Transformations of pore solution along the vertical profile of the Przezchlebie dump. Low-buffered waste undergoing changes in time from non-acidic (A – 1 year old waste) to acidic stage (B – waste layers 15 years old).

considerably affect the transformation of pore solution and leachate, and a resultant impact on the aquatic environment. Spatial and time-dependent variability of groundwater quality in the vicinity of a coal mining waste dump on the background of waste management and hydrogeological conditions will be exemplified here in the case study on the Smolnica coal-mining dump. The characteristics of material disposed, its leaching behavior and the pollution potential have been presented above, including results of long-term lysimetric studies on water balance (lysimeters SM1, SM2) and transformations of pore solution along the dump profile (SM).

III.6.4.4.1. Site characteristics

III.6.4.4.1.1. Waste characteristics and management

The Smolnica coal mining waste dump having total area $F_t = 130$ ha, thickness $H_t = 23$ m and volume $V_t = 13,845,000\ m^3$ is located along the Bierawka river (USCB, Poland) (Fig. III.6.24). At the dump, weakly buffered granular coal mining waste of moderate to elevated chloride (0.050–0.245% Cl) and mean sulfide sulfur contents ($S_s < 1\%$) has been disposed in three layers since 1965, in the general direction N–S and E–W. Sulfide reactivity expressed as a sulfide half-life $t_{1/2}$ ranges from 1037 to 1440 days. Rock material heavily compacted by vibratory rollers remains permeable to air and water and due to rather high sulfide reactivity and low buffering capacity ($\xi = C_{buf}/C_{ac} \leq 0.70$) is susceptible to acidification in time (Twardowska et al., 1988, 1990). The older N part of the dump, constructed in 1965–1980 ($F = 34$ ha, $V = 7500 \times 10^3 m^3$), from 1988 to 1997 was subject to residual coal recovery in the general direction W–E. After coal extraction by physical methods, waste has been re-disposed again. Technological processes caused disturbance of the primary constructed layers and increased exposure of waste to water and air during grinding, washing and sieving. Part E is the oldest part of the dump.

III.6.4.4.1.2. Hydrogeological conditions

The non-insulated quaternary aquifer in sandy gravel formations is underlined by impermeable tertiary muds. The free water table occurs 0.8–4.6 m below the ground surface. Groundwater in the dumping site area flows undisturbed in the general direction NE–SW to the riverbed (Fig. III.6.24).

III.6.4.4.1.3. Groundwater quality monitoring network

A local groundwater quality monitoring network (GWQM) consists of 28 wells (piezometers) installed in 1994 to yield groundwater samples from the uppermost quaternary aquifer up-gradient and down-gradient the waste management area. Water in the wells has been sampled 2–4 times a year. Isocontour maps (isopleths) of the hydrodynamic field and major water quality parameters were constructed by linear kriging using the SURFER computer program, Version 7 (Golden Software, Inc., 1999).

III.6.4.4.2. Groundwater quality transformations

Results of 9 years' (1994–2002) monitoring (Table III.6.7, Fig. III.6.25a–d) demonstrated generally stable good quality and lack of a strong anthropogenic impact on natural waters of the quaternary aquifer up-gradient of the waste dump. The leachate from the coal mining waste dump caused significant alteration of their chemical composition. It resulted in high (up to 80 times) increase of TDS and transformation of hydrogeochemical type of waters from SO_4–Ca into Cl–SO_4–Na, SO_4–Cl–Na–Ca–Mg or SO_4–Na–Ca down-gradient of the dump (Table III.6.7). Distinct trends in dynamics and directions of these transformations (Fig. III.6.25a–d) and analysis of cause–result nexus proved the controlling effect of such factors as waste age and management, as well as meteorological and hydrogeological conditions. In particular, the following general regularities were observed: (i) stable high sulfate concentrations,

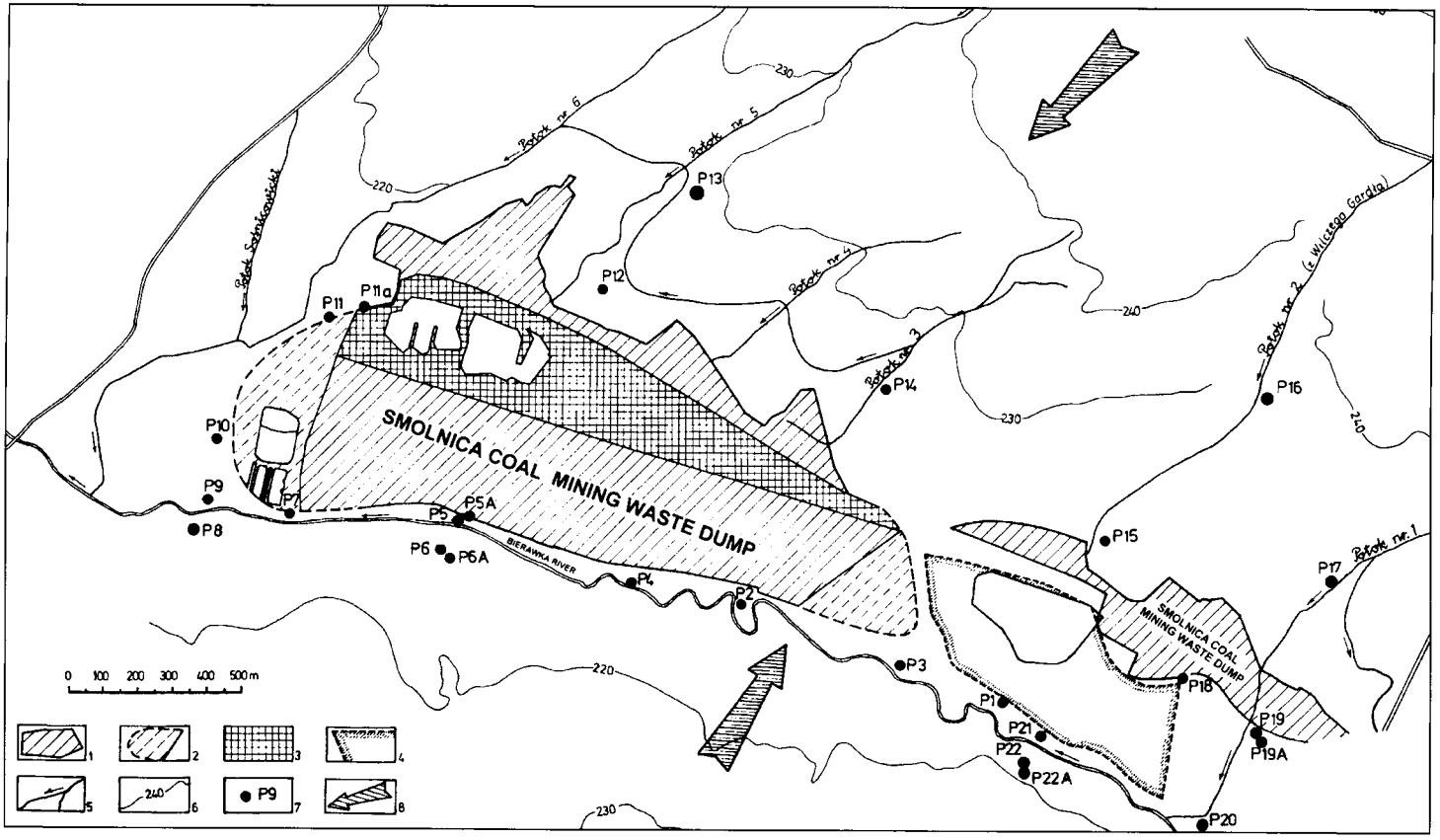


Figure III.6.24. Smolnica coal mining waste dump. Local ground-water quality monitoring network (LGWM). State in 12/1994. 1, Existing Smolnica coal mining waste dump; 2, planned final dump contour; 3, operational area of coal extraction plant; 4, planned municipal landfill; 5, water courses and rivers; 6, isopleths of ground level (m asl); 7, groundwater monitoring wells (LGWM network); 8, ground-water flow directions.

Table III.6.7. Transformations of groundwater quality in the Smolnica coal mining waste disposal site (USCB, Poland, monitoring data 1994–2002).

Parameter	Unit	Groundwater up-gradient of the dump	Groundwater down-gradient of the dump[a]			MCL for drinking water (Class A1 of surface water quality) – Polish standards[b]
			Part E: waste 20–38 years old	Central part: waste 15–30 years old + fresh rock	Part W: waste 10–20 years old	
pH, field		**5.35**–7.01	**2.51–6.41**	**5.73**–7.18	**6.13**–7.30	6.5–9.5 (6.5–8.5)
Conduct., field	μS/cm	214–466	1,855–**6,190**	**3,240–18,500**	1,212–**8,100**	2,500 (1,000)
Eh, field	mV	+146– + 344	−96.0– + 542	−78– + 144	−63– + 350	
Hardness, $CaCO_3$	mg/l	64.6–188.6	**742.6–2,363.3**	**1,067.9–4,071.9**	**543.8–2,456.4**	60–500
Ca^{2+}	mg/l	20.71–47.53	241.01–690.74	254.67–721.34	104.80–581.53	
Mg^{2+}	mg/l	3.12–16.98	34.20–**155.10**	**104.95–551.70**	**68.55–244.00**	50
Na^{2+}	mg/l	4.05–10.80	**263.73–1,174.85**	**587.55–3,403.45**	27.94–**1,368.5**	200.0
K^{+}	mg/l	0.91–2.41	8.33–20.47	19.06–90.63	12.07–87.64	
NH_4-N	mg/l	0.00–**4.96**	**1.184–10.08**	**1.00–8.68**	0.218–**6.720**	0.5 (0.5)
NO_2-N	mg/l	<0.001–0.019	<0.001	<0.001–0.004	<0.001–0.007	0.1
NO_3-N	mg/l	0.207–7.60	0.018–2.040	0.032–2.315	0.006–3.807	50.0 (50.0)
HCO_3^-	mg/l	5.49–24.12	0.00–122.03	9.15–705.97	18.31–360.0	
Cl^-	mg/l	8.16–29.58	257–**1,127**	204–**3,498**	22.22–**1,096.5**	250.0 (250.0)
SO_4^{2-}	mg/l	47.72–130.7	**1,013.3–2,846.9**	**1,958.3–7,362.4**	**495.33–3,595.6**	250.0 (250.0)
PO_4^{3-}	mg/l	0.009–0.087	0.002–0.094	0.006–0.098	0.001–0.050	5.0 (0.4)
SiO_2	mg/l	2–22	10–20	4–20	1–12	
TDS	mg/l	192–420	2,426–5,344	4,020–15,220	1,240–7,312	
COD	mg/l	7.41–54	15.20–**207.4**	24.48–**610**	9.76–**149.2**	(25.0)
C org.	mg/l	4.24–16.23	5.31–13.54	6.61–40.6	6.31–16.49	
Al	mg/l	<0.06	<0.06–**1.905**	<0.06–**0.614**	<0.06–**1.33**	0.2
B	mg/l	<0.10–0.10	<0.10–0.1	<0.1–0.6	<0.1–0.125	1.0 (1.0)
Ba	mg/l	0.059–**0.105**	0.025–0.095	0.022–0.026	0.037–0.065	0.7 (0.1)
Cd	mg/l	<0.003	<0.001–**0.070**	<0.001–**0.020**	<0.001–**0.011**	0.003 (0.005)

(continued)

Table III.6.7. (Continued)

Parameter	Unit	Groundwater up-gradient of the dump	Groundwater down-gradient of the dump[a]			MCL for drinking water (Class A1 of surface water quality) – Polish standards[b]
			Part E: waste 20–38 years old	Central part: waste 15–30 years old + fresh rock	Part W: waste 10–20 years old	
Co	mg/l	<0.005–0.04	0.001–0.09	0.05–0.15	<0.001–0.09	
Cr_t	mg/l	<0.001–0.004	<0.001–**0.275**	0.010–**0.1784**	<0.001–**0.14**	0.05 (0.05)
Cu	mg/l	0.001–0.01	<0.001–**0.075**	0.010–0.033	<0.001–0.024	1.0 (0.05)
Fe	mg/l	<0.001–**8.57**	**28.43–297.3**	**20.68–158.4**	0.02–**92.09**	0.2 (0.3)
Mn	mg/l	<0.001–**1.45**	**4.18–14.09**	**5.253–15.897**	0.03–**12.53**	0.05 (0.05)
Ni	mg/l	<0.001–**0.04**	0.017–**0.107**	0.016–**0.570**	<0.001–**0.124**	0.02 (0.05)
Pb	mg/l	<0.005–**0.015**	<0.001–**0.120**	<0.001–**0.14**	<0.001–**0.08**	0.01 (0.05)
Zn	mg/l	<0.001–0.27	<0.001–**11.93**	<0.001–0.478	<0.001–0.62	3.0 (3.0)

[a]Values exceeding MCL are in bold.

[b]Directive of the Minister of Health (2000); Directive of the Minister of Environment (2002a).

(a)

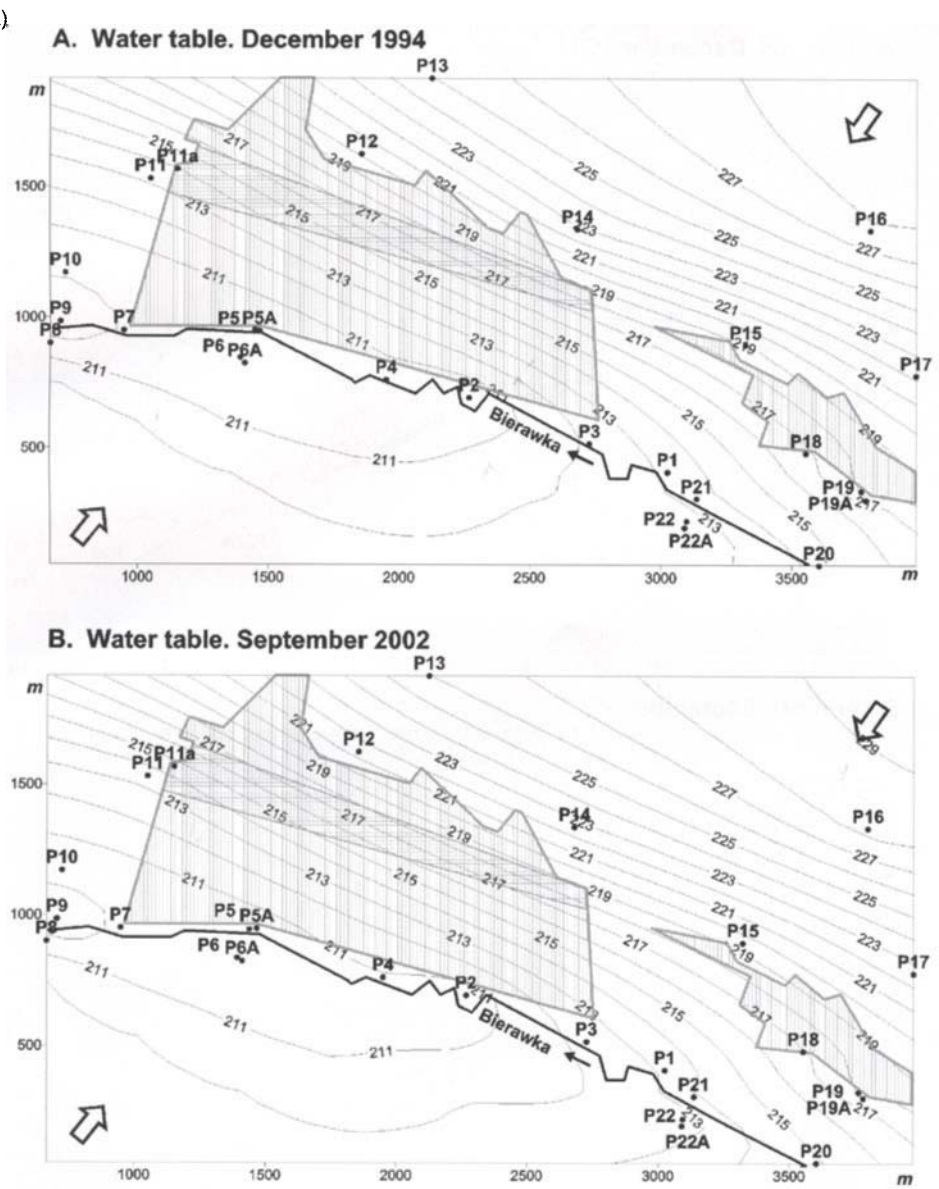


Figure III.6.25. Hydrodynamic field and distribution of contaminants in groundwater of Smolnica dump site (m asl). A, State on 08/12/1994 (sampling series I, LGWM network); B, state on 05/09/2002 (sampling series XV, LGWM network). Kriging estimates, linear model, anisotropy: ratio 2.5, angle 15 (SURFER computer program, Version 7, Golden Software, Inc., 1999). (a) Map of hydrodynamic field; (b) distribution of pH values; (c) distribution of SO_4^{2-} concentrations; (d) distribution of Cl^- concentrations.

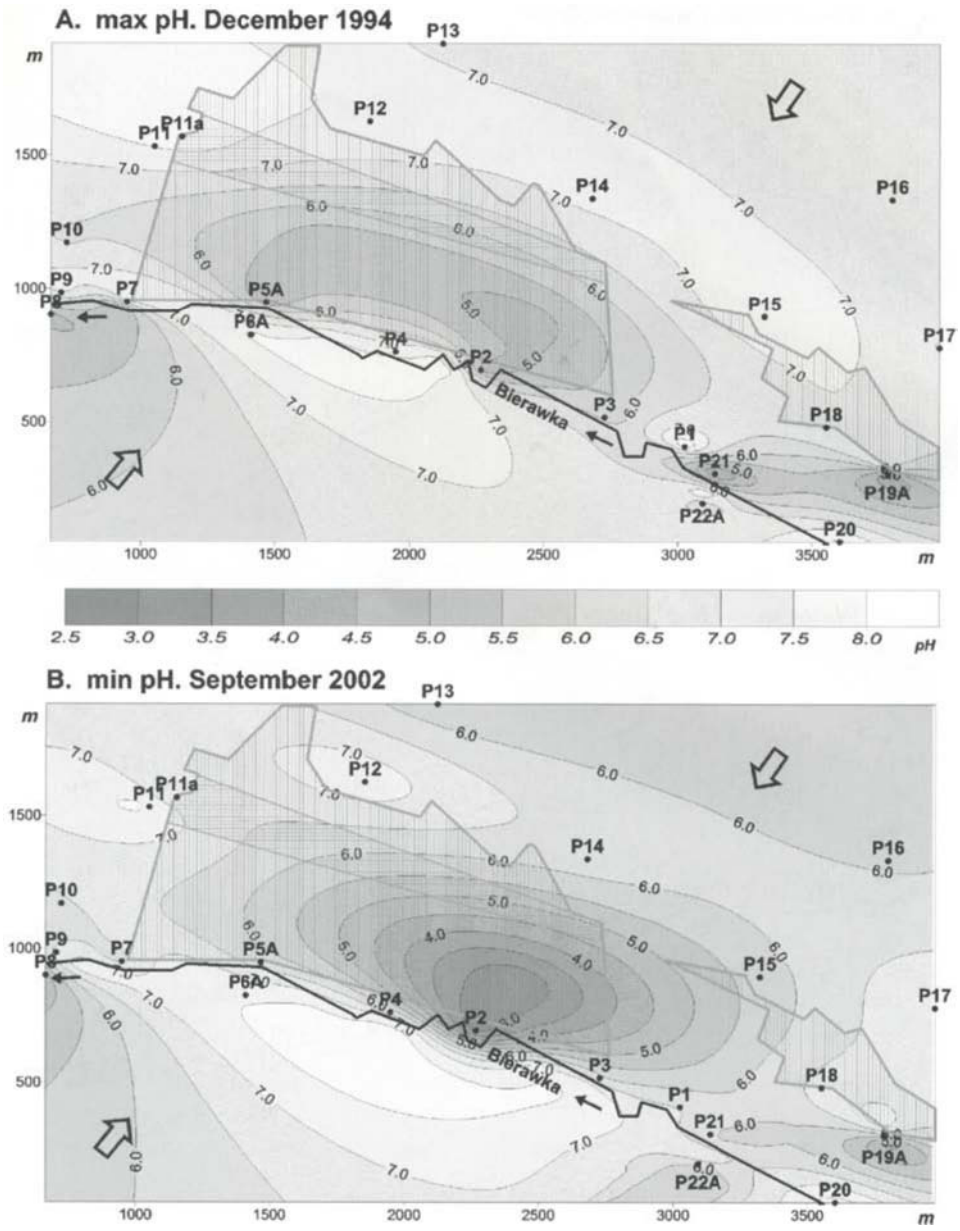


Figure III.6.25 (continued)

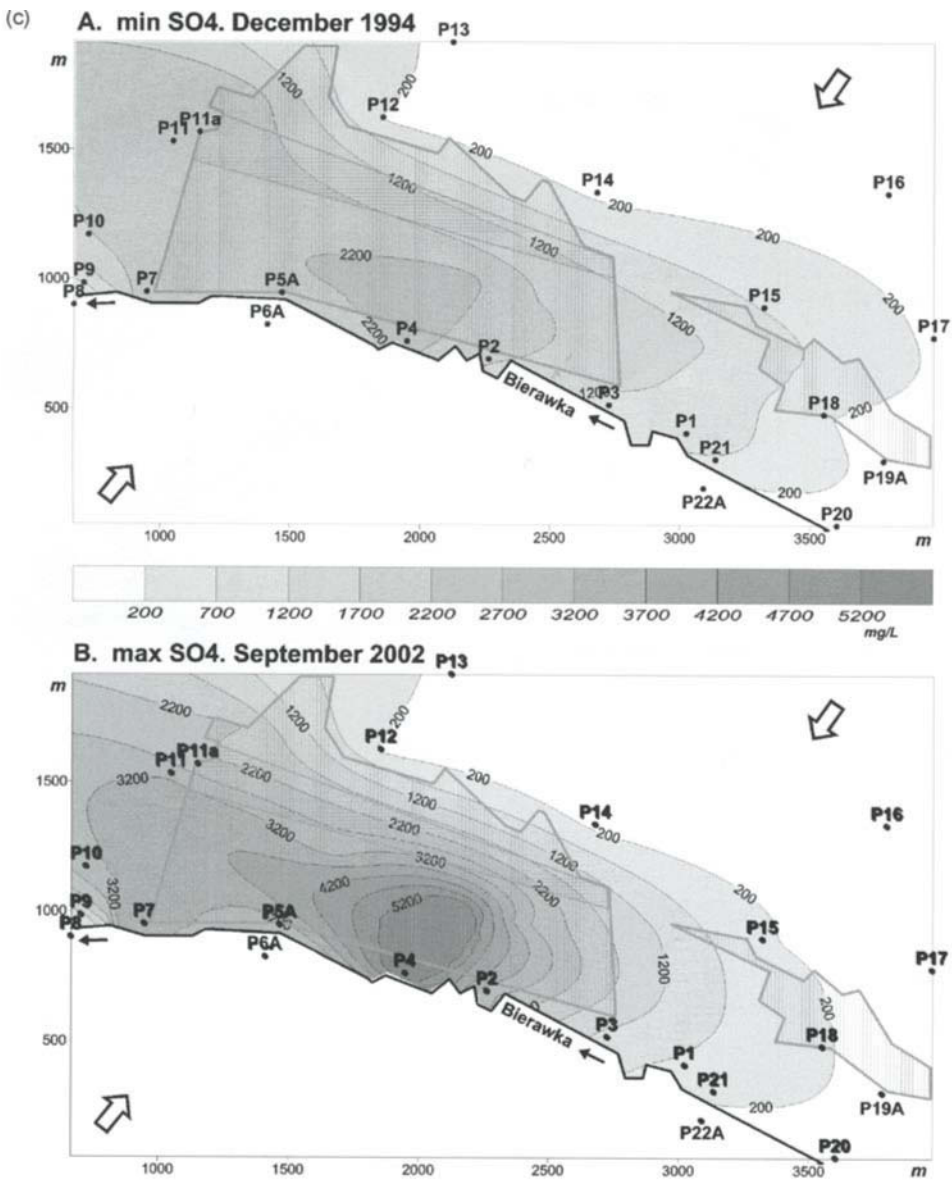


Figure III.6.25 (continued)

acidification up to pH 2.5; moderate or relatively low, gradually decreasing chloride salinity of groundwater affected by leachate from the oldest (20–38 years old) undisturbed E part of the dump; (ii) wide range of pH (mostly moderately acidic), high chloride and sulfate salinity of groundwaters receiving leachate from the central part of the waste dump, predominantly 15–30 years old, which was the most affected

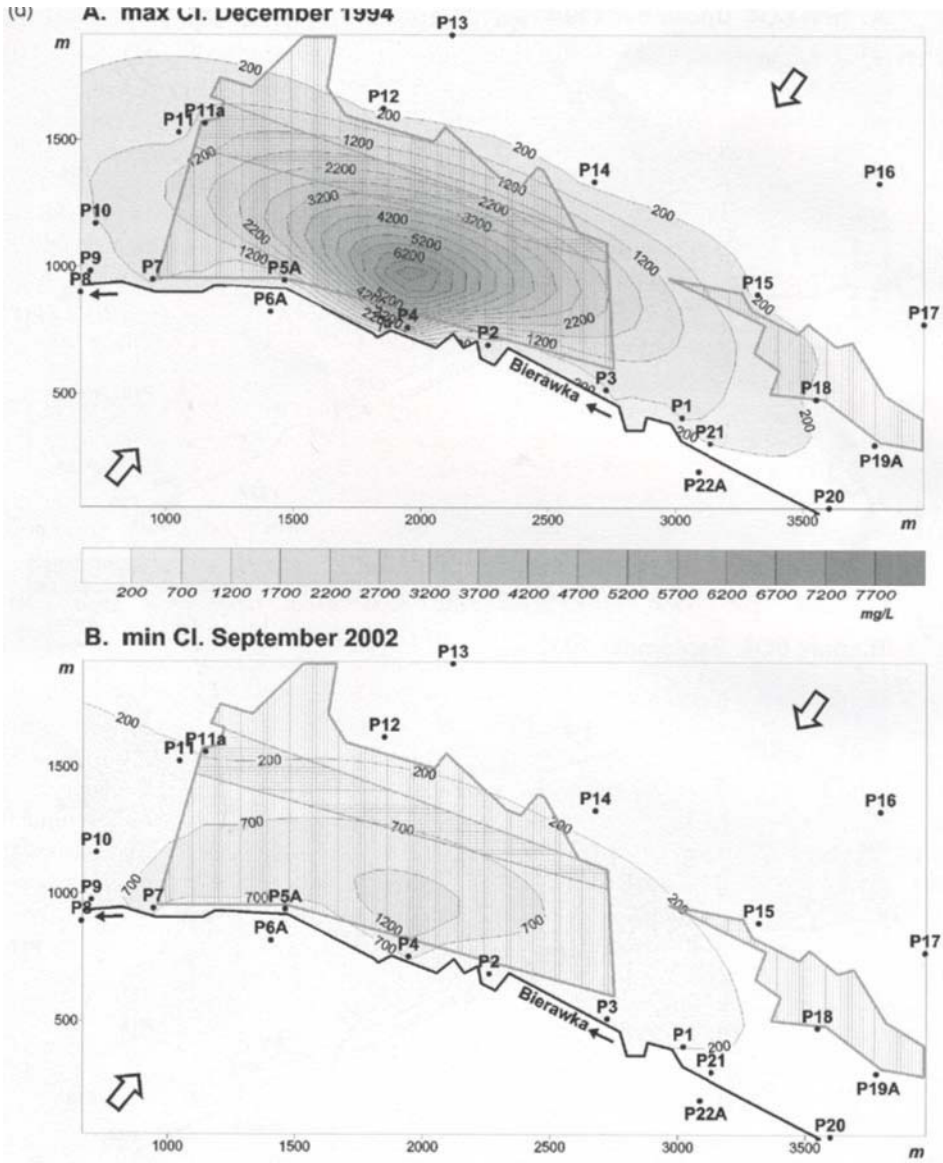


Figure III.6.25 (continued)

anthropogenically by joint impact of old waste deposits and current management operations; in these waters, the highest concentrations of chloride (decreasing trend) and sulfate (increasing trend) at weakly acidic pH were observed; (iii) pH values predominantly ≥ 6.5, decreasing chloride salinity and increasing sulfate concentrations in groundwaters receiving leachate from the W part of the dump (10–20 years old) and influenced also with coal recovery activity in the NW section. High chloride salinity

was caused by the disposal of freshly mined rock at the top of the dump, while the increase of sulfate concentrations distinctly correlated with the direction of waste extraction/disposal for coal recovery. The concentrations of constituents in groundwater down-gradient of the waste dump appeared to be influenced also by meteorological conditions: intensive precipitation after dry periods resulted in higher concentrations of sulfate being a resultant of generation/release processes. Groundwaters affected by leachate from the dump also showed high contents of Fe and Mn (1–2 orders of magnitude with respect to MCL and background concentrations) and elevated maximum concentrations of Al, Cd, Ni, Pb and Zn, particularly in waters receiving leachate from the oldest E part of the dump. The adverse alteration of groundwater quality down-gradient of the coal mining waste dump has made the impacted aquifer unfit for any use.

The natural barrier against the expansion of contaminants from the dump in the SW direction is the Bierawka river, which drains the quaternary aquifer. Therefore, in the presented case study, a strong deterioration effect of the coal mining waste dump is spatially limited. The dilution/adsorption effect of bedrock in the vadose zone causes considerable reduction of trace metal concentrations (Zn, Ni), while iron in oxic conditions tends to precipitate in the form of hydroxides, abundant in the drainage ditches of the dump.

In other sites of the USCB, though, where the dumps are sited up-gradient of the settlements, thorough degradation of the usable quaternary aquifer has occurred as a result of macro-components leaching (sulfates, chlorides, TDS) despite the well-buffered mining waste disposed and qualification of the material as non-acid generating waste. This caused a necessity of using remote sources of tap water supply for a number of settlements.

Other numerous case studies on ARD or acid mine drainage (AMD) show similar environmental behavior of mining wastes with respect to potential for acidity generation and major ion composition; the acidic leachate from metalliferous waste contains considerably higher concentrations of mobilized heavy metals due to their high content in a waste rock (Table III.6.6) (Cnoquette et al., 1995; De Vos et al., 1997; Herring et al., 1998; Munroe and McLemore, 1999). As ARD generation creates a serious environmental problem both in active and old mining waste disposal sites, the European Union with its almost 2000 mining sites, of which almost 1000 is abandoned, should pay close attention to the environmental behavior of these sites.

Waste rock geochemistry and the long-term weathering characteristics of mining waste appear to be a key issue for predicting the potential of active or abandoned mine waste disposal sites for ARD, its detrimental or toxic effect and for undertaking preventive attenuation measures (Yeates, 1993; Price and Kwong, 1997; Zahner et al., 1997; Smith, 2001).

III.6.5. Conclusions

1. Bulk non-hazardous mining waste, either disposed at dumping sites or used in civil engineering as common fill, may cause long-term deterioration of groundwater quality.
2. The most important intrinsic factors controlling the contamination potential and its spatial and time-dependent transformations are the hydraulic conductivity,

permeability to air, soluble compound contents in the freshly mined waste rock and occurrence of geochemically unstable minerals (e.g. sulfides), which cause long-term generation and release of new loads of primary (e.g. acidity, sulfates) and secondary contaminants (e.g. trace metals). The external factors comprise meteorological, hydrogeologic, hydrogeochemical and hydrological conditions and the anthropogenic impact of waste management at the disposal site.

3. Sulfidic mining wastes, among them coal mining waste exposed to atmospheric conditions, should be considered as a long-term source of groundwater contamination, lasting for decades. The specificity of this material is an occurrence of short- and long-term pollution potentials. While the short-term pollution potential originating from the initial load of soluble macro-components (TDS: chlorides, sulfates) contained in fresh wrought material is well recognized, the long-term leaching behavior induced by sulfide oxidation is often neglected due to its non-linear, time-delayed character and failure in its evaluation by a singular regulatory leach test. This leads to wrong qualitative and quantitative assessment of the environmental risk of high-volume mining waste other than hazardous, e.g. coal mining waste.
4. The contaminant release and transport within sulfidic mining waste, e.g. in coal mining waste dumps and civil engineering constructions (river and lagoons embankments, ground leveling), occurs predominantly in the vadose zone conditions of water infiltration. Water balance of a surface layer of mining waste rock about 1.5 m thick is unstable, while the infiltration water flow within the dump is, in general, constant.
5. The majority of non-compacted and compacted granular mining wastes, among them coal mining waste, are permeable to vertical water infiltration and air penetration.
6. The chemical composition of pore solution within the dump profile is determined by the vertical redistribution of contaminant loads unrestricted by equilibria constraints (chlorides and sulfates balanced by alkali and hydrogen ions), acid generation potential (sulfide oxidation), buffering capacity at pH $\approx$ 7.0 (occurrence and forms of Ca–Mg carbonates: calcite, dolomite) and solid/liquid phase equilibria (equilibrium with carbonates and gypsum, pH–Eh).
7. The highest short-term contamination potential is from waste rock having relatively high chloride salinity; the highest long-term contamination potential is due to low-buffered acid generating waste of high metal content (e.g. from metal ore mining). High acidification and long-term macro- and trace component release generally occur in weathered mining waste several years old.
8. Sulfide minerals' reactivity varies in a wide range determined by their textural form and shows certain regularity depending upon their position in the stratigraphic profile of the carboniferous sequence. The kinetics of sulfide decomposition, which can be described by a first-order reaction, generally display high stability for the particular rock material and do not show acceleration in time that would have suggested considerable changes in prevailing oxidation mechanism.
9. Just part of the total sulfide load is available for the oxidation and acid-sulfate release process. The oxidizable sulfides in the material become gradually accessible in subsequent portions; the accessibility increases in older waste material in the uppermost layer of waste about 1.0–1.5 m thick due to the weathering degradation of the rock grains, which reduces their size.

10. Buffering of generated acid loads by carbonate minerals in waste rock is based mainly on their equilibrium-constrained dissolution in microenvironments of the heterogeneous porous matrix. There is a different availability of buffer load depending on the carbonate dispersion and specific surface. This causes a tendency to acidification of a buffered material in long dry periods. Hence, to neutralize ARD permanently, buffering capacity of the material should be much in excess with respect to its acid generation potential.
11. The extent of an adverse effect and required protective measures in the dumping area are site-specific and depend also on the buffering capacity of the vadose zone bedrock and ability of receiving ground and surface waters to dilute life cycle contaminant loads released from the dump. General evidence shows deep deteriorating impact of both active and old closed mining waste disposal sites on groundwater quality.

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Further reading

Web sites for further information

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http://www.enviromine.com/ard/Eduardpage/ARD.HTM

http://www.state.sd.us/denr/DES/mining/adti.htm.http://www.enviromine.com/ard/Acid-Base%20Accounting/Quality.htm

http://www.enviromine.com/ard/Microorganisms/roleof.htm

http://www.enviromine.com/ard/Mineralogy/Petrology%20ard%20Mineralogy.htm

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III.7
Coal combustion waste

Irena Twardowska and Jadwiga Szczepańska

III.7.1. Introduction

III.7.1.1. Coal combustion as a source of energy

The large-area contamination problems caused by coal-based electric utilities in the second half of the 20th century directed efforts to the reduction of particulate and gaseous emissions from coal-fired power plants to the atmosphere. The problem of fly ash (FA) emission has been solved successfully, immediately creating another problem of environmentally safe coal combustion waste (CCW) disposal and use. In turn, reduction of gaseous emission affects the structure and properties of CCW.

Coal combustion residues are one of the most abundant high-volume waste materials. Their proportion in the total waste stream highly depends upon the role of coal in power production, and is as a rule the highest in coal producing countries (Twardowska, 2003a). Despite stepping up development of alternative sources (oil, gas, nuclear, hydro and other renewables), the position of coal in power production is still strong and is also expected to be significant in the future (see Chapter III.6).

In 2000, coal provided over 23% of global primary energy needs and generated about 39% of the world's electricity (WCI, 2002e, after IEA, 2002a). At the beginning of 21st century, coal remains to be the major fuel used for generating energy worldwide. Countries heavily dependent on coal for electricity include the ones with the highest population that are also major producers of hard coal (China, USA and India, which supply 66.6% of global hard coal production), and a number of other countries, which comprise both suppliers and importers of coal.

In China, the greatest world coal producer, in 2000 electricity generation based on coal accounted for 78–84% (IEA, 2002a; WCI, 2002e). In the USA, the second biggest coal producer after China, electric utilities burn over 90% of the total coal output (Collins, 1992) to supply 52% of the nation's electricity according to 2001 data (WCI, 2002e). The third place as a coal producer holds India (8.5% of the total global hard coal production), where unlikely other stagnating coal markets, accelerated growth of output occurs to fulfill the increasing demands in power generation. Currently, Indian coal fired power plants comprise 77% of electricity output (2000 data, WCI, 2002e). National sources for all India estimate an increase of coal consumption to 725 Mt in 2011–2012 (Prasad et al., 2000); 500 Mt (72%) of coal is slated to go in 2009/2010 for power generation (Gale, 1999). This

means an extremely challenging 2.3-fold growth in the next decade compared to the current hard coal production in the country (312.5 Mt in 2001). The ABARE report (2002) assesses the prospects for thermal coal consumption for electricity generation in India by 2010 with an average annual growth rate of about 3%, which is at much lower realistic level (WCI, 2002a, after ABARE, 2002).

A number of countries use coal as an important component in a balanced energy mix. According to the World Coal Institute (WCI, 2002e), major steam coal importers in 2001 were Japan, Republic of Korea and Chinese Taipei (Taiwan), which imported 2.1, 1.2 and 1.1% of the global output, respectively, while 15 Member States of the European Union (EU15) imported in total 145.4 Mt (3.8% of the global output). All these countries showed significant increase of steam coal import in 3 years since 1998. In the EU15 thermal coal import increased in this short period for 34% (WCI, 1999, 2002b), despite permanent general decrease of hard coal consumption in last two decades (1981–2001) and further projected declining trend by 2010 with an annual rate of −0.8% (WCI, 2002a, after ABARE, 2002).

The overall prognoses on global energy production based on coal compared to 1999 through to the year 2010 forecast an average annual growth of 1.9%. The majority of this increase is expected for electricity production in developing Asian economies, in particular in the ASEAN countries, India and China, with average annual growth rate of about 9.5, 3 and over 2.5%, respectively. Japan, Korea and Chinese Taipei (Taiwan) are projected to remain the largest importers of thermal coal (WCI, 2002a, after ABARE, 2002). In Japan, from 1975 to 1998, the total power production grew 2.3 times, while coal-based power generation increased 7.5-fold. The market share of coal-based power production in Japan increased 3.5-fold, from slightly more than 4.5% in 1975 to 15% in 1998. The Federation of Electric Power Companies in Japan estimates that coal will maintain its market share in the future composition of the Japanese power sector at the level of 20–21%, while further increase of electricity generation by 2008 up to 24% compared to 1998 is anticipated (WCI, 2000). This will assure a balanced energy portfolio for Japan and a safe broad diversity of fuels.

The growth of cost-effective coal-fired generation of electricity in some developed economies, such as the USA and Australia (1.5–2% per annum by 2010) is also expected (WCI, 2002a).

The emerging markets for coal-based electricity generation include selected developing countries, where electrification rates vary significantly (Fig. III.7.1). China in 2000 already reached the rate of electrification over 98% that was close to OECD average (99.2%); 78% (WCI, 2002e) to 84% (IEA, 2002a) of electricity in China was coal-fired. Philippines and Thailand experience dynamic growth of electrification that substantially exceeds world average (72.8%) and will shortly reach OECD level. Sub-Saharan Africa is suffering from acute energy shortage with an average of only 23%, while a number of these countries is placed much below this low level (e.g. Mozambique, Ethiopia, Uganda). South Africa greatly differs from the rest of Sub-Saharan countries: it has raised its electrification rate to 66.1% (88% of power generated is based on coal) and shows further rapid development. Similar fast growth of electrification occurs in Indonesia that is currently close to the developing countries with an average (64.2%). In India and Nigeria the electrification rate is still below 50% and requires a significant increase in power generating capacity (WCI, 2002c,d). These data illustrate both worldwide dispersion of coal use for electricity

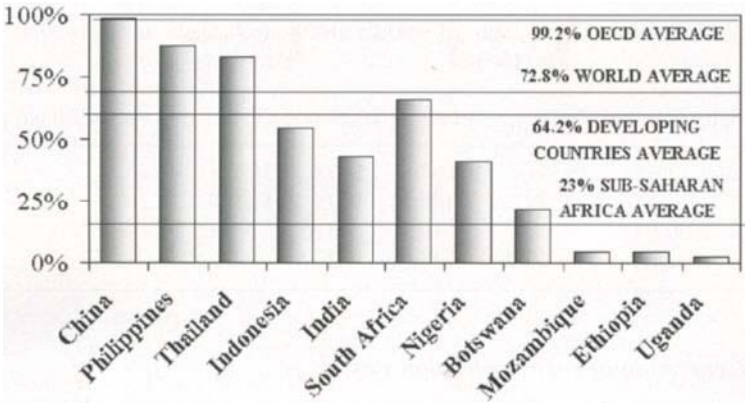


Figure III.7.1. Electrification rates for selected developing countries in 2001 (after IEA, 2002a,b).

production, and uneven present and future distribution of coal-fired power generation. African and Asian development in the area of energy to the great extent is going to be based on coal.

At present, in Asia Pacific coal has become the major source of energy generation, supplying in 2001 over 40% of primary energy in the region (WCI, 2002b). Besides China and India where coal-based electricity generation accounted 78 and 77%, respectively (2000 data), also in Australia 77% of power production is dependent on coal (WCI, 2002e).

The biggest European coal producer (2.7% of the global output in 2001) is Poland. Its electricity generation is almost entirely based on coal (96%). Besides Poland, other countries in Europe heavily dependent on coal as the source of electric power include Czech Republic (72%), and among the EU15 Member states Greece (67%), Germany (52.5%), Denmark (47%) and The Netherlands (28%). In the EU15 coal was used in 2001 for 27% of electricity generation (WCI, 2002e). In order to achieve a decrease in greenhouse gas (GHG) emissions under the Kyoto Protocol, EU15 plans to decrease solid fuel consumption, i.e. hard coal, lignite and peat that results in the negative growth rate projected by 2010.

The long-term World Energy Outlook (WEO) released in 2002 by the International Energy Agency (IEA) forecasts a 1.7% annual increase in energy demand and twofold increase in world electricity demand in the next three decades 2000–2030 (Table III.7.1). According to this prognosis, global primary coal consumption will rise at an average annual rate of 1.4% up to 2030. In all regions, coal use will become increasingly concentrated in power generation, which will account for almost 90% of the increase in demand between 2000 and 2030. In developing countries coal-based electricity is set to more than triple by 2030. Most of the increase is projected to be in India and China where large, low-cost reserves will keep coal as the dominant fuel (WCI, 2002e, after IEA, 2002b). Therefore, coal will remain the largest source of electricity generation for the first three decades of a new Millennium.

Table III.7.1. Prognosis of coal share in world's electricity balance in 2000–2030 (after IEA, 2002a,b).

World electricity balance	2000	2010	2020	2030	Average annual growth (%)
Gross generation (TWh)	15,391	20,037	25,578	31,524	2.4
Coal (TWh)	5989	7143	9075	11,590	2.2
Growth 2000–2030 (%)	0	19.3	51.5	93.5	
% of gross generation	38.9	35.6	35.5	36.8	

III.7.1.2. Generation of coal combustion waste

Coal-based power production results in generating a huge amount of CCW worldwide. Coal statistics reflect on the one hand, the range of CCW in the total waste stream, and on the other hand, non-uniformity of distribution of this waste in particular countries, producers and users of coal. Despite of the omnipresence of CCW, the statistical data concerning its generation and managing in the different countries of the world are fragmentary.

The OECD last available data for 19 member countries (without the USA, Canada, Spain and eight other OECD members) concerning waste from power generation in the 1990s gives the total as 166.66 Mt, which comprise besides CCW also other waste, e.g. from fuel oil (OECD, 1999). The largest contributions to this total were from Japan, Germany, Poland, UK, Australia and Turkey (57.3, 19.6, 18.0, 13.0, 11.0 and 8.7 Mt, respectively). In 2001, Poland produced 15.8 Mt CCW from electricity, and 3.0 Mt CCW from thermal energy generation, total 18.8 Mt (Central Statistical Office, 2002). Of these countries, which are coal producers, the exceptionally high position of Japan as a fuel importer is probably due to the high development of power-consuming industries. Earlier sources (Shao Yi, 1992) report that only 4.0 Mt of CCW was generated in this country in 1989. According to incomplete data, EC15 (without Spain, Austria, France and Luxembourg), produced a total of 49.93 Mt of waste from all the sources of power generation, and of this the contributions of Germany (39%) and the UK (26%) amounted to 65% of the total (OECD, 1999). Annual waste generation from these sources reported by EUROSTAT (2001) for 10 of 15 EC Member States for the years 1993–1999 accounted for 54.14 Mt; 71% of this amount was share of Germany (47%), and of the UK (24%). Of 29 European countries that comprise EC15, 3 associated and 11 candidate countries, data on annual waste generation from electricity and thermal energy production in this period were available only for 15 countries that produced in total 96.43 Mt of power plant waste. Germany, Poland and the UK generated 57% of this amount.

Divergence and incompleteness of both sources of the statistical data is a serious obstacle in the accurate assessment of the amount of CCW generated by OECD member states and European countries. For a number of other countries, no reliable statistics on CCW generation is available.

In the USA, in 1998 over 100 Mt of CCW were produced (Butalia and Wolfe, 1999; Chugh and Sengupta, 1999). According to American Coal Ash Association (ACAA) in 1992, 74.4 Mt of CCW was generated (Tyson, 1994). ACAA survey data for 1996

evaluate CCW amount for 92.45 Mt (Stewart, 1997, 1999). It consists predominantly of FA (58.3%), bottom ash (15.8%), boiler slag (2.5%) and FGD solids (23.4%) (Stewart, 1999).

In India, the coal consumption for power production in 1996–1997 was 196 Mt, and around 75 Mt of CCW was generated annually. This huge amount of CCW, which consists of about 80% of FA and 20% of bottom ash (BA), is due to use of high ash (30–50%) low-grade coal; thereby coal ash has been generated at an average rate of 5 t/MW/day (TIFAC, 1990). A further growth of CCW to 120 Mt at the beginning of the new Millennium (2000–2001) and up to 290 Mt in 2011–2012 has been anticipated at coal consumption for power generation of 299 and 725 Mt, respectively (Prasad et al., 2000).

III.7.1.3. Coal combustion waste disposal

The beneficial properties of CCW make it suitable for a wide array of commercially and technically proven applications. The traditional leading markets for CCW use are cement and concrete production, structural fills, road base and sub-base, as well as blasting grit/roofing granule. Other markets and reuse options for CCW as an engineering material are advancing (Collins, 1992; Cabrera and Woolley, 1994; Tyson, 1994; Butalia and Wolfe, 1999; Chugh and Sengupta, 1999; Stewart, 1999; Twardowska, 2003a,b; see also Chapter VI.8), with a goal of full use of these materials in a technically sound, commercially effective and environmentally safe way. Nevertheless, the utilization of CCW is still far from achieving this target for various reasons of a different character. Limiting factors which are of particular importance include: inadequate legislation, discrepancy between the CCW generation rates and demand for the end product, availability of competing materials for lower costs, experience of professionals involved in the production and marketing as well as the prejudice of potential end users and regulators. As a result, a large portion of the total CCW stream is still being disposed of in surface ponds or landfills. The rate of CCW disposal in a local or regional scale is a resultant of the joint effect of these factors, hence the differences between the countries with respect of CCW utilization (Twardowska, 2003a).

In 1992, CCW disposal in the USA accounted for 55.9 Mt (75.2% of the annual production) (Tyson, 1994). Also the most recent data refer to 25% of CCW utilization in the USA (Butalia and Wolfe, 1999; Chugh and Sengupta, 1999; Stewart, 1999). ACAA survey results for 1996 evaluated total CCW disposed for 69.6 Mt (75.3%), and utilized for 22.8 Mt (24.7%). Boiler slag, BA and FA are the primary CCW utilized at a rate 93.3, 30.3 and 24.7% of the amount generated, respectively (Stewart, 1999). Flue gas desulfurization (FGD) scrubber sludge and fluidized-bed combustion (FBC) products are the least utilized CCW in the USA (6.9% in 1996). Hence, about 75% of CCW are currently disposed of annually.

The data for China are limited and for 1989 (Shao Yi, 1992) CCW production was 62 Mt. Of this 22 Mt (33%) is reported to be utilized, while 67% (about 40 Mt per annum) is being disposed of.

In India, almost all CCW generated are disposed of. The data concerning the rate of utilization reported is from hardly 2–5% (Kumar et al., 1996) to 2–3% of the total amount generated (Prasad et al., 1999, 2000). CCW in India is usually disposed of hydraulically as a slurry containing 20–25% of a mixture of FA and BA in unlined surface ponds with an

open circuit. Taking into consideration the amounts of CCW already produced (75 Mt) and a forecast for 2011–2012 of 290 Mt/a, the situation with CCW management in this country is going to be critical.

In Poland, of 18.8 Mt of CCW from electricity and thermal power generation in 2001, 13.8 Mt (73.1%) was utilized, while permanent disposal of and temporary storage accounted for 4.3 and 0.71 Mt (23.0 and 3.8% of the annual production), respectively. The total amount of CCW stored in the disposal sites was evaluated by the end of 2000 as being 312.3 Mt (Central Statistical Office, 2002). Huge amounts of CCW are stored in disposal sites worldwide, and the amount of CCW at these sites is growing continuously with the intensity depending upon its utilization rate.

These data show that despite all the efforts of reuse proponents to change the way CCW are classified in the legislative arena and to consider ash, slag and flue gas desulfurization solids (FGDS) from power production entirely as beneficial raw materials (Collins, 1992; Mishra and Seth, 1999), disposed CCW must be regarded as waste.

III.7.1.4. Regulatory framework

CCW falls within the European definition of waste expressed in Council Directive 75/442/EEC on waste as last amended by Commission Decision 96/350/EC. An additional condition that the substance or object should be listed in the 16 categories of waste presented in Annex I (*vide* Chapter I, Annex A) is also fulfilled with respect to CCW, which belong to the category Q9 (residues from pollution abatement processes). The CCW are also included in the European list of wastes (Commission Decision 2000/532/EC as amended by Commission Decision, 2001/118/EC), where waste is categorized principally on the basis of origin or composition of the material. CCW are coded under category 10 (wastes from thermal processes), subcategory 10 01 (wastes from power stations and other combustion plants (except 19), codes 10 01 01, 10 01 02, 10 01 05 and 10 01 07, which comprise slag, BA and FA from hard coal and lignite, as well as FGDS. CCW are not considered hazardous wastes (Council Directive 91/689/EEC, 1991), though in view of Council Directive 75/442/EEC on waste, the disposal of CCW, as any waste, at any stage must not cause harmful effects to the environment.

In Poland, CCW disposal is regulated by the Waste Act of 27 April 2001, and the Directive of the Cabinet of 18 March, 2003. According to this Directive, disposal of FA and other CCW from coal combustion (10 01 01 and 10 01 02) is currently charged for the disposal ~US $4 per ton. Dry FGDS and slag from lime desulfurization process are charged for the disposal ~US $2 per ton.

In the USA, the basis for stepping up the reuse options is an exclusion of CCW, i.e. FA, BA waste, slag waste and flue-gas emission-control waste from fossil-fuel combustion from RCRA (1984) requirements. This exclusion is listed in 40 CFR 261.4. in the category of solid wastes that are not hazardous wastes. Despite this amendment enacted since 1980, some state regulations have set particularly stringent requirements for siting, constructing and managing CCW disposal facilities and reuse projects. Cost of CCW landfilling ranges from US $7 to $30 per ton depending upon the specific conditions (Chugh and Sengupta, 1999).

In India, no environmental regulations concerning CCW disposal and post-closure reclamation exist up to now. There are also no requirements concerning soil conservation or reclamation (CMPDIL, 1986; MOEF, 1992).

III.7.1.5. Environmental issues

The resentful approach of a certain part of decision-makers and of public opinion to CCW in the USA is based on its properties, which indicate that this material may pose an environmental risk while exposed to atmospheric conditions due to high concentration of trace metals, leachability of soluble constituents and its airborne character. The environmental compatibility of the products made with use of CCW should also be proven. The development of "clean energy" technologies and desulfurization of flue gases result in changes of the amount and properties of an end product depending upon the applied FGD process. This, in turn, influences its environmental behavior during disposal and utilization.

The structure of disposed CCW usually somewhat differs from that of CCW produced due to different proportions of kinds utilized. Because of predominance of FA, which accounts for $>70\%$ of the CCW generated in power plant (excluding FGD solids), and its lower utilization rate compared to BA and boiler slag, the proportion of FA in the total CCW disposed of increases up to $\geq 80\%$.

Traditional ways of CCW disposal are surface ponds (lagoons) or landfills. FA is transported hydraulically to surface ponds or lagoons and disposed of in a form of FA:water pulp, conventionally at slurry concentrations $\geq 20\%$ wt, or as dense slurry assuring transportability to the disposal site, approximately 50% wt (1:1). The lagoons are generally waterlogged and hence form an anthropogenic saturated zone that may easily contact with the natural vadose and saturated zones of unprotected aquifers.

In dry compacted landfills, CCW are disposed pneumatically. Landfills need about 25% of the space required by ponds of the same volume, liquid:solid (L:S) ratio is much lower than that in surface ponds. The water flow is adequate to handle the infiltration rate of atmospheric precipitation and a surface run-off in the vadose zone. Both in dry and wet disposal facilities, leaching of contaminants from FA by water will occur, though the mechanism and dynamics of the process are different due to the different water flow conditions in the saturated and vadose zones. FGDS either form an integral part of the disposed FA, or are generated and disposed separately, depending upon the applied FGD process. The disposal options for FGD solids also include ponding and landfilling of natural- or forced-oxidation dewatered sludge (Collins, 1992).

For both disposal systems, i.e. ponding and landfilling, a long-term environmental evaluation of disposed FA in relation to the actual field conditions is necessary, as it has direct environmental and economic consequences. "Pure" FA is predominant in the world's generation of CCW, in particular in the electric utilities, which either do not use the desulfurization of flue gases or use a wet or semi-dry desulfurization process with low content of FA in the end product. Hence, an evaluation of long-term environmental behavior of this kind of material is of a particular interest for the constructors and managers of dumping sites, as well as for potential end users of FA as high-volume material for structural fill.

This chapter is focused on FA characterization with respect to the long-term environmental implications of its disposal. The possibilities of CCW use for control of other sources of contamination from high-volume waste were also considered. Environmental impact of FA was exemplified in two case studies of the environmental behavior and time-delayed transformations of pore solutions in FA surface pond. The studies are presented on the background of the characteristics of FA composition and properties related to pollution potential to the environment. The impact on the groundwater quality is exemplified in the ash pond site of MSEB in Maharashtra, India. Post-closure changes of power plant waste pollution potential with respect to macro-compounds and trace metals are illustrated by the screening survey in the Przezchlebie disposal site (Upper Silesia Coal Basin USCB, Poland).

III.7.2. Properties of hard coal combustion waste related to pollution potential to the environment

III.7.2.1. Characteristics of freshly generated "pure" FA

III.7.2.1.1. Particle size distribution

Electric utilities usually burn coal supplied from several mining areas. In the USCB area, coal from different coal seams is supplied to power plants from many coal mines located within a radius of 50 km. Nevertheless, petrographical and phase composition and physicochemical characteristics of "pure" CCW from pulverized hard coal burning in conventional boilers display certain similarity and stability between years. Particle size distribution in FA is log-normal, the fraction <0.06 μm comprises over 50% wt, and ranges generally from 55 to 80% wt, while grains bigger than 260–320 μm do not occur (Fig. III.7.2). BA is a coarser and less uniform material. The fraction >1 mm may reach up to 30% wt, while the fraction <250 μm comprises about 50% wt.

III.7.2.1.2. Petrographical and phase composition

In this waste, which originates from high-temperature transformations of carboniferous rocks, amorphous components dominate over crystalline phases and range from 77 to >80%. They include a glass phase and amorphous relics of clay minerals. In petrographical composition two types of particles are predominant: irregular or oval aggregates surficially sintered or glazed, and round grains (Table III.7.2). Round grains glazed thoroughly or partially are more frequent in finer fractions. The grains partially glazed are filled with very fine dehydrated amorphous relics of clay substances. Amorphous aluminum oxide (Al_2O_3) is partially soluble in acids and alkali, though insoluble forms like corundum α-Al_2O_3 or γ-Al_2O_3 are more abundant.

Crystalline phases are minor components of FA. Among them, secondary ones are definitely dominant. Primary phases are represented entirely by quartz and potassium feldspar. Among crystalline phases, there is a considerable proportion of mullite $3Al_2O_3 \cdot SiO_2$ ($\sim 15-20$%), which prevails over phases containing iron (hematite/maghemite Fe_2O_3 and spinels: magnetite ($FeO \cdot Fe_2O_3$), hercynite ($FeO \cdot Al_2O_3$), magnesium

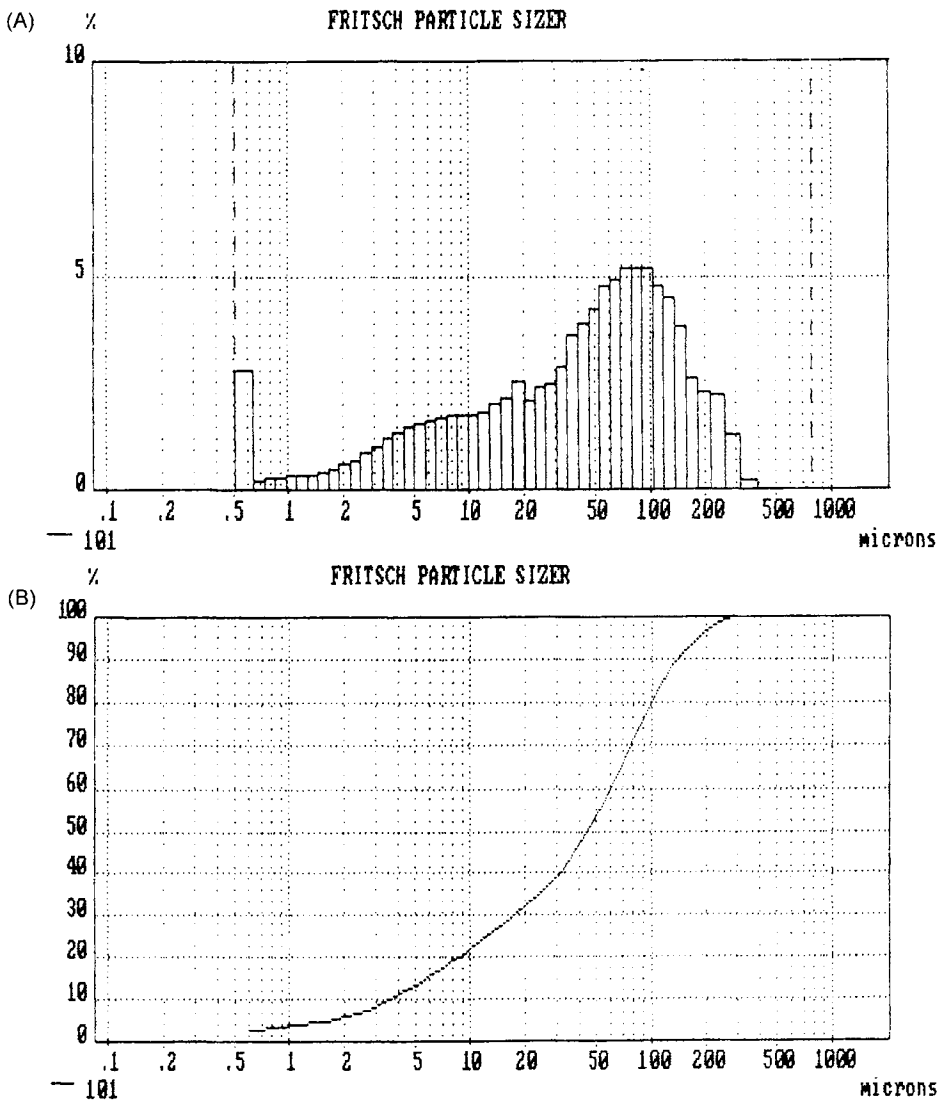


Figure III.7.2. Example particle size distribution in "pure" power plant FA. (A) Particle size frequency distribution. (B) Cumulative particle size frequency distribution.

ferrite ($MgO{\cdot}Fe_2O_3$) or mixed crystals between hercynite and magnetite). Trace or accessory amounts of sulfates occur predominantly in the form of anhydrite $CaSO_4$. Calcium oxides are present in mixed structures of C_4AF or C_2F phases. Also some amount of $Ca(OH)_2$ and phase C_4AH_{12} (hydrated calcium aluminate of $4CaO{\cdot}Al_2O_3{\cdot}12H_2O$ type) has been identified. Magnesium is present in small amounts as magnesium ferrite. FA contains also a small admixture (~3–4%) of unburnt coal (quick coke), which occurs in the form of porous particles of a skeleton structure.

Table III.7.2. Petrographical composition of FA from hard coal combustion, "pure" (FA) and containing FGD solids from dry (FA + D-FGD) and semi-dry process (FA + SD-FGD, in % v/v (after Ratajczak et al., 1999).

Components	Origin and kind of FA					
	"Pure" FA		FA + D-FGDS			FA + SD-FGDS
	R-1	L-1	R-2	R-3	O-1	L-2
Mullite aggregates[a]	57.5	47.6	22.5	35.6	10.0	34.3
Glaze spheres[b]	23.7	35.8	42.6	17.0	34.7	35.0
Unburnt coal matter	8.8	11.1	7.0	7.8	6.7	12.9
Quartz grains	2.7	2.3	1.0	1.3	1.0	3.6
Non-transparent spheres magnetically receptive	4.9	2.9	5.0	5.6	7.7	2.6
Primary and secondary carbonate aggregates[c]	–	–	21.9	32.7	39.9	11.6
Other	2.4[G]	0.3	–	–	–	–
Total	100.0	100.0	100.0	100.0	100.0	100.0

R – FA from the Rybnik power plant; L – FA from the Laziska power plant; O – FA from the Opole power plant (Poland); G – gypsum.

[a,b]In aggregates and spheres occurs an admixture of other components of FA.

[c]Primary carbonate minerals are represented by calcite, secondary minerals comprise calcium oxide, portlandite and anhydrite.

In general, the phase composition of FA from Polish power plants (Ratajczak et al., 1999) (Table III.7.3) is similar to that from other European (Garavaglia and Caramuscio, 1994) and US power plants (Mattigod et al., 1990, 1999).

III.7.2.1.3. Chemical composition

"Pure" FA from power plants of the USCB belongs to alkaline aluminum silicate material (van der Sloot et al., 1984). The ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3) = 1.3–3.9$ is close to the available data for FA from European power plants fired by hard coal, where it ranges from 1.5 to 3.6 (this value reflects alkalinity of FA expressed as the ratio of buffering and acidifying agents: the sources of acidity are sulfide oxidation and aluminum hydrolysis). For FA considered typical for Indian power plants (Mishra and Seth, 1999; Singh, 1999) this ratio ranges widely from 0.64 to 4.25 with a domination of low-buffered material with low CaO content. For eight power plants of National Thermal Power Corporation Ltd. (NTPC), the average ratio is 1.30, for National Aluminum Co. Ltd. (NALCO) power plant it is 2.35. Combustion processes result in concentration of most macro-elements (except S and C) and trace elements (except Hg, I and F) by about an order of magnitude compared to the content in the coal that is burned (Table III.7.4). In "pure" FA the prevailing form of sulfur is sulfate sulfur, which accounts for about 74% of S_t, and organic sulfur (23% S_t). Concentrations of trace metals in "pure" FA (in mg/kg) show declining order (Table III.7.3) [10^3 mg/kg] (Ba > Sr > Mn > V) $\gg$ [$\geq 10^2$ mg/kg] (Rb, Cr, Zr, Ce, Zn, Ni, Cu) > [> 10 mg/kg] (Co, Pb, La,Y, Nd, Sc, Th, Cs, As) > [$\cong$ 10 mg/kg] (Sm, Be, U, Mo, Br, Sb) > [< 10 mg/kg] (Yb, Hf, Bi, W, Se) > [10^{-1} mg/kg] (Eu, Ta, Tb, Lu, Hg, Cd, Ag) $\gg$ [10^{-2} mg/kg] (Au, Ir). Fluoride occurs in amount of 90–120 mg/kg. Comparison of the elemental composition of FA from Polish (Ratajczak et al., 1999; Twardowska, 1999a; Twardowska and Szczepańska, 2001, 2002, 2003) and other European coal-fired power plants (Garavaglia and Caramuscio, 1994; Meij and Schaftenaar, 1994) that partly use coal imported from Poland (Mukherjee and Kikuchi, 1999), as well as from Indian (Khandekar et al., 1999; Mishra and Seth, 1999; Pradhan et al., 1999; Das, 2000) and the US power plants (Mattigod et al., 1999) shows high similarity (Twardowska, 1999a; Twardowska and Szczepańska, 2002, 2003). This is due to properties of hard coal that despite of variability in different seams and regions exhibits also definite common features that also result from elements behavior during combustion and gasification (Mukherjee and Kikuchi, 1999). Only minor changes in the ranking of elements by concentration are observed. Therefore, the observations derived from environmental behavior of FA from hard coal combustion in power plants of the USCB (Poland) can be generalized to a considerable extent.

Concentrations of 16 PAHs in the "pure" FA matrix (Table III.7.5) have been found to be low (< 300 μg/kg), of this naphthalene was predominant (~80% of the total). Phenanthrene and acenapthalene were present in lower amounts, while PAHs proven to be carcinogens, including the five recommended for monitoring by WHO, seven displaying the lowest risk-based concentrations (RBC) after US EPA (Smith, 1994) and two representing priority group 1 in the list of 100 hazardous substances under CERCLA (1980) prepared by US EPA and ATSDR (1988), did not occur in detectable concentrations (analytical method: HPLC/fluorescence detection).

Table III.7.3. Phase composition of FA from hard coal combustion, "pure" (FA) and containing FGD solids from dry (FA + D-FGD) and semi-dry (FA + SD-FGD) process, qualitative identification (after Ratajczak et al., 1999).

CCW kind and origin	Mineral phase												
	CaO	Po	Mu	An	Q	C	Sk	Pl	He	Ma	Gr	Gy	Amorphous
"Pure" FA													
R-1	−	−	++	−	++	−	−	−	−	+	−	−	+++
L-1	−	−	++	+?	++	−	−	+?	−	+?	−	+?	+++
FA + D-FGDS													
R-2	++	−	++	++	+	+	−	−	−	+?	−	−	++
R-3	++	−	++	++	+	+	−	−	−	+?	−	−	++
O-1	+	−	+	+	+	++	−	−	−	−	−	+?	++
FA + SD-FGDS													
L-2	−	+	+	+?	+	+?	−	−	−	+?	−	−	++

R – FA from the Rybnik power plant; L – FA from the Laziska power plant; O – FA from the Opole power plant (Poland).
Mineral symbols: An – anhydrite; C – calcite; Gr – granite; Gy – gypsum; He – hematite; Ma – magnetite; Mu – mullite; Pl – plagioclase; Po – portlandite; Q – quartz; Sk – potassic feldspar.
Occurrence of the identified phase: +++, abundant; ++, mean; +, low; +?, trace, close to the detection limit, or a presence that cannot be excluded due to coincidence of diffraction peaks; −, lack or below the X-ray detection limit.

Table III.7.4. Elemental composition of pure FA from different coal-fired power plants compared to coal.

Constituents	The Netherlands[a]		Italy[b]	India			USA[c]	Poland[d,e]		
	Coal	FA	FA	Coal[f]	FA[g]	Coal ash[g]	FA	"Pure" FA[d]	Rybnik PP[e]	
									1973–1995	1997–mean
Major constituents (wt %)										
Al	1.65	15.0	14.0	0.85	14.94 (12.43–19.29)	12.76–13.90	8.88–15.13	12.77 (10.03–13.95)	12.81–14.66	13.95
C	73.2	4.3		78.11						
Ca	0.14	1.2	1.27	0.20	0.94 (0.07–3.43)	1.43–1.55	0.87–4.40	2.51 (0.61–4.63)	1.46–2.64	2.93
Cl	0.06	0.004								
Fe	0.51	4.7	5.03	0.75	3.42 (1.49–5.41)	2.79–2.80	8.27–19.93	5.48 (4.74–6.70)	4.69–9.90	5.67
K	0.17	1.5	2.26	0.074	0.52 (0.08–0.94)	0.81	1.55–2.38	1.32 (0.71–2.36)	1.76–3.76	0.71
Mg	0.08	0.7	0.71	0.038	0.43 (0.28–0.72)	0.84–3.06	0.32–0.46	1.36 (0.49–1.66)	1.03–1.52	1.61
N	1.6	0.3		1.56						
Na	0.04	0.4	0.3	0.051	0.19 (0.07–0.28)	0.36	0.01–0.84	1.38 (0.29–2.18)	0.38–0.91	2.18
P	0.01	0.10				0.24	0.25–0.44	0.26 (0.12–0.34)	0.065–0.34	0.21
S	0.7	0.1	0.39	1.89	0.14 (0.03–0.87)		0.50–0.87	0.33 (0.10–0.78)	0.18–0.58	
Si	2.82	25.7	23.3		29.01 (25.92–30.24)	26.51–27.22	19.97–24.47	26.75 (22.53–28.50)	21.37–24.64	23.15
Ti	0.08	0.8	0.9	0.045		0.72	0.54–0.86	0.58 (0.44–0.67)	0.16–1.10	0.60
Trace elements (mg/kg)										
Ag								0.84 (<0.4–1.7)		<0.4
As	3.7	34	40	3.72			10–149	37.3 (2–120)	15–48	17
B	43	163								
Ba	158	1438	1000	67.50	400	120–350	466–1702	1264.3 (927–1600)		1528
Be	3.3	29	16					11.2 (7–21)		8.0
Br	5.4	1.6						12.4 (7–21)		7.0
Cd	0.10	0.9	0.2	0.06				1.3 (0.5–2.7)		<0.5
Ce	17	151						124.8 (114–141)		48

(*continued*)

Table III.7.4. (Continued)

Constituents	The Netherlands[a]		Italy[b]	India			USA[c]	Poland[d,e]		
	Coal	FA	FA	Coal[f]	FA[g]	Coal ash[g]	FA	"Pure" FA[d]	Rybnik PP[e]	
									1973–1995	1997–mean
Co	5.8	52		2.29	14	5–25		44.6 (21–74)	12–122	36
Cr	14.4	131	133		145	40–100	179–319	154.7 (87–230)	20–253	170
Cs	1.0	9						20.5 (13–27.3)		22.6
Cu	16.6	151	130	6.28	72	20–60	66–165	123.4 (70–167)	30–199	104
Eu	0.4	4						2.3 (2.0–2.7)		2.3
F	80	127							90–120	
Ga	2.0	18			50	15–25	24–52		85	
Hf	1.2	11						5.2 (4.5–6.0)		4.9
Hg	0.16	0.23						1 (<1)		<1
I	2.2	0.6								
La	7.6	69			108	15–20		62.2 (51.1–70)		65.2
Mn	46	415	431	12.40			117–380			
Mo	3.0	27					19–81	11.2 (<5–15)	10	7.0
Ni	11	98	105	6.10			112–155	138.8 (45–276)	32–151	93
Pb	8.5	77	68	3.67	95	10–30	24–69	195.2 (43–507)	47–223	69
Rb	9.2	84		5.05			103–188	145.8 (120–176)		176
Sb	0.8	7	5.0				<10–80	9.5 (4.2–4.14)	7.5	5.6

Sc	3.3	30						27.12 (18.3–31)		29.2
Se	2.2	13	13	1.29	10	1–8	9–13	9.7 (<3–43)	<1–1.02	<3
Sm	1.8	16						10.7 (9.1–12.1)		11.4
Sr	107	971	1000		164	40–350		704 (406–1214)		543
Th	2.9	26	26	1.342	112	39–85		23 (21–25.1)		25.1
Tl	1.0	9	2.0							
U	1.5	13	10	0.436	21	8–27	16–25	10.6 (7.6–13.7)		7.6
V	29	262	197		321	55–150	179–374	278 (129–459)	500–570	244
W	1.0	9						6.4 (<3–9)		<3
Y					47	20–50		60.2 (46–84)		50
Zn	24	218	65	11.89	295	180–460	135–390	199.2 (16–507)	70–389	135
Zr							156–244	170 (162–179)	70–80	162

[a]After Meij and Schaftenaar (1994).
[b]After Garavaglia and Caramuscio (1994).
[c]After Mattigod et al. (1999).
[d]After Ratajczak et al. (1999).
[e]Twardowska (2003a–c) and Twarowska and Szczepanska (2003).
[f]After Khandekar et al. (1999).
[g]After Khandehar et al. (1999), Mishra and Seth (1999), Pradhan et al. (1999) and Das (2000).

Table III.7.5. Concentrations of polynuclear aromatic hydrocarbons (16 PAH), and polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) in power plant FA, "pure" (FA) and containing FGD products from dry (FA + D-FGD) and semi-dry (FA + SD-FGD) process.

Kind and origin of CCW	PAH (μg/kg)				PCDD, PCDF (tetra- to octa-) (ng/kg)			
	16 PAH (EPA)	6 PAH[a] (WHO)	7 PAH[b] (EPA)	2 PAH[c] (EPA)	PCDD	PCDF	PCDD + PCDF	I-TEQ
"Pure" FA								
L-1	262.9	2.7	3.0	<0.06	12.51	5.46	17.98	0.69
FA + D-FGDS								
R-2	311.6	3.8	2.9	<0.06	40.15	1.31	41.46	0.05
O-1	182.0	2.8	3.0	<0.06	25.02	7.87	32.89	0.36
High-FA + SD-FGDS								
L-2/su	42.9	0.9	2.2	<0.06	70.81	6.49	77.29	0.72
L-2	40.8	1.9	2.3	<0.06	2.26	0.84	3.11	0.04
Low-FA + SD-FGDS								
DB	39.1	5.0	3.0	<0.06	5.56	3.95	9.50	0.31
Range of RBC (US EPA data, after Smith, 1994), μg/l, μg/kg								
Tap water	0.92–1500	0.92–1500	0.92–920	0.92	1.1[H]			
Residential soil	8800–3100 × 10^3	8800–3100 × 10^3	8800–8800 × 10^3	8800	10,000[H]			
Industrial soil	39,000–41,000 × 10^3	39,000–41,000 × 10^3	39,000–39,000 × 10^3	39,000	46,000[H]			

R – CCW from the Rybnik power plant; L – CCW from the Laziska power plant; O – CCW from the Opole power plant (Poland); DB – CCW from the DRAX "B" power plant (Denmark); su – start-up phase. H – sum of hexachlorodibenzo-*p*-dioxins only.

16 PAH by US EPA: Naphthalene, acenaphtylene, acenaphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene.

[a]6 PAHs recommended for monitoring by WHO (Fluoranthene Flth, benzo[b]fluoranthene BbF, benzo[k]fluoranthene BkF, benzo[a]pyrene BaP, benzo[ghi]perylene BghiP, indeno[1,2,3-cd)pyrene INP.

[b]7 PAHs proven carcinogens after US EPA: Benzo[a]pyrene BaP, dibenz[ah]anthracene DBahA, benzo[b]fluoranthene BbF, benz[a]anthracene BaA, indeno[1,2,3-cd]pyrene INP, benzo[k]fluoranthene BkF, chrysene CHR.

[c]2 PAHs the strongest carcinogens after US EPA: Benzo[a]pyrene BaP, dibenz[ah]anthracene DBahA.

An earlier evidence of PCDDs and PCDFs identification in FA and flue gases from municipal waste incinerators, fossil-fuelled power plants, fireplaces, etc. (DCC, 1978; Rappe, 1980) suggested that these hazardous compounds could be formed in any combustion process. The analysis of FA for PCDD and PCDF confirmed their occurrence in this material, but in much lesser, ng/kg range (Table III.7.5), which is in conformity with the more recent data (Huang and Buekens, 1995). Opposite to the referred data (DCC, 1978; Rappe, 1980; Huang and Buekens, 1995), in analyzed material PCDDs were definitely major constituents. They comprised 70% of the total PCDD + PCDF yield in the "pure" FA.

III.7.2.1.4. Radioactivity

The process of coal combustion results also in the increase of radioisotope concentration in FA. For the 25 years' period 1977–2002, the increase of ^{226}Ra, ^{232}Th and ^{40}K content in FA compared to coal ranged from 2- to 4.5-times (Twardowska, 2003c). Radioisotope content in FA is in general considerably higher than mean concentrations in the lithosphere (Table III.7.6), but still more than an order of magnitude lower than the threshold level 10 kBq/kg of total Ra-isotopes, which qualifies waste as a radioactive material in compliance with Polish Standard PN-88/Z–70071. According to Polish Standards for stowing materials PN-93/G–11010, FA can be thus unrestrictedly used for hydraulic stowing of mine workings. All FA fulfill also the criterion ^{226}Ra < 350 Bq/kg and ^{228}Ra < 230 Bq/kg, which defines a permissible level for the disposal of and using a material for civil engineering works at the surface. The natural radioactivity level of FA in many cases, however, exceeds parameters $f_1 \leq 1$ and $f_2 \leq 185$ established by the National Polish Institute of Construction Techniques for assessing the applicability of material for production of construction materials. These parameters, which define the maximum acceptable level of γ- and α-radiation, respectively, are being evaluated as follows:

$$f_1 = 0.00027C_K + 0.0027C_{Ra} + C_{Th} \leq 1, \qquad f_2 = C_{Ra} \leq 185,$$

where C_K, C_{Ra} and C_{Th} are the concentrations of isotopes ^{40}K, ^{226}Ra and ^{228}Ra.

FA that does not fulfill these requirements cannot be used for production of construction materials. Variable f_1 and f_2 coefficients for Polish FA imply a requirement of analysis for radioactivity level of every portion of FA, which is considered to be used for this purpose. Scarce data for Indian FA showed increase of the radioactivity level for ^{226}Ra in the range from 6.2 to 4.2-fold compared to coal and from 5.0 to 2.6-fold compared to soil, and exceeded the average value for soil from >2 to >5 times. Concentrations of ^{228}Ra exceeded the corresponding concentrations in coal from 8.9 to 4.5 times and in soil from 7.5 to 2 times, and average value for soil from >2 to >3.5 times. Elevated concentrations of U and Th in FA from combustion of coal from the Talcher coalfields in India (Table III.7.4) also suggest the need of paying heed to this question, which up to now is beyond consideration in that country and has been commented as negligible on the basis of an unknown number of samples analyzed for ^{226}Ra and ^{228}Ra, which indeed displayed the concentrations within safety limits (Raghuveer, 1999).

Table III.7.6. Range and mean concentrations of radionuclides in coal combustion waste compared to coal and lithosphere (Poland and India).

Material	Concentration of radionuclides (Bq/kg)			Radiation coefficients[a]	
	^{40}K	^{226}Ra	^{228}Ra	f_1	f_2
Rybnik power plant, Silesia, Poland (1977–1997)[b]					
FA	917 (497–1106)	116 (< 18.5–197)	78 (43–122)	0.90 (0.47–1.26)	116 (< 18.5–197)
FA + D-FGDS[b]	746 (666–805)	103 (57–124)	88 (74–102)	0.86 (0.79–0.94)	103 (57–124)
Boiler slag	756 (336–908)	93 (28–153)	68 (30–103)	0.74 (0.35–0.98)	93 (28–153)
All Polish power plants (1980–1995)[c]					
FA	701 (33–1386)	124 (< 1–395)	89 (< 1–194)	0.91 (0.04–1.44)	124 (< 1–395)
Boiler slag	541 (1–1260)	95 (2–335)	70 (1–210)	0.70 (0.04–1.63)	95 (2–335)
(1996–2000)[d]					
FA	716 (20–1664)	114 (8–363)	90 (2–206)	0.89 (0.07–1.77)	114 (8–363)
Boiler slag	591 (20–1120)	99 (5–482)	77 (1–188)	0.75 (0.04–2.08)	99 (5–482)
2001[e]					
FA	680 (56–1062)	119 (11–268)	92 (2–141)	0.90 (0.04–1.36)	119 (11–268)
Boiler slag	590 (57–1047)	89 (9–198)	73 (5–130)	0.71 (0.16–1.19)	89 (9–198)
Coal (1977–1997)					
Coal	316 (115–438)	37 (21–81)	24 (14–34)	0.28 (0.16–0.39)	37 (21–81)
Lithosphere					
Soil and rock	380 (100–700)	25 (10–50)	25 (7–50)		
Indian power plants (after Raghuveer, 1999)					
Coal ash		55.5–133	55.5–82.5		55.5–133
Coal		9–31.5	6–21		9–31.5
Construction materials					
Concrete/cement		33–74	30–85		33–74
Brick		52–96	37–126		52–96
Lithosphere					
Soil		26 (11–52)	26 (7–48)		26 (11–52)
Rock, stone, sand		15–111	4–167		15–111

[a]Coefficients defining applicability of material for production of construction materials with respect to the natural γ- and α-radiation. Regulatory limits: $f_1 < 1$ (for γ-radiation); $f_2 < 185$ (for α-radiation) (ITB, 1995).

[b]Data on routine analysis of CCW from Rybnik power plant for radioactivity carried out by Laboratory of Radiometry, Central Mining Institute in 1977–1997; data for FA + D-FGDS are from 1990 to 1997.

[c]After Central Statistical Office, 1997 (data of the Central Laboratory of Radiological Protection).

[d]After Central Statistical Office, 2001 (data of the Central Laboratory of Radiological Protection).

[e]After Central Statistical Office, 2002 (data of the Central Laboratory of Radiological Protection).

III.7.2.2. Effect of FGD processes on FA composition

III.7.2.2.1. Process characterization

The FGD processes, which have been developed as a part of clean energy technologies, may exert a considerable effect on the properties of FA, depending upon the composition and proportion of FGDS and the FA in the end product (EP). In general, widely used technologies of FGD can be defined as dry, semi-dry, mixed and wet processes, which differ by the reagent used, method of the reagent injection and the kind of the reaction product (e.g. Collins, 1992; Anonymous, 1995a–c; Blaszczak and Buzek, 1998; Punshon et al., 1999). In the dry methods, the reagent is injected in the dry form, and the end product is also dry. In the semi-dry methods, the reagents are injected thoroughly or partially wet, while the end product is dry. In the wet methods, both the input reagent and the reaction product are wet. The majority of currently used methods are based on lime in the form of limestone, quicklime, slaked lime or dolomite lime as a reagent for binding SO_2. This results in calcium compounds enrichment in the end product, which is highly dependent upon the used desulfurization technology (Twardowska, 1999b).

In the dry method, limestone or pulverized limestone is injected into the boiler furnace, where the calcium carbonate decomposes thermally to form calcium oxide and carbon dioxide. A portion of SO_2 and all of the SO_3 reacts with CaO to form $CaSO_4$. The flue gas desulfurization solids in the dry process (D-FGDS) are the newly formed $CaSO_4$ and the unreacted excess of CaO. They are carried along with the coal FA out of the boiler, forming the end product (FA + D-FGDS), which is highly alkaline due to the excess of CaO with respect to the initial SO_2 (Ca:S = 2.5–3.1). Due to a low efficiency of desulfurization (20–40% for conventional pulverized coal fired boilers) and sorbent use (10–15%), the dry processes are being replaced by semi-dry or wet methods and generally treated as transitory ones. For fluidized-bed boilers (FBB), end product also consists of FA and spent limestone sorbent containing $CaSO_4$, unreacted CaO, MgO and inerts (Collins, 1992; Mukherjee and Kikuchi, 1999). The efficiency of this process ranges from 85 to 95% due to different operational parameters.

The semi-dry desulfurization process consists of injecting a pulverized suspension of slaked lime into the flue gas flowing through the reactor, where calcium hydroxide reacts with SO_2 in flue gas. The temperature of the process is 15–20°C higher than the dew-point of a Ca:S ratio of 1.2–1.8. The primary reaction component is $CaSO_3$, which further partially oxidizes into $CaSO_4$. The final end product is separated from the flue gas in the bag filters or electrostatic precipitators. The end product (FA + SD-FGDS) is a dry powder, which consists of FA and the reaction products of the injected slaked lime and the SO_2 in the flue gases containing $CaSO_3$, $CaSO_4$, $Ca(OH)_2$, $CaCO_3$ and moisture. The efficiency of the process is from 70 to 80% up to 90%. Efficiency of sorbent use is about 45%. These processes are offered by a dozen firms (e.g. ABB-NID one-stage process). Due to addition of FGDS, the amount of the end product, i.e. FA along with FGDS, increases by 20–30%.

Combined methods are coupling elements of the dry and semi-dry processes, i.e. pulverized limestone injection into the boiler with post-furnace humidification in an activation reactor, e.g. ER (Rybnik) or LIFAC process (Anonymous, 1995b,c). The first stage is a typical dry process. In the second, post-furnace stage of the combined process,

the flue gas is moisturized by injecting water into a specially designed activation reactor, with, or without addition of slaked lime. Within this reactor, the unreacted CaO is converted into $Ca(OH)_2$, which readily reacts with SO_2. The efficiency of desulfurization is similar as in the semi-dry process, and reaches 80–90%. By closely controlling the parameters of the process, in particular the temperature in the reactor, the CaO conversion and SO_2 reduction can be maximized, up to >90%. Due to addition of FGDS, the amount of the end product, i.e. FA along with FGDS increases by 20–30%. The end product is similar as in the one-stage semi-dry process described above (FA + SD-FGDS). In some semi-dry processes, FA and the reaction product of desulfurization are collected separately. In this case, dry end products consist of "pure" FA and low-FA flue gas desulfurization solids (low-FA-FGDS). The compositions of end products from dry and semi-dry desulfurization process are presented in Table III.7.7.

Currently, the most worldwide spread desulfurization methods are wet processes, mainly based on the limestone as a sorbent of SO_2 (Punshon et al., 1999). In the USA, they account roughly for 80% and in Germany for 90% of all the applied desulfurization processes. The process consists in a sorption of SO_2 in a water suspension of ground limestone in scrubbers and adsorption columns. The end product is calcium sulfate and sulfite crystals in the form of water suspension separate from FA. The excess of Ca used in the process is low (Ca:S = 1.03–1.05) and the pH of the suspension is 5.5–6.0. The efficiency of the desulfurization process exceeds 90%. The wet FGD processes do not influence the properties of other CCW (FA, BA, slag), but cause formation of

Table III.7.7. Phase composition of end products from dry (FA + D-FGDS) and semi-dry FGD process (FA + SD-FGDS) with high- and low-FA content.

FGD process	FA + D-FGDS (Rybnik PP)	FA + SD-FGDS			
		High-FA[a]		Low-FA[b]	
		LIFAC	ABB-NID (Laziska PP)	RYBNIK (Rybnik PP)	FLÄKT (DRAX-B PP)
Phase composition (% wt)					
Fly ash	85	50–70	>80	2–4	9–12
$CaSO_3$	0.011	10–15	5.55	31–42	40–50
$CaSO_4$	3.54	10–15	3.14	12–14	7–12
$CaCl_2$	1.00		ND	1–2	1–4
$CaCO_3$	1.53	5–15	7.55	9–10	2–4
$Ca(OH)_2$	Trace			29–36	8–15
CaO	10.0	Trace	Trace		Trace
Moisture	ND	2–5	2–5	2	1–3
Crystal water	ND				7–11
Neutral compounds	ND		ND		3–5

ND – not determined.

[a]LIFAC, ABB-NID – flue gas desulfurization process with high-FA content in the end product.

[b]RE-RYBNIK, FLÄKT – FGD process with low-FA content in the end product.

a considerable amount of FGD solids that create problems with their management. The proportion of FGD solids with respect to other CCW in the USA accounts for about 28% (Collins, 1992) to over 23% (Stewart, 1999). The environmental behavior of FA when the wet desulfurization of flue gases is used does not differ from that of the "pure" FA from the power plants not using FGD process. The FGD products in the form of suspension contain 5–15% of solids before dewatering and need further fixation for stabilization.

In 1990, the total utilization of FGDS in the USA as a percentage of production accounted for 1.1% (Collins, 1992), in 1992 it was reported to be 2% (Tyson, 1994), and in 1996–1997 it reached 6.9–7% (Butalia and Wolfe, 1999; Stewart, 1999), while the utilization of other CCW accounted in total for 24.8% of production in 1992 and remained at the same level in 1996–1997 (24.7%). In Germany, FGDS use, mainly in the wallboard industry, is considerably higher. Recent research and demonstration projects have indicated that dry and wet FGD materials can be safely and cost-effectively utilized also in highway construction, mine reclamation and agricultural applications (Butalia and Wolfe, 1999; Punshon et al., 1999).

III.7.2.2.2. Characteristics of FA properties resulting from FGDS admixture

The admixtures of FGDS significantly influence properties of end products, depending upon the applied technology of desulfurization (Twardowska, 1999b). The final end product of the dry desulfurization process (FA + D-FGDS) is FA (~70–80%) with the reaction products from the dry desulfurization process (D-FGDS). They consist of unreacted CaO and reaction products, mainly anhydrite $CaSO_4$, as well as minor amounts of $CaCO_3$ and $CaCl_2$ (Table III.7.7). The chemical composition of FA + D-FGDS showed significant increase of S_t, Ca and carbonates compared to the "pure" FA (Table III.7.8). Due to the presence of unreacted CaO, the end product is reactive and highly alkaline. The high proportion of FA (70–80%) moderates reactivity of the FGD reaction products.

The end product of the semi-dry process consists of dry FA and the reaction products of the injected limestone and SO_2 in the flue gases. The reaction products from FGD consist of calcium compounds: sulfite $CaSO_3$, sulfate $CaSO_4$, hydroxide $Ca(OH)_2$, carbonate $CaCO_3$ and accessory amount of chloride $CaCl_2$. The composition of the end product from the semi-dry desulfurization processes, in particular the proportion of calcium compounds, depends upon the proportion of FA, which differs significantly for different systems and varies from 2 to 75%. Accordingly, the end products can be thus either high- or low-FA material. The content of $CaSO_3$, which is a main component of the end product, generally ranges from 10 to 60%, $CaSO_4$ occurs in accessory amounts, and $Ca(OH)_2$ prevails over $CaCO_3$ (Table III.7.7).

The proportion of FA and FGD reaction products determines the chemical composition of the end product of a semi-dry process (FA + SD-FGDS) (Table III.7.8). The end product of semi-dry ABB-NID process implemented at the Laziska power plant (Poland) displayed several times higher sulfur and calcium contents compared to the pure FA from the same plant. The alkalinity of the end product expressed as the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3)$ (van der Sloot et al., 1984) was close to that of a pure FA. Because of the presence of chemically unstable sulfides, the end product showed thixotropic properties.

Table III.7.8. Elemental composition of FA containing FGD solids from dry (FA + D-FGDS) and high-FA semi-dry process (FA + SD-FGDS) compared to pure FA.

Element	Rybnik power plant		Opole power plant	Laziska power plant	
	FA (1973–1993)	FA + D-FGDS (1990–1995)	FA + D-FGDS (1993–1994)	FA (1994–1995)	FA + SD-FGDS (1995)
Macro-elements (% wt)					
Al	13.94 (12.82–14.60)	11.74 (9.96–13.26)	10.46 (8.93–11.84)	14.53 (14.49–14.58)	10.83
Ca	**2.12 (1.47–2.63)**	**8.62 (6.59–10.66)**	**13.63 (11.68–16.05)**	**2.84 (2.82–2.89)**	**8.12**
Cl	0.21	ND	ND	ND	ND
Fe	6.68 (4.69–9.91)	5.45 (4.27–6.73)	5.36 (5.05–5.52)	5.10 (4.86–5.13)	4.45
K	2.36 (1.76–2.76)	1.79 (1.59–2.08)	1.99 (1.72–2.32)	2.48 (2.39–2.58)	1.73
Mg	1.18 (1.03–1.52)	0.97 (0.88–1.03)	1.66 (1.39–1.84)	1.81 (1.58–1.87)	1.17
Na	0.58 (0.39–0.91)	0.53 (0.35–0.69)	0.67 (0.59–0.74)	0.46 (0.44–0.48)	0.53
P	0.18 (0.06–0.35)	0.31 (0.22–0.37)	0.16 (0.09–0.21)	0.28 (0.26–0.29)	0.30
S	**0.37 (0.18–0.78)**	**1.78 (1.16–1.97)**	**1.11 (0.77–1.72)**	**0.30 (0.28–0.32)**	**2.22**
Si	22.47 (21.52–24.82)	18.40 (15.69–20.57)	18.99 (17.38–20.81)	22.85 (22.82–22.88)	20.54
Ti	0.53 (016–1.10)	0.59 (0.13–1.16)	0.64 (0.57–0.67)	0.68 (0.61–0.75)	0.50
Trace elements (mg/kg)					
As	42 (33–48)	27 (12–39)	20 (15–22)	26–28	26
Ba	1528	879–1066	1230 (1047–1346)	1372 (1262–1385)	913–1052
Cd	2.7 (<0.5–5)	1.2–1.6	3.1 (1.2–5)	1.7 (0.5–2.5)	1.2
Co	61 (12–102)	59 (16–92)	41 (31–49)	40	18–30
Cr	166 (20–253)	156 (40–197)	130 (107–160)	143 (122–165)	56–136

Cu	120 (30–197)	121 (25–151)	147 (129–182)	134 (98–170)	31–88
F	105 (90–120)	105	ND	ND	ND
Ge	<5	<5	<3	<3	<3
Mn	580 (360–840)	590 (200–650)	590 (550–660)	720	ND
Mo	7–10	<5–7	<3–9	15	6
Ni	109 (32–151)	108 (35–132)	90 (78–105)	90	24–69
Pb	112 (21–223)	84 (45–174)	92 (67–108)	64 (50–90)	22–104
Sb	5.6	5.4–5.9	7.8	9.5–11.6	4–16
Sr	543	438–487	725 (568–948)	630	368–444
Tl	ND	1.76	1.7	2.7	0.65
V	244–500	183–220	270	251	178–185
Zn	218 (70–280)	193 (80–260)	175 (116–220)	193 (143–225)	36–190

Elements showing distinct increase in FA + FGD compared to pure FA are bold; ND – not determined.

Comparison of data leads to a general conclusion that despite many different and variable sources of coal supply to power plants (usually, to each power plant from several, up to 20, mines and coal seams of the USCB), the general pattern of trace element occurrence in FA matrix remained similar within the years studied. The occurrence of D-FGD products in FA generally resulted in a decrease of metal concentrations in FA + D-FGDS as an effect of addition of low-metal FGD solids, though no strong effect of reaction products from dry desulfurization (D-FGD products) on trace metal concentrations in FA + D-FGDS has been observed. The concentration range of each metal for representative samples FA + D-FGDS compared to "pure" FA was within the deviation caused by the heterogeneity of fuel in the different power plants and did not show regular trends due to the relatively low proportion of D-FGDS in the end product. Nevertheless, comparison of metal contents in FA(R) and FA + D-FGD(R) analyzed in parallel suggested the reducing effect of D-FGDS admixture on the end product (Tables III.7.8 and III.7.9).

On the other hand, up to 2–3-fold decrease of metal concentrations in high-FA end product containing SD-FGD products has been found. This can be explained by the "diluting" effect of trace metal-free reaction products (calcium sulfite, sulfate and carbonate compounds), comprising up to 60% of the high-FA + SD-FGD end product.

An extremely low trace metal content occur in the low-FA + SD-FGD solids. They appeared to be approximately 5–10 times lower than these in the high-FA + SD-FGD end products. This proves FA is the main source of trace metals in the end products from the FGD process.

Therefore, FGD solids from dry and semi-dry FGD processes may have a considerable effect on the end product properties and release of constituents from this material due to its influence on pH, contents and forms of sulfur and calcium compounds, as well as on concentrations of trace elements. With respect to trace element contents, FGD products caused a positive "diluting" effect on the FA (Tables III.7.8 and III.7.9).

Concentrations of the total 16 PAHs in the FA matrix containing D-FGD solids ranged from 182 to 312 μg/kg. They appeared to be close to those of "pure" FA, also with respect to quantitative composition and proportions of PAH compounds. While no distinct effect of dry FGD process on PAH occurrence was noticed, the semi-dry process results in reduction of 16 PAHs content both in high-FA + SD-FGDS and in low-FA + SD-FGDS close to an order of magnitude, mainly due to the decrease of naphthalene content, which was a dominant compound (Table III.7.5).

In FA with FGDS, concentrations of dioxins and dibenzofurans occur in the low, ng/kg, range. The low formation of these compounds in highly effective power plant boilers is mainly due to complete combustion resulting in non-soothing flames. The highest concentrations of PCDDs and PCDFs were found in the end product from dry desulfurization of flue gases (FA + D-FGDS), where also the highest PAHs content occurred. In the "pure" FA, PCDD + PCDF content was about half of that found in FA + D-FGDS, while PAHs were present within the same range. Both high-FA and low-FA semi-dry desulfurization processes cause about an order of magnitude reduction of these hazardous compounds in the end product. Also in this material, opposite to the referred data (DCC, 1978; Rappe, 1980; Huang and Buekens, 1995) PCDDs were definitely the major constituents. They comprised in the "pure" FA 70%, in FA + D-FGDS 76–97%, and in FA + SD + FGDS 58–72% of the total PCDD + PCDF yield.

Table III.7.9. Concentration of trace metals in parallel samples of power plant FA, pure and containing FGD solids from dry and semi-dry process with high- and low-FA content.

CCW	Concentration of trace metals (mg/kg)									
	As	Cd	Cr	Cu	Ni	Pb	Sb	Se	Tl	Zn
"Pure" FA										
R-1	41.0	<2	170	104	93	69	ND	<3	ND	135
L-1	28.0	1.56	46.8	62.7	58.0	80.9	11.60	<1.07	2.66	97.6
FA + D-FGDS										
R-2	17.0	1.32	40.8	45.9	44.1	51.7	7.45	<1.02	1.76	106
O-1	2.85	1.62	54.1	65.8	49.0	67.3	8.19	<0.99	1.70	154
High-FA + SD-FGDS										
L-2/su	16.0	1.10	38.7	41.7	39.9	45.1	8.00	<1.07	1.57	69.6
L-2	<1.02	1.22	23.1	31.1	24.4	21.6	4.06	<1.05	0.652	35.9
Low-FA + SD-FGDS										
DB	<1.05	<0.50	3.63	2.45	3.57	4.84	0.714	4.79	0.053	7.32
Range of RBC (US EPA data, after Smith, 1994), mg/l, mg/kg										
Tap water	0.011	0.018	0.180	1.40	0.73	3.7×10^{-6}	0.015	0.180	0.0029	11.0
Residential soil	23	39	390	2900	1600	0.0078	31	390	6.3	23,000
Industrial soil	310	510	5100	38,000	20,000	0.1	410	5100	82	310×10^3

FA – pure power plant fly ash; FA + D(FGD) – FA containing reaction products from dry FGD process; FA + SD(FGD) – FA containing reaction products from semi-dry flue gas desulfurization process; (R) – Rybnik power plant; (O) – Opole power plant; (L1) – Laziska power plant; (L2/su) – start-up stage of ABB-NID semi-dry desulfurization process, high-FA end product; (L2) – Laziska power plant, operational stage of ABB-NID semi-dry desulfurization process, high-FA end product; (DB) – DRAX-B power plant, FLAKT semi-dry desulfurization process, low-FA end product.

The reduction of PCDD + PCDF content in end products from the SD-FGD process was mainly due to the dramatic decrease (>80%) of PCDD concentrations (Table III.7.5).

Blending FGD reaction products results also in the reduction of FA + FGDS radioactivity compared to the "pure" FA (Table III.7.6).

Therefore, FGDS from dry and semi-dry FGD process may have a considerable effect on the end product properties and release of constituents from this material due to influence on pH, content and forms of sulfur and calcium compounds and concentrations of trace metals. With respect to trace metals content, FGD products exert positive "blending" effect on the FA. The semi-dry desulfurization process causes considerable reduction of organic compounds of a proven carcinogenicity, though their occurrence is generally low and non-problematic. The phase and chemical composition of FGDS in dry ($CaSO_4$, residual CaO) and semi-dry process ($CaSO_3$, $CaSO_4$, $Ca(OH)_2$, $CaCO_3$) will affect also the environmental behavior of the disposed or utilized end product.

III.7.2.3. Hydrogeological parameters of FA

Both from the environmental and technological aspects, hydrogeological parameters of FA:water mixtures are of a special importance, in particular hydraulic conductivity k (m/s), the time of solidification t_s (days) and penetration resistance R (kPa). These parameters define circulating conditions of pore solution in the material and permeability to air, which determine the extent of contaminant migration and sealing properties of FA:water mixture.

III.7.2.3.1. Hydraulic conductivity

The presented data show that CCW contain high concentrations of mainly inorganic contaminants, of which trace metals are of a special concern due to high mobility and proven toxic effect of many of them (some metals are also proven carcinogens). This material disposed of in surface impoundments or exposed to the atmospheric conditions when used as a structural fill, may be a source of a serious contamination of groundwater resources, provided the toxic compounds can be mobilized from the matrix and migrate to the aquatic environment. From this standpoint, the hydrogeological parameters defining the ability of solutions to penetrate through the waste layer are crucial for evaluating pollution potential of the waste, besides the concentration of contaminants in the material and their susceptibility to mobilization. The major parameters, which define filtration properties of material, are effective porosity n_e responsible for transport of solutions and hydraulic conductivity k. In turn, total porosity, pore structure and the specific surface of the material play an important role in release and migration of contaminants. The typical pore structure and hydraulic properties of FA, "pure" and containing reaction products from the dry desulfurization process (FA + D-FGDS) in the form of solidified mixture 1:1 (wt) with distilled water, is presented in Table III.7.10 and in Figures III.7.3–III.7.5. The effective porosity n_e of these wastes ranged from 16.9 to 26.4%, which is characteristic of materials of high and very high porosity (Pazdro and Kozerski, 1990). The FA + D-FGDS has much lower porosity due to the cementitious effect of calcium carbonate and sulfate, though still considerably higher than natural clays. The values of hydraulic conductivity for "pure" FA at the level of $k \geq 10^{-8}$ m/s do not fulfill the criteria of impermeability both

Table III.7.10. Hydraulic conductivity parameters of CCW compared to natural soils.

Material		Density (g/cm^3)		Porosity (%)		Pore specific surface (m^2/g)		Mean pore diameter (μm)	
No.	Kind, symbol[a]	Bulk, ρ_d	Specific, ρ_s	Total, n_t	Effective, n_e	Total, S_t	Capillary voids, S_e	Total, d_t	Capillary voids, d_e
"Pure" FA									
1	R-1	1.1773	1.6037	26.58	26.40	0.461	0.250	1.9599	3.5816
2	L-1	1.0479	1.3658	23.24	21.13	4.913	0.402	0.1806	2.0068
FA + D-FGDS									
3	R-2	1.0620	1.2830	17.23	16.03	1.231	0.231	0.5271	2.7581
4	O-1	1.0306	1.3329	22.68	22.25	1.463	0.316	0.6018	2.7369
Natural soils									
5	Clay	2.1441	2.7048	20.73	11.23	7.583	0.236	0.0510	0.8883
6	Loam	1.9401	2.4427	20.25	2.25	22.514	0.019	0.0188	2.3949

R – FA from Rybnik power plant; L – FA from Laziska power plant; O – FA from Opole power plant (Poland).

[a]"Pure" FA – power plant FA without desulfurization products; FA + D-FGDS – FA containing reaction products from dry FGD process.

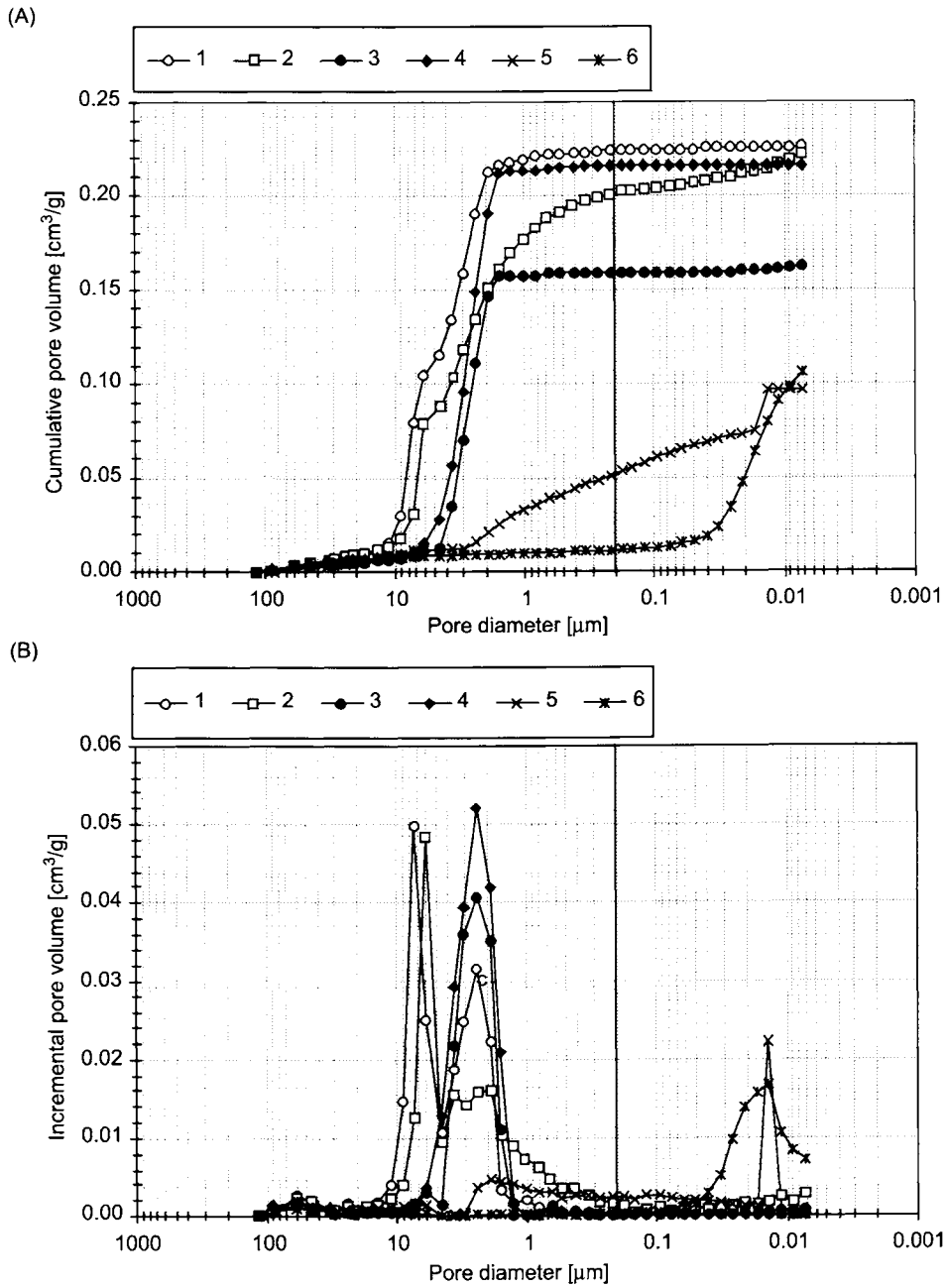


Figure III.7.3. Pore structure of solidified CCW: water mixtures (1:1 wt) compared to natural soils. (A) Cumulative and (B) incremental pore volume (cm^3/g) vs. pore diameter (µm). 1 – "pure" FA from the Rybnik power plant; 2 – "pure" FA from the Laziska power plant; 3 – FA + D-FGDS from the Rybnik power plant; 4 – FA + FGDS from the Opole power plant; 5 – clay; 6 – loam.

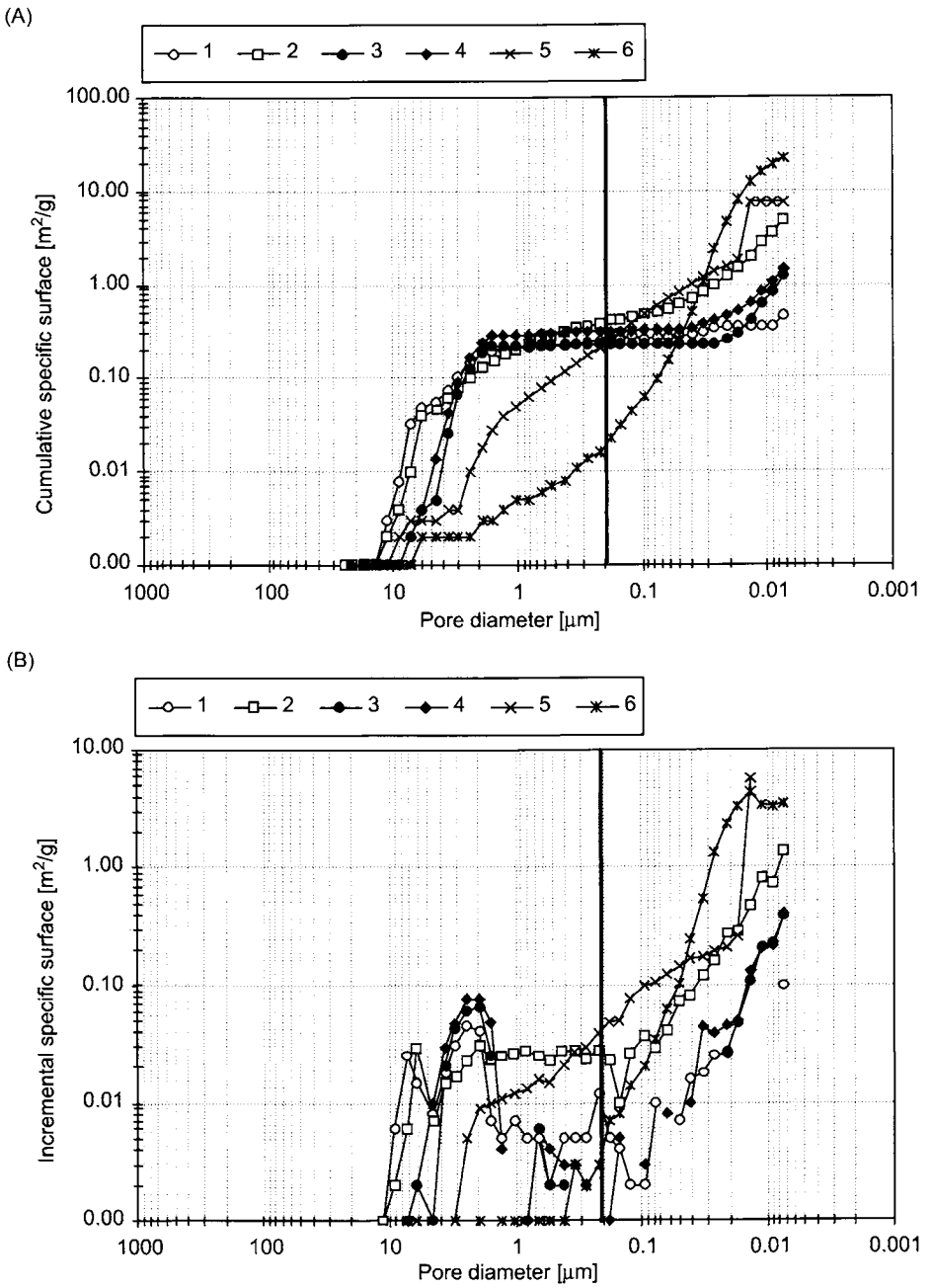


Figure III.7.4. Pore structure of solidified CCW: water mixtures 1:1 (wt) compared to natural soils. (A) Cumulative and (B) incremental specific surface (m^2/g) vs. pore diameter (μm). 1 – "pure" FA from the Rybnik power plant; 2 – "pure" FA from the Laziska power plant; 3 – FA + D-FGDS from the Rybnik power plant; 4 – FA + FGDS from the Opole power plant; 5 – clay; 6 – loam.

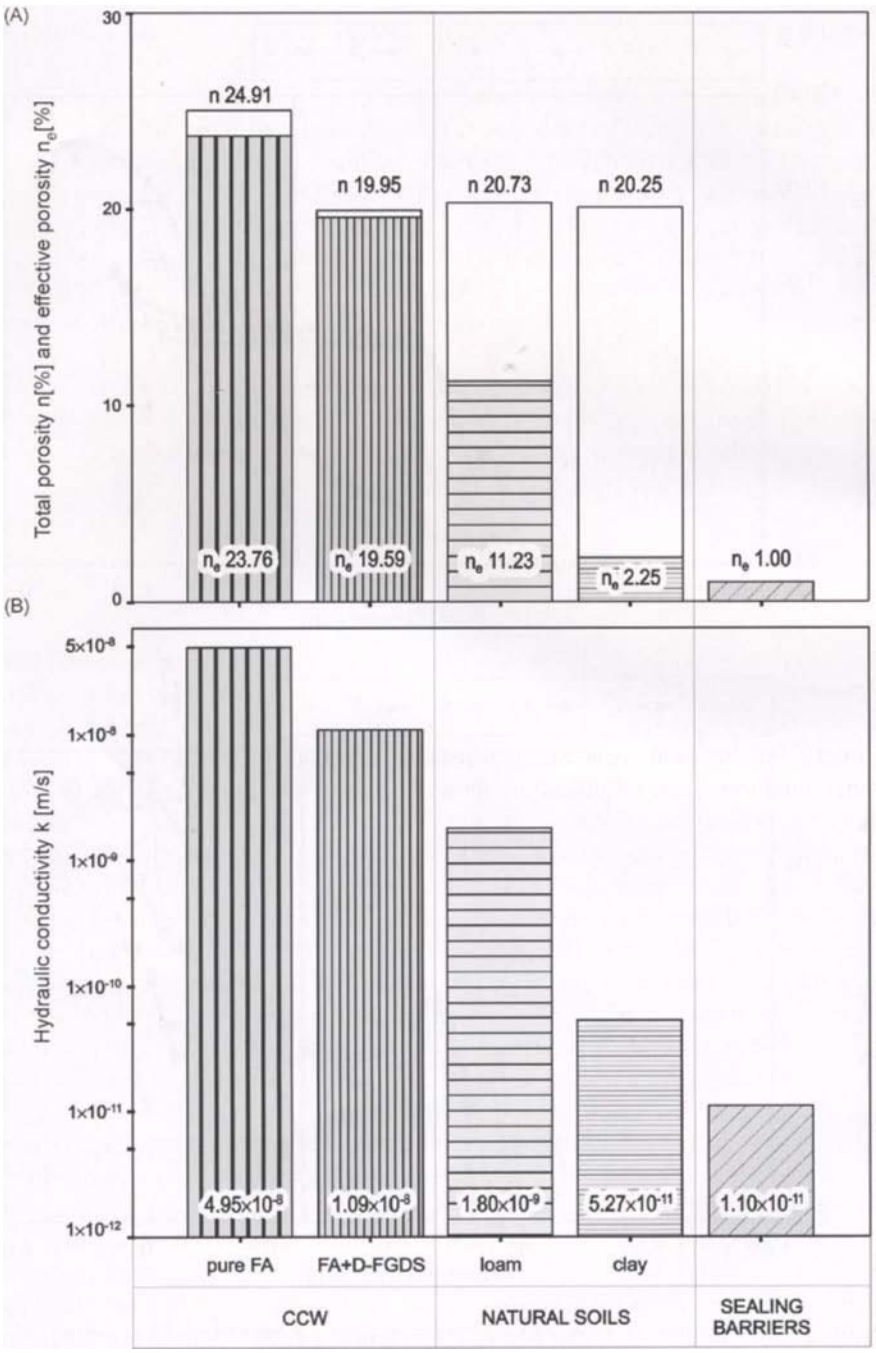


Figure III.7.5. Hydraulic properties of solidified CCW: water mixtures 1:1 (wt) compared to natural soils and sealing materials. (A) Total porosity n (%) and effective porosity n_e (%); (B) Hydraulic conductivity k (m/s). 1 – "pure" FA from the Rybnik power plant; 2 – "pure" FA from the Laziska power plant; 3 – FA + D-FGDS from Rybnik power plant; 4 – FA + FGDS from Opole power plant; 5 – clay; 6 – loam.

for horizontal flow (Pazdro and Kozerski, 1990) and for a vertical infiltration (Table III.7.11, Witczak and Adamczyk, 1994). The FA + D-FGDS has a hydraulic conductivity an order of magnitude lower than "pure" FA ($k = 10^{-9}$–10^{-8} m/s) and hence fulfills the criterion of impermeability for horizontal flow in groundwater reservoirs. These values, though, classify it as a weakly sealing material with respect to vertical infiltration (Witczak and Adamczyk, 1994). The rocks considered in hydrogeology as practically impermeable to a horizontal flow in an aquifer ($k = 1.0 \times 10^{-8}$ m/s) (Pazdro and Kozerski, 1990) do not assure sufficient barrier properties with respect to the vertical infiltration of water from the surface to the groundwater layer. The mean infiltration rate of atmospheric precipitation in Poland accounts for 100 mm/yr, which is adequate to the vertical infiltration rate of 3.2×10^{-9} m/s. This means that the infiltration water may percolate through the rocks of the hydraulic conductivity $k = 3.2 \times 10^{-9}$ m/s at a gradient = 1. Therefore, FA mostly does not fulfill the criteria of impermeability both with respect to the horizontal and vertical water flow. The leaching and transport of contaminants from the FA layer to the groundwater by the percolating water can thus occur.

III.7.2.3.2. Penetration resistance

Generally, all the mixtures of FA with water (1:1 wt) after solidification (16–24 days) were characterized by high *R*-values, ranging from 1000 to 19,000 kPa, i.e. 1–2 orders of magnitude higher than the ones of natural cohesive soils such as boulder clay (Fig. III.7.6A,B). For this soil, penetration resistance accounts for 190 kPa. Therefore, the FA:water mixtures after solidification showed excellent sealing properties against air penetration (Twardowska, 1999a,b, 2003b).

The *R*-values of mixtures based on pure FA appeared to be the lowest (1100–1200 kPa) (Fig. III.7.6A). Mine water mixtures which were 1:1 wt with FA + D-FGDS and FA + SD-FGDS displayed *R*-values roughly an order of magnitude higher than the ones with pure FA (Fig. III.7.6B). The pattern of $R = f(t)$ for 1:1 mixtures with water of different salinity consisting of pure FA, FA + D-FGDS and FA + SD-FGDS suggested that in the solidification process of these end products different mechanisms were involved: Phase 0 – instant chemical binding (FA + SD-FGDS); Phase I – gravitational dewatering and evaporation losses (FA, FA + D-FGDS, FA + SD-FGDS); Phase II – chemical binding (FA + D-FGDS).

The changes of penetration resistance of pure FA:water mixtures appeared to be very slow. It was a one-phase process, where almost entirely phase I was involved, while the role of phases 0 and II were negligible. The process of solidification and changes of *R*-value of water mixtures with end products of dry desulfurization process FA + D-FGDS showed different, specific for this kind of material two-phase pattern of *R*-values. In the initial phase I, which lasted up to 5 days, the *R*-value was low. After this time, a sharp increase of *R*-value occurred due to the chemical interaction of matrix with a pore solution (phase II). The chemical process of solidification was similar to the hydration and cementation of a lime mortar. Mixtures consisting of FA + D-FGDS showed the shortest solidification time (15–20 days) and the highest *R*-values (13,000–19,000 kPa). Use of high-salinity water for mixture preparation resulted in an increase of *R*-value of

Table III.7.11. Classification of rocks as protective barriers insulating groundwaters against vertical infiltration (after Witczak and Adamczyk, 1994).

Proposed class name (after Witczak and Adamczyk, 1994)	Vertical hydraulic conductivity k, m/d (m/s)	Examples of rock	Class name
Practically non-insulating	1×10^{-1} ($> 1.1 \times 10^{-6}$)	Loamy sand, sandy loam, loam/low-fissure rocks	Very highly permeable
Very weakly insulating	From 1×10^{-1} to 1×10^{-3} (from 1.1×10^{-6} to 1.1×10^{-8})	Silt loam, sandy clay loam, low-fissure rocks	Highly permeable
Weakly insulating	From 1×10^{-3} to 1×10^{-5} (from 1.1×10^{-8} to 1.1×10^{-10})	Clay loam, silty clay loam	Medium permeable
Medium insulating	From 1×10^{-5} to 1×10^{-6} (from 1.1×10^{-10} to 1.1×10^{-11})	Sandy clay	Low permeable
Well insulating	From 1×10^{-6} to 1×10^{-7} (from 1.1×10^{-11} to 1.1×10^{-12})	Lean clay	Very low permeable
Very well insulating	$< 1 \times 10^{-7}$ ($< 1.1 \times 10^{-12}$)	Boulder clay	Practically impermeable

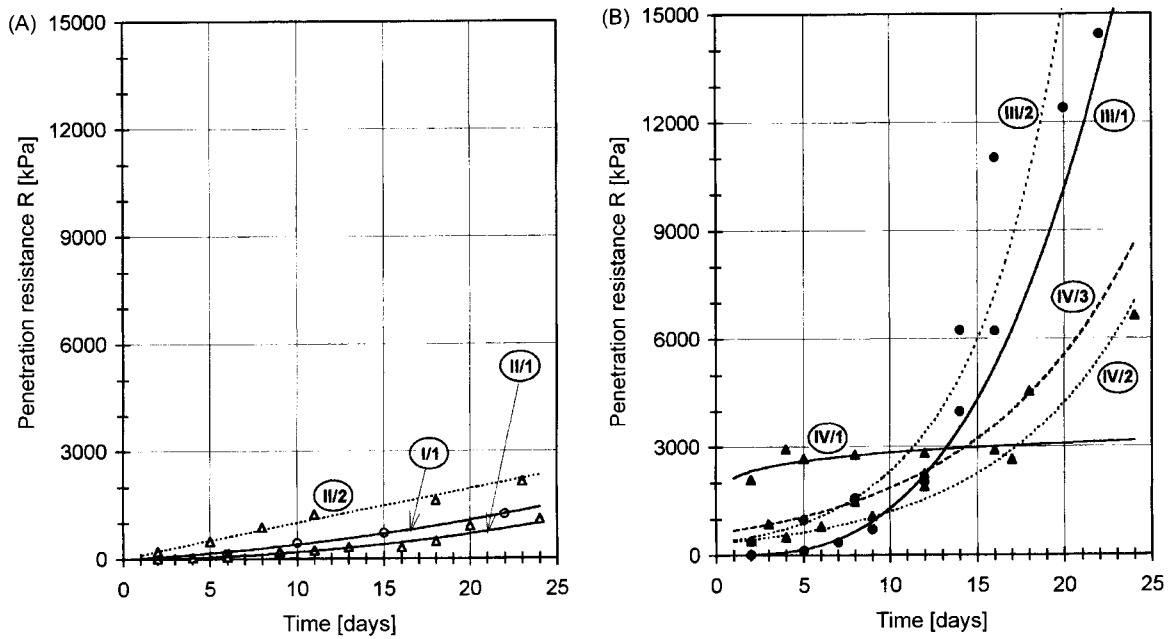


Figure III.7.6. Kinetics of solidification and increase of sealing properties of FA: water mixture (1:1, wt) against air penetration. A – "pure"FA; I/1 – low-alkaline "pure" FA from the Rybnik power plant (LA-FA). Mine water of Cl–SO_4–Na type, TDS 3.9 g/l, pH 8.15; II/1 – high alkaline "pure" FA from the Laziska power plant (HA-FA). Mine water of Cl–SO_4–Na type, TDS 3.9 g/l, pH 8.15; II/2 – high-alkaline "pure" FA from the Laziska power plant (HA-FA). Synthetic saline water of Cl–Na type, TDS 50.0 g/l, pH 7.2; B – FA + FGDS; III/1 – FA + D-FGDS, Rybnik power plant. Mine water of SO_4–(Cl)–Na–Ca type, TDS 2.9 g/dm^3, pH 8.06; III/2 – FA + D-FGDS, Rybnik power plant. Synthetic saline water of Cl–Na type, TDS 50.0 g/l, pH 7.2; IV/1 – FA + SD-FGDS from ABB-NID process, Laziska power plant. Mine water of SO_4–(Cl)–Na–Ca type, TDS 2.9 g/l, pH 8.06; IV/2 – FA + SD-FGDS from ABB-NID process, Laziska power plant. Synthetic saline water of Cl–Na type, TDS 50.0 g/l, pH 7.2; IV/3 – FA + SD-FGDS from ABB-NID process, Laziska power plant. Saline mine water of Cl–Na type, TDS 59.2 g/l, pH 7.23.

FA + D-FGDS mixtures. The effect of saline water was similar to that observed for mixtures with pure FA.

During the solidification of water mixtures with end products of the ABB-NID semi-dry desulfurization process (high-FA + SD-FGDS), the major role in the changes of *R*-value occurred for phases 0 and I. In the short-term phase 0, which lasted up to 2 days, the *R*-values depended both on chemical composition of water and characteristics of the matrix. The changes of *R*-value in this phase appeared to be specific for high-FA + SD-FGDS mixtures and were attributed to the fast chemical reactions, mainly of chemical water binding in matrix (Fig. III.7.5B). After phase 0, these mixtures showed considerable *R*-values (from 300 to 2100 kPa), from 1 up to >2 orders of magnitude higher than the respective *R*-values for mixtures with pure FA and also with FA + D-FGDS. In the next phase I, the characteristics of a matrix seemed to be the most important. In a long period up to 25 days the slow gradual, almost linear increase of *R* up to >7000 kPa occurred. In the phase 0, the highest *R*-values were displayed for the mixture of high-FA + SD-FGDS with a moderately mineralized water. In the phase I, use of highly saline mine water did not cause increase of *R*-value of these mixtures compared to low or moderately mineralized water. The long period of solidification and certain thixotropic properties of FA + SD-FGDS mixtures with water reduce the reuse potential of this end product as a sealing material against air penetration, particularly in a wet climate.

III.7.3. Pollution potential from FA

III.7.3.1. Weathering transformations of "pure" FA

The chemical composition of FA shows that this material is highly enriched in major and trace elements compared to the parent rock of its origin. Reliable assessment of the potential environmental impact of FA stored in the disposal sites or used for the production of construction materials that will be exposed to the atmospheric conditions during their life cycle, or application as soil amendment, which becomes increasingly popular in some countries, in particular in India, requires a knowledge of the qualitative and quantitative weathering transformations of FA in time under the actual field conditions. These transformations, which resulted from contact of FA with water, exert a determining influence on the leaching behavior of macro- and trace elements. Here, the transformation of pollution potential of "pure" FA from hard coal combustion has been discussed as a most abundant kind of CCW disposed and stored in FA ponds worldwide.

In general, in the FA weathering model, four major phases have been distinguished (Janssen-Jurkovičová et al., 1994). In the *phase 1*, intensive dissolution of highly soluble salts and oxides, along with ion exchange occurs between the liquid and solid phase at the surface of FA particles. The most characteristic aspect for this phase is an exothermic process of CaO hydration accompanied by a strong rise of pH values above 11–12. The major processes in *phase 2* consist of the devitrification of the amorphous glass phase at high pH, exposure of the amorphous relics of clay minerals filling FA particles, release of amphoteric constituents and formation of secondary phases at gradually decreasing pH values. In the *phase 3*, diffusion processes are considered to be predominant, and a slower continuation of the development of the secondary amorphous Mg–Al–Si phases exposure

at the interface with the glass matrix occurs. The further aging processes in the *phase 4*, are considered to result in formation of clay minerals (kaolinite, smectite) at lower pH < 9–10 at the interface between solution and amorphous phase (or zeolites at pH > 9–10).

Janssen-Jurkovičová et al. (1994) attribute the decrease of pH to the dissolution and screening by precipitates of a more reactive exterior glass phase and exposure to leaching of a less reactive interior one. It seems, though, that this process should be explained rather by the proven exposure of interior amorphous relics of clay minerals due to the devitrification of a glassy superficial phase. This results in the development of the aluminum hydrolysis reactions. Different sources refer to equilibrium with gibbsite $Al(OH)_3$ or aluminum hydrolysis as solubility controlling factors for Al (Schofield and Taylor, 1954; Hem, 1968; Brookins, 1987; Hutchinson and Ellison, 1992; Garavaglia and Caramuscio, 1994; Blaszczak and Buzek, 1998). In the FA, amorphous aluminum hydroxides along with silica are the prevailing phases. The pH of a solution determined by the hydrolysis reaction of aluminum ions is close to pH 5.0. The pattern of pH formation at the wash-out (I) and dissolution (II) stages observed in the simulated leaching cycle (Twardowska and Szczepańska, 2002) and field studies presented below fits well with this scheme.

Our own observations of weathering transformations of "pure" FA from Polish power plants during long-term column leach experiments and field surveys showed massive macro-constituent release at highly alkaline pH 9.8–12 in *phase 1*, which occurred with subsequent decrease of pH. The dynamics of macro-constituents release were adequate to wash-out stage I of leaching presented in Chapter III.1, and the stabilization of leaching at a relatively low level at pH which had decreased to < 7–7.5 in *phase II* (which is adequate to dissolution stage II). A number of secondary minerals were also formed in stage II. The extent of pH increase in *phase 1* and subsequent decrease in *phase 2* was found to be highly dependent upon the CaO content and the value of the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3)$. At the mean concentration in FA of CaO ≤ 3% wt and the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3) \leq 3.0$, the pH values in *phase 1* are less alkaline (pH 11–10) and the decrease of pH in *phase 2* is faster and deeper, up to pH < 7–6. This material was termed as low-alkaline (LA). At CaO at the level ≥4% wt and the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3) > 3$, the pH values in the *phase 1* are strongly alkaline (up to pH ≥ 12) and their decrease in the *phase 2* is slower and stabilizes at the slightly alkaline level (up to pH 7.5). This material was consequently termed high-alkaline (HA).

The newly formed minerals observed in the different parts of weathered FA layer were portlandite $Ca(OH)_2$ and calcite $CaCO_3$ as products of CaO hydration and carbonation by atmospheric CO_2. The typical secondary mineral was ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, hydrated calcium aluminates of C_4AH_n type ($4CaO\cdot Al_2O_3\cdot 12H_2O$), and occasionally calcium sulfaluminates of $C_3A\cdot CaSO_4\cdot H_{12}$ type or in the form of mixed crystals with C_4AH_{12} phase. As a transitory mineral, gypsum $CaSO_4\cdot 2H_2O$ was also present, which showed gradual depletion in time. These minerals, along with amorphous phases, are in conformity with phases observed by de Groot et al. (1989) and Janssen-Jurkovičová et al. (1994) in weathered FA from Dutch power plants and seem thus to be typical for FA weathering transformations at the transitory *phase II* and stabilization *phase III*. These observations comprise, though, a relatively short period of time and do not supply

a satisfactory knowledge on a life-cycle environmental behavior of FA in actual field conditions.

Though FA has become for years a focus of extensive studies in order to develop a reliable unified and systematic approach to evaluation of the leaching behavior of inorganic granular waste based on general geochemical principles (van der Sloot et al., 1984, 1991, 1993, 1994, 1996, 1997; van der Sloot, 1996; Tiruta-Barma, 2000; Twardowska and Szczepańska, 2001, 2002, 2003), there are still significant uncertainties in the long-term prognosis of environmental impact of this waste placed at disposal sites or used for large-area application (e.g. for soil amendment), in particular of impacts on groundwater and soil (Ghuman et al., 1999; Rowe et al., 2001; Twardowska et al., 2003; Wang et al., 2003; Ziemkiewicz, 2003a,b). Long-term environmental impact of FA ponds in different stages of weathering of waste material was exemplified in two case studies: (i) an operational ash pond sited in the Erai River basin (MSEB, Chandrapur, Maharashtra, India); (ii) a reclaimed FA pond in the dewatering stage of the post-closure period sited in a disused sand quarry (Silesia, USCB, Poland). Selection of these sites remote from each other was inspired by two premises. On one hand, it was intended to show the similarity of the leaching behavior of hard coal FA from different sources, on the background of the disposal/management approach. On the other hand, lack of FA ponds under operation in Silesia enabled parallel field leaching studies at the initial stages of leaching in the same area.

III.7.3.2. Leaching behavior of FA at the (I) wash-out and (II) dissolution stages (a case study: ash pond under operation, MSEB, Maharashtra, India)

III.7.3.2.1. Characteristics of a disposal site

The FA pond construction and management is typical for the current FA disposal practice in India based on the least cost. The major method of CCW utilization is wet disposal in the surface ponds sited in the areas of unprotected aquifers, with open water circuit and overflow discharge of surplus water to the nearest river. The slurry consists of a mixture of FA and BA in the general proportion 80/20, as it is generated in the power plant (Prasad et al., 1999). Controls over these sites have been given a low priority due to failure to recognize the adverse environmental impact of the disposed CCW. This waste is considered harmless, predominantly on the basis of short-term leaching tests simulating (II) dissolution stage at a lowest rate of release and applied to a freshly generated material (Singh and Gambhir, 1996; Singh, 1999) or monitoring of surplus overflow impact on the river water quality (Raghuveer, 1999).

A surface pond for disposal of coal ash slurry from the Maharashtra State Electricity Board (MSEB) at Chandrapur was sited in 1983–1984 in the Erai River basin, in the submerged depression with a total area of 27 km^2 in the valley of Kankaiya nallah (stream), a tributary of the Erai River (Fig. III.7.7). The stream water was impounded by constructing a masonry dam across the catchment near Chargaon village, thus giving rise to a large settling pond. No specific lining has been provided to insulate the pond from the aquifer. The pond filling is being performed by progressively extending the ash slurry pipeline and changing its alignment. Ash slurry is disposed at the rate of approximately 50,000 m^3/day and contains 20–23% v/v of ash. The ash pond has a storage capacity of approximately 116 million m^3 and is expected to fill in 30 years. The excess water as

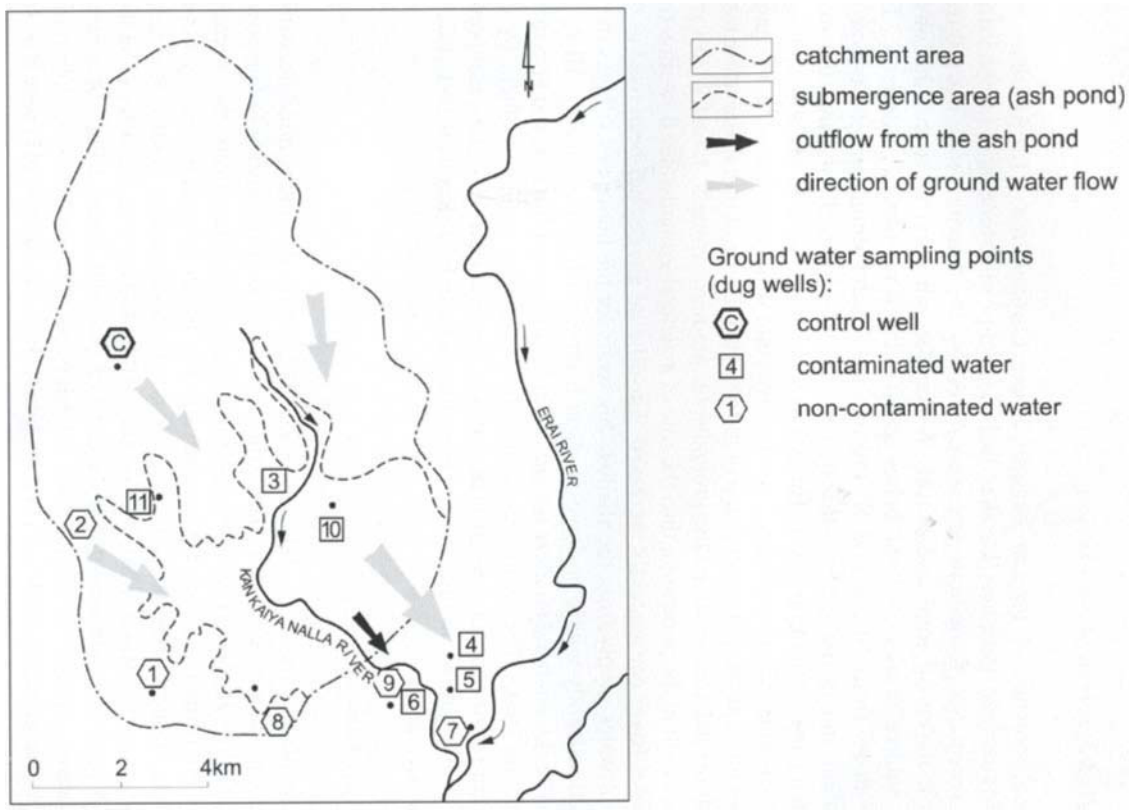


Figure III.7.7. General map of MSEB coal ash pond under operation (Maharashtra, India) and location of groundwater sampling points (wells). C – control well upgradient of the ash pond; 1–8, 10, 11 – dug wells; 9 – outflow of excess water from the ash pond; 11, 3, 10 – contaminated aquifer within the ash pond; 4, 5, 6 – contaminated aquifer down-gradient of the ash pond; 2, 1, 8, 7 – non-contaminated well water beyond the impact of the ash pond.

the overflow passes the weir in the spillway area is discharged directly into the Kankaiya nallah.

The average annual precipitation (1346 mm/a) is distributed within the year in a way typical for the region: heavy rains of a monsoon period are followed by 7 months of dry weather. Temperature ranges from 10 to 45°C.

III.7.3.2.2. Hydrogeological conditions

The geological structure of the site includes Upper Carboniferous (Talchir shale and pebbly sandstone) and Permian (Barakar and Kamathis sandstone and carbonaceous shale). The recent age formations are represented by the laterite rocks and alluvial sediments with layers of sand and gravel. Within the ash pond area, the shallowest unprotected aquifer occurs 3–10 m below ground level in alluvial sediments. The groundwater flows from NE, E and W towards the central drainage watercourse of Kankaiya nallah and in the general direction from NW–NE to SE towards the main drainage watercourse of the Erai River. The difference in water table in the post monsoon and summer season is 2.5 m on average, which proves that surface infiltration is the major source feeding this aquifer. After formation of the pond a build-up of 6 m in the water table below the submerged area modified the groundwater gradients from N, E and W towards the Kankaiya nallah in the pond area, thus the role of a general groundwater flow direction towards the Erai River consequently increased. The alluvial aquifer has been used as the main source of water supply from the shallow dug wells for the numerous villages in the area sited predominantly within or down-gradient from the ash pond area (Fig. III.7.7).

In this area, leaky confined aquifers occur both in Kamathis and Barakar and also in the Talchir sandstone strata. The hydraulic connection of aquifers endangers them by the potential infiltration of contaminants from the surface. The Kamathis sandstone is reported to form the best aquifer in the area, while the potential of Barakar and Talchir progressively decrease.

III.7.3.2.3. Ash characteristics

This material contains particles 1–150 μm in size. The chemical composition falls within the range of component concentrations occurring in CCW elsewhere, also in Polish power plant waste (Table III.7.3). Phase composition does not differ from the average. Amorphous non-vitrified phase and glaze prevail. The major component of crystalline phases is quartz; minor phases are magnetite, hematite and mullite. With a low mean CaO = 2.0% wt and the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3) \approx 2$, this ash can be thus classified as low-alkaline aluminum silicate material (van der Sloot, 1996), of a rather moderate buffering capacity. Discharge from the ash pond and leachate from a laboratory column test conducted in the conditions of dissolution stage (II) showed pH range 8.0–6.0 (Singh and Gambhir, 1996; Singh, 1999), which indicates a potential for acidification.

III.7.3.2.4. Survey of groundwater quality in the vicinity of CCW disposal site

In the ash pond under operation, in conformity with the *phases 1, 2* and *3* of the FA weathering model (Janssen-Jurkovičová et al., 1994), two generic leach patterns of

the disposed material are anticipated to occur (van der Sloot et al., 1993, see also Chapter III.1): wash-out stage (I), when the soluble compounds unrestricted by equilibria limitations are readily released from the freshly generated material after its disposal at the site, at high pH; dissolution stage (II) when the leached loads are controlled by solubility of constituents limited by equilibria constraints, at pH decreasing to the lower values close to neutral. The resultant concentration and pH values will depend upon the proportion of the CCW freshly disposed and already washed out, of the different pattern of compounds release, as well as on the dilution potential and water quality of the recipient groundwater stream. Hydrogeological/hydrological parameters of the pond are determined by the two major water streams under the saturated zone conditions: (1) outflow of the excess water from the pulp over the weircase discharged directly to the surface recipient (river) and (2) vertical infiltration of water through the CCW layer to the groundwater stream and horizontal flow of groundwater in the general direction towards the Erai River.

A survey conducted by AIC Watson Consultants Pvt. Ltd. (1996) to evaluate the impact of the ash pond on the usable groundwater resources in the area, in order to undertake adequate remedial measures, was commissioned by MSEB in response to the World Bank request. The problem of a possible deterioration of the groundwater quality by the seepage from ash pond was brought to the notice of the MSEB during the supervision of the power plant facilities in 1994. The quality of the groundwater within the ash pond and in its vicinity was assessed in 1996 on the basis of water sampling from 11 dug wells in the villages, as well as from the discharge of the overflow water from the ash pond (Fig. III.7.6). Water was sampled in triplicate with an interval of 2 weeks. As a control, the dug well in Chalbardi village up-gradient of the ash pond was selected as the one unaffected by the ash disposal.

The survey (Fig. III.7.7, Table III.7.12) showed significant adverse changes of water quality in the shallowest unprotected alluvial aquifer within and down-gradient of the pond, which was revealed mainly in the multiple increase of macro-constituent concentrations typical for the leachate from the power plant ash (TDS, chloride, sulfate hardness, Ca, Mg). Contents of trace elements (B, Cd, Cr(VI), Pb, Hg), fluoride and nitrate also distinctly increased compared to the background concentrations. Nevertheless, except Hg which showed permanent excess concentrations, trace metals only occasionally exceeded MCL (Cd, Pb) due to pH values (7.4–8.3) within the stability field for the majority of these elements (Garrels and Christ, 1965; Brookins, 1987; van der Sloot et al., 1994, 1996). The most dramatic changes, which disqualify this water, occurred within the ash pond (wells 11, 3 and 10). Down-gradient of the ash pond (wells 4, 6, 5) water quality, though improved due to dilution, was still not fit for use. There is groundwater deterioration due to the adverse impact of the ash pond on the macro-component concentrations. Low concentrations of contaminants, which are present in the excess water, are discharged as an overflow through the weir. These contaminants result from the high proportion of ash used in the slurry prepared with fresh water in an open circuit. There is a short contact time of the ash with the water in the slurry and in the surface layer of the ash pond. These data, along with the accelerated laboratory leach tests, which are inadequate relative to the actual field conditions, are often used as a proof of a lack of adverse impact of unlined ash ponds on groundwater resources (Singh and Gambhir, 1996; Singh, 1999). The release of macro-contaminants at a high rate during the vertical

Table III.7.12. Groundwater quality in sampling points located in the vicinity of coal ash pond site and direction of groundwater flow in wash-out I and dissolution II stages (MSEB Chandrapur, Maharashtra, India); concentrations in mg/l (mg/dm^3).

Parameter	Location of sampling points with respect to coal ash pond and the direction of groundwater flow												DWS[a] (MCL)	DL
Sampling points	Control well up-gradient	Wells up-gradient			Well shielded by riverbed	Discharge (overflow weir)	Wells within the ash pond			Wells down-gradient				
	C	2	1	8	7	9	11	3	10	4	5	6		
Color	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1	<0.5	<0.5	<0.5	<0.5	<0.5	5	0.5 Hazen
Odor	OL	OL	OL	OL	OL	SU	OL	OL	OL	OL	OL	OL		
Turbidity	0.19	0.66	0.18	<0.01	<0.01	7.2	<0.01	0.2	0.13	0.1	<0.01	0.16	5	0.01
pH	8.35	7.66	7.75	7.81	7.79	7.96	7.51	7.45	7.37	7.41	7.67	7.36	6.5–8.5	0.1
Alkalinity $CaCO_3$	**268.5**	**266.7**	**319.3**	**236**	194.7	82	**560**	**360**	**512**	**320.7**	**717.33**	**322**	200	–
Total dissolved solids (TDS)	330	438.7	810	394.7	359.3	290	**3513**	**2716**	**2122.7**	**1824.7**	**1332**	**1173**	500	–
Total hardness $CaCO_3$	194	286.7	**460**	264	216	168	**1172**	**1010**	**720.7**	**884**	147.33	**660**	300	–
Calcium Ca	48	78.13	**90.4**	72.3	69.9	57.6	**174.13**	**190.4**	**93.87**	**156.1**	24	**178.4**	75	–
Magnesium Mg	36	22.2	**56.9**	20.3	9.4	5.83	**179.65**	**129.8**	**118.1**	**109.8**	21.22	**52**	30	–
Chloride Cl	16.56	44.16	82.84	47.4	21.28	28.4	**817.4**	**733.4**	**377.4**	**384.3**	75.09	183.9	250	–
Sulphate SO_4	150	1	88.3	1.73	81.3	97.5	**658**	**376.7**	**435.8**	**210**	**317.5**	83	200	0.1
Fluoride F	**1.41**	0.94	0.66	0.5	0.041	**1.68**	**1.24**	0.428	**1.107**	0.78	**1.55**	0.263	1	0.018

Nitrate NO_3	0.24	0.52	2.47	0.69	0.21	0.109	*5.98*	*4.58*	*3.36*	*4.95*	0.3	3.62	45	0.01
Arsenic As	0.001	0.0065	0.011	0.016	0.0071	*0.037*	0.0072	0.011	0.03	0.011	0.006	0.0064	0.05	0.001
Boron B	0.07	0.097	0.126	0.054	0.054	*0.45*	*0.318*	*0.211*	*0.383*	*0.179*	*0.43*	*0.107*	1	0.01
Cadmium Cd	<0.001	0.0013	0.0027	0.003	0.005	0.001	*0.008*	*0.007*	**0.02**	*0.006*	*0.0057*	*0.0063*	0.01	0.001
Chromium Cr^{6+}	0.006	0.0063	0.0057	0.004	0.004	0.01	*0.008*	*0.012*	*0.008*	*0.008*	*0.0075*	0.0063	0.05	0.001
Copper Cu	0.011	0.0061	0.0073	0.004	0.005	0.003	0.016	0.013	0.009	0.011	0.0157	0.014	0.05	0.001
Iron Fe	**0.31**	**0.388**	**0.325**	0.247	0.173	0.55	0.213	**0.516**	0.152	0.205	0.2027	0.174	0.3	0.001
Mercury Hg	<0.001	**0.0025**	**0.0037**	**0.004**	**0.002**	**0.006**	**0.002**	**0.004**	**0.005**	**0.005**	**0.002**	0.001	0.001	0.001
Lead Pb	0.016	0.004	0.012	0.005	0.005	0.0007	**0.06**	**0.054**	*0.023*	0.051	0.0047	*0.031*	0.05	0.001
Selenium Se	0.004	0.008	0.013	0.005	0.006	0.0096	0.0058	0.007	0.006	0.008	0.005	0.004	0.01	0.001
Zinc Zn	0.037	0.107	0.068	0.035	0.052	0.012	0.0073	0.053	0.061	0.096	0.067	0.086	5	0.001
Phenols	0.001	**0.015**	**0.022**	**0.022**	**0.025**	**0.028**	**0.28**	**0.04**	**0.037**	**0.039**	**0.026**	**0.083**	0.001	0.001
α radiation Bq/l	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	Absent	0.04
β radiation Bq/l	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	Absent	0.08

C – Control groundwater from Chalbardi village, DL – detection limit.

Value – exceeds MCL; *Value* – exceeds the background level.

Sampling points (Fig. III.7.6): 1 – Tadoli village, 2 – Ghodpeth village, 3 – Kachrala village, 4 – Tirwanja village, 5 – Kawathi village, 6 – Chhota Nagpur village, 7 – Wichota village, 8 – Chargaon village, 9 – discharge from FA pond, 10 – Awanda village, 11 – Gunjala village.

[a]DWS – Drinking water standard established by Bureau of Indian Standards according to IS 10500, 1991 = SDWA/EPA.

percolation through both the freshly generated and previously disposed ash layers has a significantly longer contact time which is generally neglected.

Adequately carried out and interpreted standard leach tests would have ensured reliable short-term risk assessment from any granular material including CCW at the wash-out (I) and dissolution (II) stages (Twardowska and Szczepańska, 2002). Archival data (Zawisza et al., 1990, 1993) on pre- and instant post-closure monitoring of the drainage, leachate and circulation water from the closed circuit and of the groundwater quality at the predominating dissolution stage II of constituent release from the disposed low-alkaline FA at the Przezchlebie fly ash pond (USCB, Poland) confirm the discussed pattern of leaching behavior of FA at this stage (Table III.7.13).

In the presented case of coal ash disposal pond of MSEB (Maharashtra, India), a further extension of groundwater deterioration in space and time is anticipated during the planned 30 years long disposal of power plant ash in a huge area. In the presented survey, contamination of the deeper aquifer has not yet been observed. However, in the long run, the hydraulic connection of aquifers poses a serious threat due to downward development of contamination (Twardowska et al., 1999, 2003).

III.7.3.3. Leaching behavior of FA at the delayed release (III) stage (a case study: fly ash pond of Rybnik power plant in the post-closure period, USCB, Silesia, Poland)

The above study exemplifying the pollution potential of a power plant ash pond in the operational period, which lasts usually for several years and reflects wash-out (I) and dissolution (II) stages, was discussed for the case study of ash pond in Maharashtra, India. While the short-term risk assessment to the environment from CCW is easy to define, the long-term prediction is much more difficult due to the complicated nature of kinetically determined long-range transformation processes, which might be easily overlooked. The leaching behavior of FA in the surface pond in the post-closure period at the delayed release (III) stage (van der Sloot et al., 1993, see Chapter III.1) is exemplified here in the case study on the Przezchlebie fly ash surface pond of Rybnik power plant (USCB, Silesia, Poland).

III.7.3.3.1. Location and characteristics

The fly-ash pond for disposal of Rybnik power plant wastes was sited in an unused 20 ha sand quarry having a maximum depth of 20 m (Fig. III.7.8). The hydraulic disposal of FA to the pond in a closed circuit started in 1979 and lasted for 12 years. In 1982–1983 due to construction of embankments of coal mining wastes, the FA disposal in the pond was continued above the surface level. The location of pulp outlet was changed several times.

The total area of FA disposal increased to 53 ha and its volume reached 23 million m^3. In the following years, the construction of the pond was further developed through increasing the height of embankments and construction of new sections. The anthropogenic FA layer 25–30 m thick replaced finally the extracted primary sand layer.

Since 1984, the amount of FA disposal decreased, up to the site closure in 1991. In the post-closure period, due to gradual dewatering of the pond, hydrogeological conditions within the FA layer changed from saturated to vadose zone conditions. In order to control

Table III.7.13. Monitoring of groundwater quality in the area adjacent to the Przezchlebie fly ash pond of the Rybnik power plant (USCB, Poland) prior to and after the site closure (after Zawisza et al., 1993).

Parameter	Monitoring wells (Quaternary aquifer)			Drainage outlet	Effluent below the front dam	Collecting reservoir in water circuit	Effluent below the railway	MCL for drinking water[a]
	P1b	P1a	P10					
Quality parameters prior the site closure (1989–1991)								
pH	8.3–6.5	6.6–6.4	8.3–7.9	8.0–9.1	7.3	7.8–8.4	7.8	6.5–9.5
Cl	19.6–13.5	29.4–31.2	23.4–25.0	**888–685**	**734**	**700–684**	**940**	250
SO_4	247–204	**276**–190	10.7–9.1	**1829–1215**	**1648**	**1263–1214**	**2351**	250
TDS	13,848–9220	2118–908	351–62	4366–2972	3467	3143–2913	5896	
Quality parameters after the site closure (1992–1993)								
pH	6.6–8.1	6.9–8.3	7.5	8.7	8.0–7.5	8.5–7.4	8.0–7.5	6.5–9.5
Cl	17–20	32–10	20	**665**	**277**–192	**600–713**	**1107–975**	250
SO_4	222–207	248–209	7.0	**1370**	**1609–605**	**1360–1254**	**2795–1885**	250
TDS	3158–2111	621–550	117	3680	3541–1575	3481–3650	6852–7222	

Values exceeding MCL are bold.

[a]Polish regulations: Directive of the Minister of Health (2000).

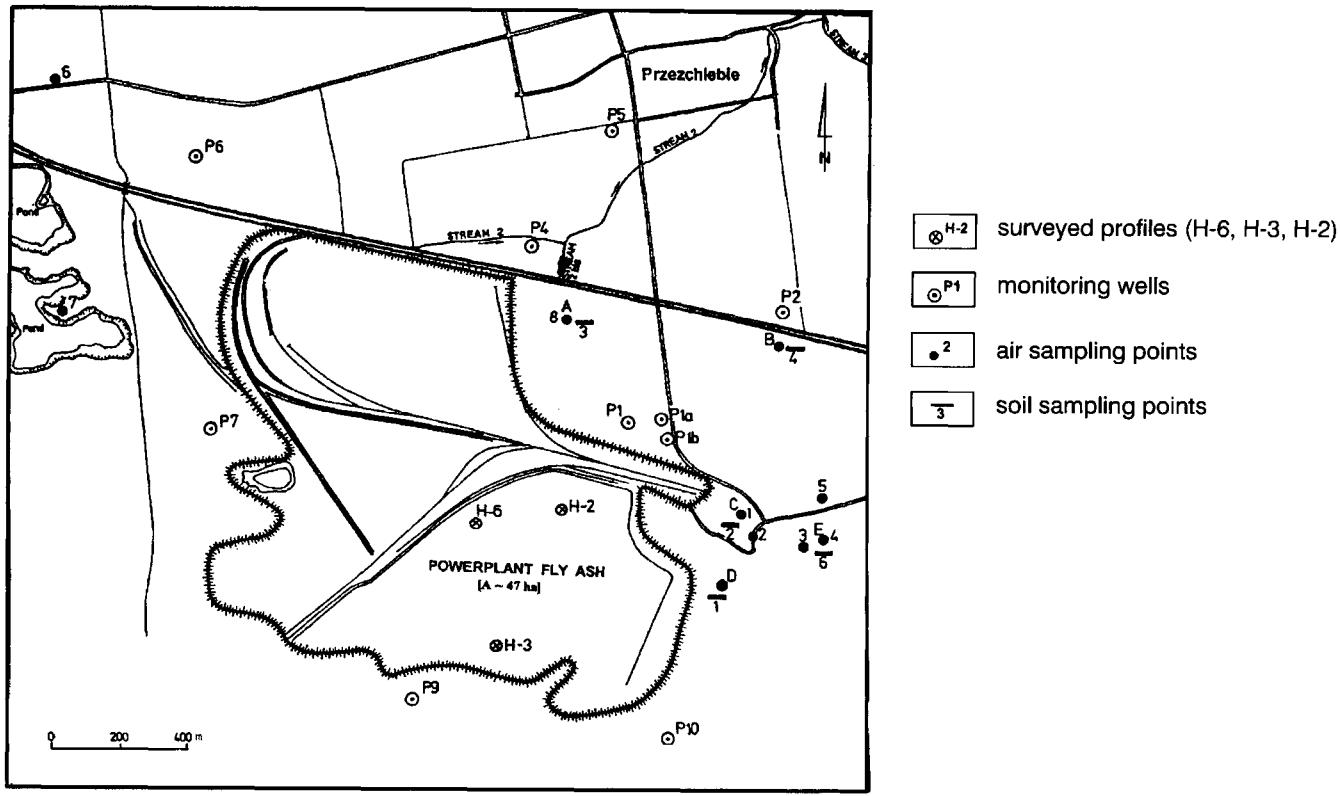


Figure III.7.8. General map of the Przezchlebie fly ash pond of the Rybnik power plant (Silesia, Poland) in the post-closure period. Location of monitoring wells (P1–P10) and screening boreholes (H-2, H-3, H-6).

dusting, the dump surface was stabilized by carbamide resins spread from a helicopter and in the following years it was reclaimed by grass cover. Due to full reuse of FA in Silesia, no new surface ponds have been constructed since then.

III.7.3.3.2. Meteorological and hydrogeological conditions

Annual precipitation in the area ranges from 559 to 866 mm; pH of the precipitation in the area adjacent to the pond in the W–E direction of dominating winds ranged in 1989–1993 from acidic to close to neutral (pH 3.5–7.4, mean 5.6).

The geological structure of the site is represented by Quaternary, Tertiary and Triassic sediments. The Quaternary formations in the site area are about 20 m thick in the W and about 50 m thick in the E directions. They comprise both permeable (sand and sand gravel) and low permeable sediments (clays and silts). The upper Quaternary aquifer in sandy sediments is of discontinuous character. The water table, at a depth 0.3–4.7 m under the ground surface, is free and only locally it is tense.

The Quaternary groundwater monitoring network includes 10 wells, drainage, leachate and reservoir of circulating water, where only basic parameters (pH, TDS, Cl, SO_4, Fe and Mn) were measured (Fig. III.7.8, Table III.7.13). After site closing, the monitoring of groundwater terminated.

III.7.3.3.3. Fly ash characteristics

FA from the Rybnik power plant has been characterized in detail in the previous subchapters, in Tables III.7.2–III.7.10, and in Figures III.7.2–III.7.6 as a representative material of typical composition and properties. FA from the Rybnik power plant can be classified as LA aluminum silicate material with CaO ranging from 2.07 to 3.70% wt, mean 2.98% wt and the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3) = 1.7–3.6$, mean 2.6. In this respect, this range is typical for "pure" FA from European power plants fired by hard coal.

III.7.3.3.4. Methods of field survey

The applied procedure of evaluating long-term leaching behavior of "pure" FA at the disposal site should have been both reliable and fast, which could be assured by direct measurements. The field survey conducted in 1993 was based on the assessment of qualitative and quantitative transformations of pore solution in FA layer at the Przezchlebie pond in the post-closure period. The pond after dewatering was already converted into an anthropogenic vadose zone. This newly formed zone was sampled along the vertical profile in the three drilled boreholes up to 11 m deep (H-2, H-3, H-6) (Fig. III.7.9). FA core samples of a natural moisture content were transported in air-tight plastic bags to the laboratory, where pore solution was extracted by the pressure method under nitrogen and analyzed for the metal content by standard methods using ICP-OES technique (ICP Perkin Elmer Plasma 40). For anionic compounds, a High Throughput Capillary Electrophoresis System Model 270A-HT Perkin Elmer was applied. The elemental speciation in pore solution and QA/QC testing was performed with use of a geochemical computer programs WATEQ 4F and Visual MINTEQ ver. 2.01.

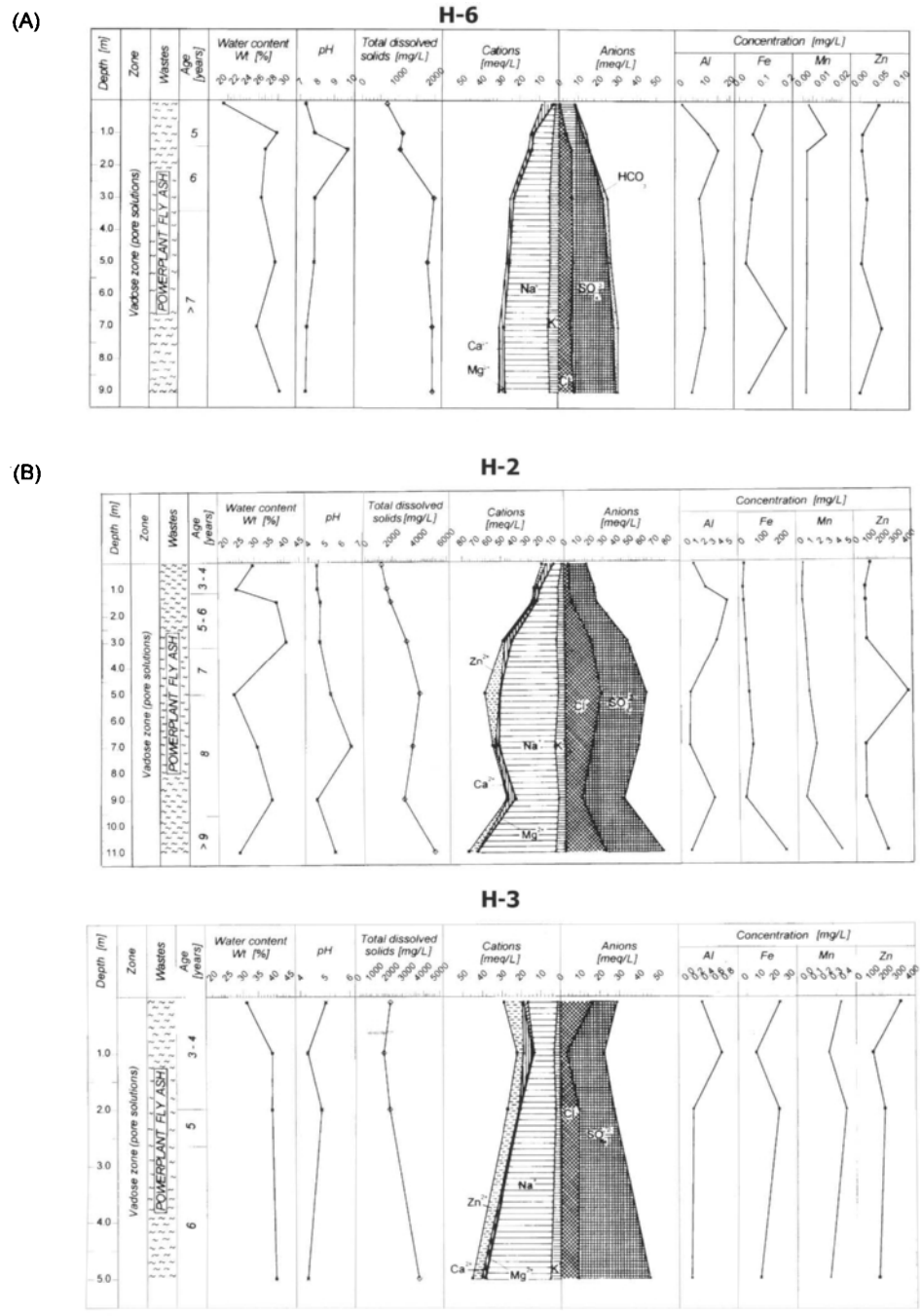


Figure III.7.9. Hydrogeochemical profiles of macro-components in pore solutions in the layer of alkaline FA from the Przezchlebie fly ash pond of the Rybnik power plant in the post-closure period. (A) Dissolution (II) phase (profile H-6); (B) Delayed release (III) phase (profiles H-2 and H-3).

III.7.3.3.5. Field screening studies

The results of analysis of pore solutions along the three vertical profiles of the FA disposal pond in the post-closure period after 12 years operation displayed the pattern of leaching behavior at the delayed release (III) stage that has not been considered or reported before with respect to FA. The material disposed in the pond is of a different hydraulic conductivity, from high in the non-compacted to moderate in compacted state ($k = 10^{-3}$–10^{-4} cm/s) typical for fine and mean sands, and has a high porosity ($n = 0.58 - 0.50$). After closure, the water flow pattern changed during the dewatering of the FA layer from saturated zone conditions typical for the operating stage into vadose zone conditions, when vertical percolation of atmospheric precipitation had started. Chemical composition of pore solutions along the FA dump profiles displayed significant transformations, which reflected both the altered water flow (vertical downward redistribution of ions) and the equilibria conditions. The comparison of the pore solution characteristics along the H-6, H-2 and H-3 profiles reflected the character of these changes (Table III.7.14, Figs. III.7.9, III.7.10a–e). While the pore solution in FA in H-6 profile, which showed lower specific density, hydraulic conductivity and moisture content still reflected the dissolution stage II under operating conditions (pH 7–10), the composition of pore solution in the looser FA profiles H-2 and H-3 indicated alteration of buffering properties of the system that could be defined as delayed release III stage. It resulted in the decrease of pH from alkaline values to acidic ones, ranging from 4.3 to 6.5, and release of trace metals in accordance with the changed stability conditions. The composition of pore solutions along the profiles H-2 and H-3 compared to H-6 suggested that the major buffering mechanisms controlling pH after depletion of carbonates comprised reactions involving hydrolysis of aluminum ions from amorphous phases exposed to the direct contact with percolating water due to the devitrification of glaze. The first stage hydrolysis reaction:

$$(Al{\cdot}6H_2O)^{3+} + H_2O = (AlOH{\cdot}5H_2O)^{2+} + H_3O^+ \qquad \log K \approx 5 \qquad \text{(III.7.1)}$$

Further weathering transformations of the solid phase were directed to formation of the secondary minerals within the amorphous phase, which was reported also by Janssen-Jurkovičová et al. (1994). Composition of pore solutions and phase analysis of material indicated that these processes in simplified form can be described as equilibrium–non-equilibrium reactions between kaolinite and gibbsite at the stage of their formation, and dissolved silica and water, discussed by Garrels and Christ (1965). In particular, the following reactions that involve amorphous phase might be considered as major ones controlling pH and ionic composition of pore solutions at this stage:

- Second stage of aluminum hydrolysis and gibbsite formation:

$$2Al^{3+} + 6H_2O = Al_2O_3{\cdot}H_2O(c) + 6H^+$$
$$\log K = 5.7 = \log[Al^{3+}] + 3pH \qquad \text{(III.7.2)}$$

- Dissolution of silica and kaolinite formation that may congruently limit the activity of dissolved aluminum:

$$2Al^{3+} + 2H_4SiO_{4(aq)} + H_2O = H_4Al_2Si_2O_9(c) + 6H^+$$
$$\log K = 1.0 = \log[Al^{3+}] + \log[H_4SiO_4] + 3pH \qquad \text{(III.7.3)}$$

Table III.7.14. Concentration range of constituents in pore solutions along the vertical profiles of the Przezchlebie fly ash pond of the Rybnik power plant (USCB, Poland) in the post-closure period: Dissolution II (profile H6) and delayed release III stages (profiles H2 and H3).

Parameter constituent	Concentration in pore solution (mg/L, mg/dm^3)							
	Profile H-6 (0.1–9.0 m)		Profile H-2 (0.1–11.0 m		Profile H-3 (0.1–5.0 m)		MCL[a] (Polish)	RBC[b] US EPA
	Min	Max	Min	Max	Min	Max		
pH	7.50	*9.80*	*4.46*	*6.50*	*4.29*	*5.04*	6.5–9.5	
μS cm^{-1}	961	2150	1194	1913	1119	1756	2500	
Macro-constituents								
TDS	681	1976	1198	5079	1564	3712		
Ca	31.98	112.62	2.95	110.73	5.95	98.60		
Mg	0.269	3.250	2.17	7.17	4.18	26.26		
Na	26.10	*516.90*	150.25	*1393.53*	*231.28*	*765.64*	200	
K	66.60	216.87	72.10	320.00	55.64	202.44		
NH_4-N	< 0.05	*1.67*	0.32	*1.26*	< 0.05	*1.22*	0.5	3.70
NO_3-N	6.41	15.03	6.55	18.40	10.85	37.40	50.0	58.0
Cl	19.24	*294.60*	108.15	*1116.06*	108.60	*589.62*	250	
SO_4	*362.69*	*1054.26*	*687.31*	*2134.09*	*581.64*	*1742.05*	250	
HCO_3	38.44	147.05	< 0.50	4.27	< 0.50	< 0.50		
SiO_2	4.83	17.26	65.46	281.18	135.19	313.66		
PO_4	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	0.2	
Trace elements								
Ag	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	0.01	0.18
Al	*0.744*	*15.260*	< 0.060	*4.662*	< 0.060	*0.663*	0.2	110
B	< 0.01	*3.064*	*2.869*	**7.987**	**3.343**	**10.460**	1.0	3.30
Ba	0.069	0.204	0.096	0.341	< 0.002	0.488	0.7	2.60
Be	< 0.002	< 0.002	< 0.002	**0.012**	**0.002**	**0.007**		0.0016
Cd	< 0.003	< 0.003	*0.013*	**0.175**	**0.045**	**0.167**	0.003	0.018

Cr	*0.059*	*0.170*	< 0.010	*0.97*	*0.121*	*0.310*	0.05/0.03	37/0.18
Cu	0.069	0.200	< 0.005	0.036	< 0.005	0.042	1.0	0.73
F	*1.62*	**7.85**	**8.03**	**33.76**	**12.98**	**30.17**	1.5	2.20
Fe	0.027	0.191	*3.891*	*209.30*	*7.222*	*23.59*	0.2	
Li	0.537	**3.512**	0.430	**4.000**	0.345	**2.548**		0.73
Mn	< 0.002	0.012	**0.081**	**4.061**	**0.222**	**0.399**	0.5	0.18
Mo	0.088	**1.480**	0.086	**1.412**	0.090	**0.361**		0.18
Ni	< 0.025	< 0.025	< 0.025	*0.062*	< 0.025	< 0.025	0.03	0.73
Sr	0.503	1.304	0.229	1.784	0.152	1.565		22.0
Ti	< 0.005	< 0.005	< 0.005	0.050	< 0.005	0.040		
V	0.076	**1.120**	< 0.010	**0.900**	0.020	0.115		0.26
W	< 0.010	0.400	1.044	7.800	1.910	7.700		
Zn	0.004	0.052	**57.33**	**382.31**	**102.80**	**308.86**	3.0	11.0

Values in *italic* exceed Polish MCLs for drinking water: Values in **bold** exceed RBC by US EPA.
[a]MCL for drinking water (Polish regulations: Directive of Minister of Health, 2000).
[b]RBC by US EPA, 1994 (Smith, 1994).

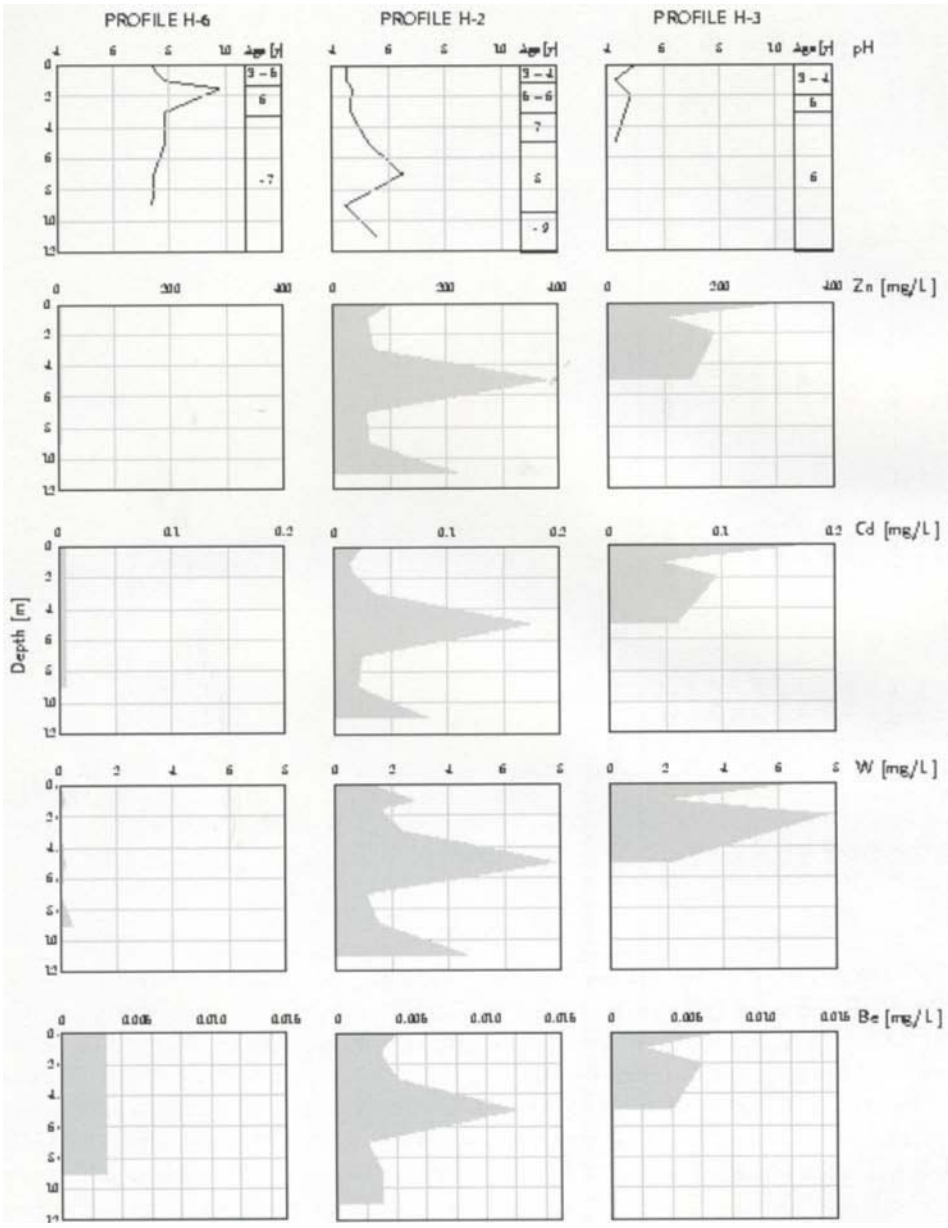


Figure III.7.10a. Chemical transformations of pore solutions along the vertical profiles of the Przezchlebie fly ash pond in the post-closure period: patterns of trace metals distribution along the profiles of FA layer vs. pH values in the dissolution (II) (profile H-6) and delayed release (III) phases (profiles H-2 and H-3). (a) pH-controlled high increase (Zn, Cd, W, Be).

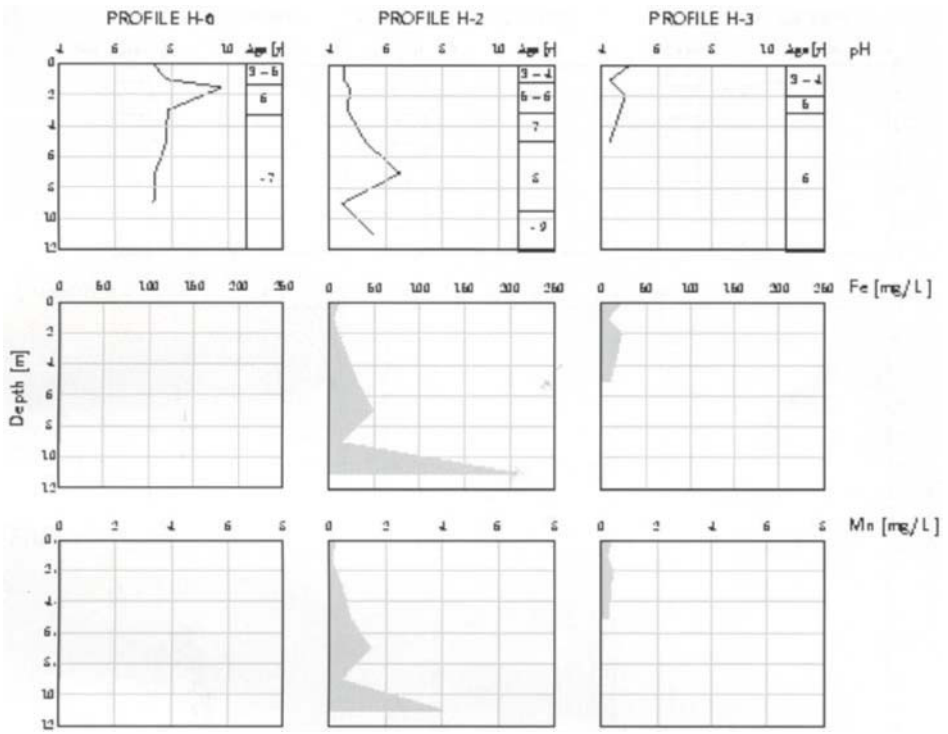


Figure III.7.10b. Chemical transformations of pore solutions along the vertical profiles of the FA pond in the post-closure period: patterns of trace metals distribution along the profiles of FA layer vs. pH values in the dissolution (II) (profile H-6) and delayed release (III) phases (profiles H-2 and H-3). (b) pH-dependent high increase (Fe, Mn).

The solubility product for the dissolution of solid amorphous silica to form dissolved silica is $10^{2.6}$. At this value the stability of kaolinite was found to be the greatest (Garrels and Christ, 1965). More complicated composition and nature of relations between the solid and liquid phase in the system FA – pore solution resulted in the formation of predominantly mixed crystal phases. Depletion of dissolved Al^{3+}, acidification of pore solution and simultaneous considerable increase of dissolved silica along the profiles H-2 and H-3, as well as formation of ettringite and other minerals of hydrated sulfaluminate type as secondary crystalline phases, confirmed this general scheme of reactions occurring in the delayed release III stage and explained the nature of acidification of pore solutions.

This dissolution resulted in a large non-linear release of heavy metals from the FA and a significant increase in contamination potential of the FA with respect mainly to the groundwater and eventually soils in adjacent area in case of uncontrolled dusting (decrease of pH in leachate to 4.3–4.5) and delayed extensive release of Zn, Mo, Mn, Li, F, Cd, Be, B in hazardous concentrations, and Fe, Cr, Al, SO_4, Cl, NO_3, NH_4, K, Na and TDS several times above their MCL values for drinking water. The chemical composition of pore solutions displays a pattern reflecting equilibria limitations for particular metals and their

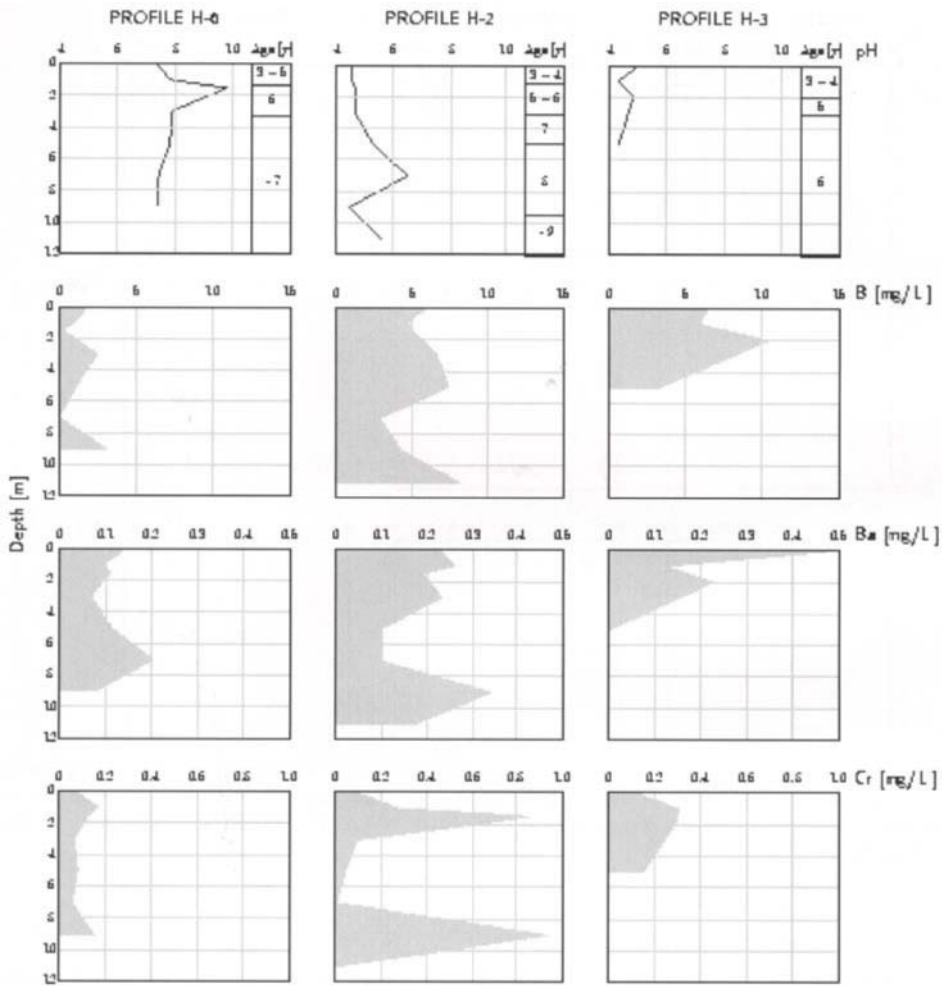


Figure III.7.10c. Chemical transformations of pore solutions along the vertical profiles of the FA pond in the post-closure period: patterns of trace metals distribution along the profiles of FA layer vs. pH values in the dissolution (II) (profile H-6) and delayed release (III) phases (profiles H-2 and H-3). (c) pH-controlled moderate increase (B, Ba, Cr).

stability fields under the different pH–Eh conditions along the vertical profiles of FA layer, including changes from oxic conditions in the surface layer to locally anoxic environment in the deeper layers. In general, in conformity with pH–Eh-stability fields (Garrels and Christ, 1965; Brookins, 1987), metals can be grouped in accordance to similar release-dissolution response to pH as the controlling parameter, e.g.: I: (Zn–Cd–W–Be) (Fig. III.7.9a); II: (Fe–Mn) (Fig. III.7.9b) (reverse pH-dependent increase). Several metals show weak (III: B, Ba, Cr) (Fig. III.7.9c) or no influence of pH (IV: Li, Mo, Sr) (Fig. III.7.9d), while Al, Cu and V (Fig. III.7.9e) display opposite behavior

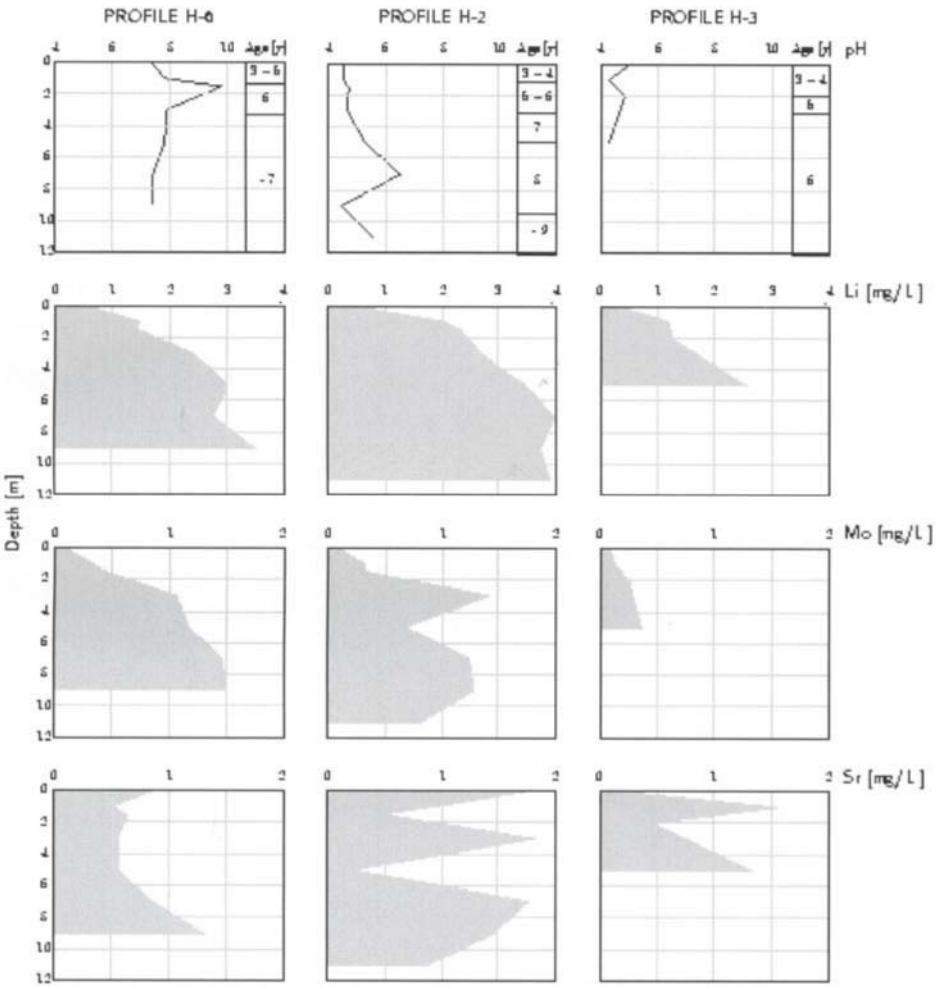


Figure III.7.10d. Chemical transformations of pore solutions along the vertical profiles of the FA pond in the post-closure period: patterns of trace metals distribution along the profiles of FA layer vs. pH values in the dissolution (II) (profile H-6) and delayed release (III) phases (profiles H-2 and H-3). (d) Weak influence of pH (Li, Mo, Sr).

(immobilization at pH 4.3–5.0), in case of Al well explained by formation of clay minerals and other aluminates. Leaching behavior of oxyanions appeared to be less pH-controlled and showed either high susceptibility to release in a wide range of pH in compliance with wide stability field (Mo), or lower dissolution rate at low pH (V). Molybdenum is a known toxin highly enriched in FA, therefore its unrestricted mobility is to be considered at every case of FA disposal or bulk use in the conditions of extensive environmental exposure. Other oxyanions of high toxicity such as As and Se, also considerably enriched in FA, were not analyzed in this survey. Other sources (Mattigod et al., 1990, 1999) report high

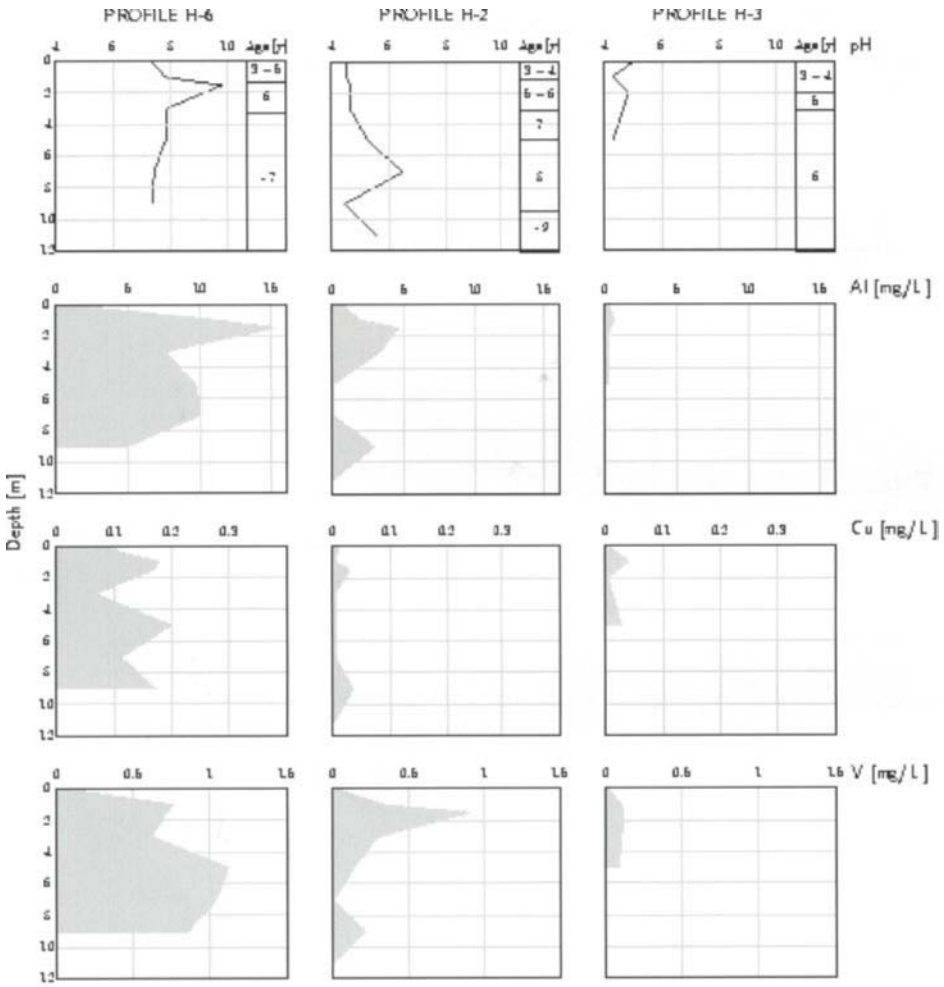


Figure III.7.10e. Chemical transformations of pore solutions along the vertical profiles of the FA pond in the post-closure period: patterns of trace metals distribution along the profiles of FA layer vs. pH values in the dissolution (II) (profile H-6) and delayed release (III) phases (profiles H-2 and H-3). (e) Immobilization at low pH (Al, Cu, V).

leachability of these elements from fossil-fuel combustion residues. Studies on speciation of As and Se during FA leaching (Eline et al., 1994) suggested sorption-controlled leaching process, while pH was to be a parameter controlling the kind of sorption phase and binding strength with respect to arsenate and selenite. At alkaline pH, Ca-minerals (portlandite or ettringite) and at acidic pH, amorphous iron oxides were considered as sorption phases, this last process to be modeled using a simplified sorption complexation model.

The speciation of pore solutions with the use of WATEQ 4F geochemical assessment computer program, showed occurrence of trace metals released to solution in the delayed

release (III) stage predominantly as free ions or associated with sulfur as $MeSO_{4(aq)}$. Dissolved silica was specified as $H_4SiO_{4(aq)}$, which is in conformity with the mechanism of transformations and chemical composition of pore solution in the delayed release III stage.

Leaching characteristics of coal combustion FA deposits in the natural conditions, although similar to that reported by other investigators (de Groot et al., 1989; van der Sloot et al., 1991, 1996; Ghuman et al., 1999; Danker et al., 2001) shows significant differences in comparison with the data obtained in laboratory leaching tests. These differences are also emphasized by other authors (Fällman and Hartlén, 1994; Janssen-Jurkovičová et al., 1994; Meij and Schaftenaar, 1994; Twardowska and Szczepańska, 2002). Due to the much more complicated nature of the environmental interactions, the distortion of the time scale may cause serious qualitative and quantitative errors in prediction of the leaching behavior of the material. In particular, kinetically determined processes and reactions such as weathering, dissolution of amorphous phases and formation of secondary minerals, as well as effect of flow conditions upon the actual composition and ionic strength of pore solutions, is not adequately considered in these tests. Correct prediction of the leaching behavior of trace elements from the material requires the precise modeling of processes occurring within the macro-components of a material under the exposure conditions, which influence the factors controlling trace metal release (pH, Eh, specific surface and pore structure, organic matter, complexing agents) (van der Sloot, 1996; van der Sloot et al., 1997; Tiruta-Barma et al., 2000; Twardowska and Szczepańska, 2002).

In general, the study proved (i) possibility of discontinuous non-linear time delayed increase of pollution potential of disused non-hazardous large-volume waste in the dumping sites to the hazardous level due to externally or intrinsically induced transformations of the environmental exposure and alteration of controlling factor values; (ii) inconsistency of the laboratory leaching tests and the actual leaching behavior of trace metals, particularly at the conditions when composition changes are dictated by kinetically determined reactions. The tests reflected entirely wash-out (I) and dissolution (II) stages but not the delayed release (III) stage; (iii) and demonstrated the necessity of life-cycle screening/monitoring of CCW dumping sites for contaminant release as a function of the primary factors (pH–Eh, ionic strength, ionic composition of solute) and secondary controlling factors (L/S–liquid to solid ratio, water flow conditions) along the vertical profile of an anthropogenic or natural vadose zone. These data are to be utilized in the development of the long-term predictive hydrogeochemical models and their field validation, and for providing an early warning and remedial actions with respect to the particular site. The development of a reliable model requires parallel observations of hydrogeological conditions as well as of transformations occurring in the solid phase over time as a function of the exposure conditions.

The formation of pH (and Eh) as a function of time-dependent (kinetically defined) processes appeared to be a key issue for a correct prediction of the leaching behavior of waste with respect to inorganic trace elements controlled by the precipitation/dissolution reactions. With respect to As and Se (as arsenate and selenite), which were found to be the most important redox species in FA, the sorption-controlled leaching model with pH as a parameter defining the sorption phase and the reversibility of the process was suggested (Eline et al., 1994).

It should be added that so-called "low emission" from the FA pond (wet and dry deposition of FA particulates from the dump surface in the direction of dominating winds)

can also adversely influence soils in the areas adjacent to the site: soil acidification in sampling point 1 to pH 4.2–4.9 compared to the background pH 5.4–7.7 in the area closest to the Przezchlebie fly ash pond (USCB, Silesia, Poland) (Fig. III.7.7) in the direction of dominant winds was already reported (Zawisza et al., 1993). In view of growing popularity in developing countries of concept of CCW (FA or coal ash) bulk use as a soil amendment, the processes not only within anthropogenic vadose zone layer, but also waste–soil interaction in the natural unsaturated zone should be the objective for long-term prediction. The studies carried out so far (Hockley et al., 1992; Sajwan et al., 1999) do not give yet strong basis for long-term prediction of these interactions for different systems.

III.7.4. Conclusions

Coal combustion, which currently generates about 39% of the world's electricity, will continue to be a major source of world power well into third Millennium. With 67% of world's coal output currently devolved to China, the USA and India, and heavy dependence of these countries on coal for power generation, a low rate of CCW use (33% (e), 25 and 2–5%, respectively) reflects the scale of FA disposal. Only few countries – small CCW generators – utilize it to the extent of 90–100%. Anticipating the highest world's energy growth based on coal in Asia in the first decades of the Millennium indicates that this is the most critical area with respect to CCW management in the near future.

About 10-fold higher concentration of trace elements compared to coal/lithosphere, the occurrence of highly leachable macro-components, high hydraulic conductivity and observed acidification of the most abundant low-alkaline FA in a long-range time due to devitrification of glass phase, generation of secondary minerals and regeneration of primary minerals from their amorphous relics are the major factors that lead to the conclusion that the potential risk to the environment from FA should be evaluated as high. The nature and extent of the risk varies at the different stages of weathering. The beneficial property of FA is its high penetration resistance, 1–2 orders of magnitude exceeding that of natural cohesive soils. It can thus be eventually used as a sealing material against air penetration.

Occurrence of xenobiotics (PAHs, PCDD, PCDF) in FA was found to be low. The radioactivity level of FA has been found to pose no risk to the environment and health provided it is not used for the production of construction materials. For this purpose, FA material cannot be used unrestrictedly and should be tested for the level of α- and γ-radiation before use.

Dry and semi-dry desulfurization processes generally caused the addition of calcium- and sulfur-containing compounds to FA reaction products from FGD process. Their proportion and kind in the end product depends on the applied process. Generally, an admixture of FGD solids results in a significant increase of leachable sulfate compounds, but also in much higher buffering capacity and lower concentrations of xenobiotics and trace metals in this product due to the "diluting" effect of FGDS, as well as generally low susceptibility to release due to permanent moderately alkaline to neutral pH values.

The leaching behavior of "pure" FA disposed in ash ponds appears to display all three basic stages of leaching, i.e. wash-out (I), dissolution (II) and delayed release (III) stages. In the first two stages, the contamination potential of FA is governed predominantly by the release of macro-components at pH values ranging from alkaline to close to neutral, hence the leaching of the majority trace elements is low, except of oxyanions of a wide stability field in solution (Mo, As, Cr(VI)). The deterioration of groundwater quality by high concentrations of leachable macro-components (TDS, chloride, sulfate, Ca, Mg) and also Mo, As and Cr(VI) may already render the shallow unprotected aquifer unusable at these stages, as was demonstrated in the case study on the MSEB ash pond in Maharashtra, India. In the dissolution stage (II) of the lowest dynamics of component leaching controlled by the equilibrium with gypsum, the sulfate content in leachate is high enough to render the groundwater non-potable. Equilibrium concentrations of macro-constituents in both stages are developed in a water stream due to a vertical redistribution of constituent load in the vadose zone or during down-gradient flow of water through the ash layer in the saturated zone of an ash pond.

The highest pollution potential to unprotected aquifers from the FA disposal was found to occur in the post-closure period in the delayed release (III) stage where the massive release of trace elements (Zn, Mo, Mn, Li, F, Cd, Be, B) occurred in hazardous concentrations, and Fe, Cr, Al, SO_4, Cl, NO_3, NH_4, K, Na and TDS were several times above MCL for drinking water. Despite years of extensive studies on FA focused on developing a reliable evaluation of the leaching behavior of granular waste, the information on the full three-stage cycle of FA leaching is still unsatisfactory. While a systematic approach to release of trace metals and also other inorganic components of waste as a function of controlling factors such as L:S (liquid to solid ratio) and pH is well advanced, a weak side of a long-term prognosis is a lack of the reliable long-term prediction model for controlling factors, in particular for pH changes due to proton release ion based on the one hand on the general geochemical principles, and on the other hand on the specificity of a material and a site. This has been the main reason for a failure in recognition of a long-range time-delayed possibility of FA acidification and hence of a massive release of trace metals in hazardous concentrations. The change of pH (and Eh) as a function of time-dependent (kinetically defined) processes appeared to be a key issue for a correct prediction of the leaching behavior of waste with respect to inorganic trace elements.

There is also evidence that easily detectable, obvious and visible adverse impact of ash disposal ponds on unprotected aquifers in their vicinity quite frequently remains neglected

induced changes of controlling parameters. A field validation by means of a life-cycle monitoring/screening of waste disposal site is the most reliable instrument for the evaluation of the actual situation and the verification of predictive models, which eliminate a chance of the wrong decision. For these purposes, monitoring of the anthropogenic and natural vadose zone in the disposal site is the best source of early-warning information. Considering the high costs of the equipment and its maintenance for the stationary vadose zone monitoring, the concept of mobile installations for a periodical survey of factors controlling release of contaminants (e.g. pH, Eh and conductivity) along the vadose zone profile of CCW and a detailed survey of controlled contaminants (concentrations of constituents in pore solutions, in particular of trace elements) in the case of detected systematic changes should provide the required information on the behavior of a material and particular contaminants in a waste in the most cost-effective way. Therefore, we consider monitoring is required to provide an early warning and to permit effective remedial actions.

Direct analysis of pore solutions gives the most reliable results and can be based either on temporary drillings, or on stationary sets of porewater samplers. The first option seems to be the most convenient and cost effective, in particular in the developing countries with the limited availability of a trained staff and difficulties in maintaining the permanent monitoring network.

The presented case studies confirm that CCW from coal combustion, though considered non-hazardous and fit for use in a multitude of commercially proven applications, should not be treated the same way as a natural raw material despite of a strong pressure of proponents of this approach, among them of the ACAA (Stewart, 1999). Uncontrollably disposed, this waste may pose a high short-term risk to shallow unprotected aquifers and soil, and its further non-linear time-delayed increase, which would render an area environmentally problematic. Another conclusion that should be derived, is a need of a careful long-term environmental evaluation of a bulk use of FA under the conditions of the vast environmental exposure of the unprocessed material, e.g. as soil amendments. It should take into consideration the possibility of soil contamination with trace elements in all stages of geochemical transformations.

To facilitate CCW disposal and utilization in an environmentally safe way and to prioritize its use, besides reliable environmental risk assessment prediction models, testing procedures, and life-cycle monitoring, countries that are high CCW generators need national strategies of power plant waste control, treatment and disposal methods within a general waste management strategy. These strategies should provide a legislative and regulatory framework within which adequate enforcement procedures can be implemented that would make uncontrollable FA disposal highly unprofitable. The enforcement procedures should comprise a well-balanced system of precepts, prohibitions and charges for disposal (fees, penalties) that would encourage power plants as waste generators to support financially the environmentally safe utilization of CCW by the waste reuse industry on a cost-benefit basis, in order to reduce charges for the disposal and to assure competitiveness of these products in the market. The current practice in India shows that under the conditions of the lack of the Resource Conservation Act and of financial incentives for CCW end users from waste generators, their products cannot compete financially with natural raw materials, and a fast growth of FA market remains a wishful thinking. The lack of properly working system of finance transfer from waste generators to

utilization industries seems to be a serious obstacle for growing of CCW market also in the USA, despite of an adequate and properly implemented regulatory framework.

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PART IV

Advances in solid waste characterization and monitoring

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IV.1
The changing face of environmental monitoring

David Friedman

IV.1.1. Introduction

During the past 30 years, analytical chemists have witnessed fundamental changes in both the technology and the policies of environmental monitoring. This chapter will look at two types of changes. We will first examine the changes taking place in monitoring policy, and second at the efforts being made to shift from laboratory analysis to field analysis.

The policy shift that will be looked at is the movement from a reference method system to a performance-based system. In this chapter, we will look at why regulatory agencies and the public initially adopted the reference method or technology approach to monitoring, the benefits and drawbacks of this decision, and the changes that are now taking place to eliminate the problems. We will highlight what the current movement to change from a technology to a performance-based approach to monitoring will have on the scientific community, the laboratory community, the consulting companies who serve government and private sector clients, the regulated community, and the regulatory agencies who are responsible for implementing the environmental programs.

The second area that will be addressed in this chapter are the efforts being made to improve monitoring quality while reducing data gathering costs by emphasizing field analysis. In addition to eliminating the costs and problems associated with preserving and shipping samples to the laboratory, the almost real-time nature of on-site analysis offers the data user tremendous potential savings. We will highlight some recent developments in the areas of field sampling and analysis and look at how these developments are impacting environmental monitoring and what additional changes we might expect to see.

IV.1.2. Monitoring policy

IV.1.2.1. Reference method approach

Beginning in the 1960s, the Congress of the United States enacted a series of laws to protect the nation's air, water, and land. Among the most important of these statutes, from the standpoint of monitoring, were the Clean Air Act (1963), the Clean Water Act (1973), the Safe Drinking Water Act (1974), the Resource Conservation and Recovery Act (1976), and the Comprehensive Environmental Response, Compensation, and Liability Act (1980).

These laws required the Environmental Protection Agency (the Agency or EPA) to establish criteria and procedures to assure the safety of the air we breathe, the water we drink, and the land we use for recreation and as a source of food.

In carrying out its mandates under these laws, the Agency recognized the need to be able to monitor the various environmental media. Such monitoring was needed to quantify the type and magnitude of the problems and to monitor compliance with the controls that would be needed to correct the problems and prevent future problems.

As it began to implement the air and water programs, the Agency realized that appropriate methodology for measuring the pollutants of interest at the levels of concern was generally not available. New techniques were needed and scientists in EPA, the private sector (e.g. instrument manufacturers), and academia responded with the development of many new measurement techniques. Many, such as quadruple mass spectrometers as detectors for gas chromatography and inductively coupled argon plasma emission spectrographs, required a fairly high level of sophistication and expertise if one wanted to be confident of the validity of the results. However, it was recognized early on that if the environmental programs were to be successful, one could not depend on having cadres of experienced analytical chemists gathering the monitoring data. For example, the drinking water programs require each of the many hundreds of public water supply systems in the United States to conduct periodic monitoring of the quality of the water that they distribute. Many of these systems are small and cannot afford to always employ highly sophisticated chemists conducting the analyses. Often, the systems would have to make use of well-trained technicians rather than chemists. A similar situation presented itself in the air monitoring arena. Here the vast majority of the monitoring is performed by local government agencies. Some of these agencies face the same staffing constraints as their drinking water counterparts.

It was not only the Agency that was concerned with this situation. The companies, the federal, state and local government agencies, and the laboratories and other organizations that assist the regulated community in complying with the regulations issued to implement the statutes were also concerned. They were especially apprehensive since, under the law, the regulated entity is criminally and civilly responsible for the quality of the data used to demonstrate compliance. The regulated entities wanted requirements that were clearly described so that they could be certain that they were correctly complying with the regulations, enforcement agencies needed clearly defined requirements so that they could easily determine if a regulated entity was in compliance, and the various supporting organizations (e.g. the engineering companies, the commercial laboratories, the instrument manufacturers) needed clear monitoring requirements in order to make it easier to bid on work and to deal with clients that often had only limited expertise in the field of environmental monitoring.

In response to these concerns, a two-pronged approach was adopted by EPA's air and water programs. They consisted of a combination of detailed, rigorously defined protocols for carrying out the required monitoring coupled with quality control and documentation requirements to ensure that the required procedures were being followed. Alternative methods approval systems were established by each regulatory program (e.g. drinking water, waste water, air emissions) to provide a mechanism for the regulated community (and for the innovation industry to get approval for their new products) to be allowed to use a monitoring technique or methodology other than one of the ones published by EPA.

Changes to this approach began in the early 1980s with implementation of the hazardous waste (RCRA) program. While the Agency continued to develop and publish methods for use in complying with the RCRA monitoring requirements, it attempted to build flexibility into the system by not mandating that the promulgated methods be used. For most of the regulatory program, monitoring requirements specified what parameters were to be determined and regulatory action levels specified, the regulations did not mandate use of any specific method(s). However, this philosophy of flexibility did not take hold in the monitoring community. A number of the states and many of the permit writers and compliance officials, when implementing the RCRA program required the regulated community and its supporting laboratories to use the methods that EPA published in its RCRA testing methods manual "*Test Methods for Evaluating Solid Waste*" (SW-846).

The next major milestone took place with the establishment of the EPA program to clean up abandoned, contaminated sites under the Comprehensive Environmental Response, Compensation, and Liability Act. The Agency's Superfund program, as it is commonly called, found itself in the position of needing to analyze a tremendous number of samples to determine which sites were contaminated, the nature and extent of the contamination, and what priority should be assigned to cleaning up the site. The amount of sampling and analysis required overwhelmed the Agency's own laboratory capability. To address this problem, EPA established the Contract Laboratory Program (CLP).

The purpose of the CLP was and is to serve as a means for EPA to efficiently and effectively purchase laboratory services from the commercial laboratory community in a manner that ensures free and open competition. Because of the large number of samples that need to be analyzed and the wide variety of analytes that were of interest to the Superfund program, a two-component system was established. In the routine services component, the Agency determined that a relatively small menu of selected analytical techniques could be used to analyze the vast majority of the soil and water samples that formed the bulk of the samples that the program would have to be analyzed. Given the nature of the government procurement process and the need of the potential bidders for clearly defined requirements, the CLP program selected a number of analytical techniques and codified the techniques into rigidly defined methods. In addition, to ensure the utility of the resulting analytical data in any future legal action, detailed reporting and record keeping requirements were placed on participating laboratories. A fundamental construct of the CLP was the concept of laboratory interchangeability. For each type of analysis that was needed, identical contracts were awarded to several laboratories. As a sample was collected by one of the many sampling teams, a sample management office distributed samples with an eye toward evening out the workload in the various laboratories. Samples from the same site might, in fact, end up being sent to several different laboratories for analysis. The rigorous specification of how the laboratory was to conduct the analysis, which was inherent in the CLP methods and contracting process, ensured uniformity of results.

The reference method or technology-based approach came to be adopted for many EPA and state regulatory programs because it offered the Agency, the states, local regulatory agencies, the regulatory community, and the laboratory community a number of advantages.

The technology-based approach eased the burden on federal and state permitting staffs in several ways. By limiting the universe of potential methods to those that have been

evaluated and approved by the national program, it simplifies the selection of appropriate testing methods. By having national program offices specify the applications for which a method was appropriate, it eliminates the need for the local permit issuing staffs to assess the suitability of proposed methods for each facility. In addition to reducing the level of expertise and experience needed by the regional and state personnel involved in the permitting and enforcement of permits and regulations, by issuing and requiring the use of detailed, relatively prescriptive monitoring methods it makes it possible for the laboratory community to use less experienced, less well-trained analysts in carrying out the analyses. Finally, from the viewpoint of the regulated community, the technology-based approach is much easier and less expertise intensive with respect to identifying appropriate testing methods, convincing regulatory agencies of the appropriateness and scientific validity of proposed compliance methods, and contracting for and overseeing outside analytical services.

In assessing the efficiency of current regulations and permits and the desirability or need for the Agency to make changes in regulatory programs trend data is critical. In assessing the data on either a facility-specific, industry-specific, or area-specific basis, the issue of data comparability looms large. The fewer the methods that are employed in conducting the monitoring, the more rigorously defined and specified the analytical procedures that are used; and the more complete and consistent are the quality control and documentation procedures that are employed, the easier it is to compare and evaluate the monitoring data and to determine trends.

Just as the technology-based approach eases the process that a regulated entity needs to go through to select an appropriate outside laboratory, the use of uniform, detailed, measurement methods and quality control procedures and requirements simplifies the task of the federal and state inspectors in determining compliance with regulatory and permit requirements. It is much easier to determine if an analytical method was performed according to a specified procedure than it is to determine if the data meets a set of data quality objectives.

As mentioned earlier, the Superfund Contract Laboratory Program is basically a mechanism for the procurement of a large volume of relatively routine analytical services. In order for the laboratory community to accurately bid on such services, for EPA to be able to compare bids, and for EPA to be able to maintain a system of interchangeable suppliers a program with rigorously defined, consistently employed, and consistently performed analytical methods was deemed to be essential. A technology-based analytical methods program was selected when the program was initiated. The rigorousness of the approach was an advantage to the other federal agencies and the private sector organizations that were involved in contaminated site remediation. These organizations were able to use the EPA methods and procedures in implementing their own laboratory services procurement programs. A side benefit of the CLP adoption of the technology-based approach was the cost savings that resulted. These savings were due to the fact that the laboratories were able to redesign their internal procedures and dedicate instruments and staff to conducting large numbers of a particular type of analysis using the same steps and instrument conditions for all samples without regard to client or source. This resulted in a tremendous decrease in per sample analytical costs for analyses such as gas chromatography/mass spectrometry, atomic absorption spectroscopy, inductively coupled plasma atomic absorption spectroscopy, and high performance liquid chromatography.

In addition to the savings inherent in using fewer analytical methods, the higher volume per method encouraged and resulted in the automation of some more commonly used methods.

IV.1.2.2. Performance-based measurement system approach

While, as just shown, the technology-based approach to regulatory monitoring specification offered many benefits, it also presented a number of serious disadvantages. These included: serving as a road block to the development and use of new monitoring technologies and often requiring the use by the regulated and enforcement communities of less efficient methods and approaches. Therefore, in addition to increasing the costs to the regulated and regulatory communities by promoting use of older, less efficient technologies, the technology-based approach serves as a major barrier to innovation. It should be pointed out that because of these disadvantages, the aforementioned CLP program has been moving away from the prescriptive, reference method approach. At this time, a significant percentage of the CLP work is done under a system whereby each user of analytical services specifies project-specific method requirements. This gives the laboratory greater flexibility in selecting the most appropriate method for a given situation.

EPA has initiated a number of complementary efforts to maintain the benefits of the technology-based approach while giving the monitoring community the flexibility it needs to improve the quality of the monitoring while, at the same time, lowering the cost of the required data gathering. These efforts include:

- streamlining EPA's various methods approval processes,
- integrating methods across programs,
- changing from a technology- to a performance-based system of monitoring specification,
- the Agency's XL Program (Excellence and Leadership) that offers the regulated community the opportunity to employ innovative approaches which improve the environment and reduce compliance costs,
- assisting the private sector in obtaining impartial evaluations of new monitoring technology and in promoting the results of the evaluations, and
- increasing the level of support provided to academia and other non-profit organizations involved in developing innovative monitoring technologies.

Under EPA's current regulatory monitoring structure, review and approval of alternative or new monitoring technologies and methods are conducted by the various regulatory programs. For example, the Office of Air and Radiation is responsible for the methods used to comply with the Clean Air Act, the Office of Water with the Clean Water Act and the Safe Drinking Water Act, and the Office of Solid Waste with the Resource Conservation and Recovery Act. Each office has developed its own procedures for obtaining approval for a new technology and its own mechanism for making new methods available to the public. Beginning in 1994 with an effort by the Office of Solid Waste, the Agency began to remove regulatory requirements to employ specific methods when complying with Agency monitoring requirements and to streamline its methods approval processes in order to speed up the introduction of new measurement technologies (US EPA, 2000). The Office of Solid Waste effort resulted in a proposed rulemaking in 2002

(US EPA, 2002). On a parallel path, the Office of Water proposed to streamline its methods approval process (US EPA, 1995). The goals of the streamlining effort included:

1. decreasing the time and Agency resources required to approve new analytical techniques and improved methods,
2. provide for an increase in the number of methods that are approved for use each year,
3. increase participation of outside organizations in the method development process, and
4. improve overall program quality.

At the same time as EPA is moving to implement the performance approach (Crumbling, 2000; US EPA, 2000), the National Environmental Laboratory Accreditation Program (NELAC), the standards setting body for the United States' federal–state–tribal national environmental laboratory accreditation program, is working to change its accreditation standards to adopt the performance approach (NELAC, 2002).

However, success of the new approach will not be easy. A change of this magnitude will require major efforts by all members of the environmental community. Two areas where these efforts will be especially important are in education and in promoting risk taking.

A whole generation has grown up believing that the route to quality data is to follow methods and procedures issued by government and other standards setting organizations. Analysts have put aside the scientist's philosophy of critically examining the validity of suggested methods or approaches in light of the properties of the samples being tested. The education and re-education process will have to address this problem. It will have to train the analytical community in how to select the most appropriate, most cost-effective approach to obtaining the information needed to solve the problem while meeting the data quality objectives. Similarly, those members of the environmental community overseeing the studies need to learn how to evaluate analytical data quality against the data quality objectives rather than to look at whether a given method was used or whether all the steps of the published procedure were followed.

A second part of the problem deals with breaking down the aversion to risk that has been built into the system. How can the engineers who develop sampling and analysis plans for the regulated community and the permit officials who have to approve the plans be given an incentive to take risks? Trying new approaches will help the regulated community save money and offers government the potential for better environmental decision making. However, trying new and untried approaches presents risk. New methods and testing strategies do not always work out. Mistakes have negative time and cost consequences. Since in the long run, taking a creative approach to monitoring will save the regulated community and the public money and improve the quality of the decision making, clients must be understanding when a study has to be redone and government officials must be understanding when monitoring schemes are found not to yield the needed data.

In conclusion, the performance-based approach will help to:

1. streamline the adoption and use of new analytical technologies,
2. improve the comparability of data obtained from different studies,
3. help assure that methods used for gathering data actually work in the particular samples being analyzed,

4. simplify operations for laboratories analyzing similar types of samples but for different regulatory programs,
5. encourage innovation in environmental monitoring technology, and
6. result in more reliable, faster, and cheaper data monitoring.

IV.1.3. Field monitoring technology

While the changes taking place in monitoring policy are important, the changes taking place on the technology side will have no less of an impact. In this chapter, we will briefly look at one of the more active areas of environmental monitoring research – on-site analysis. The area of "field" or "on-site" analysis covers a number of areas. For purposes of this discussion, we can categorize the technology into three areas. These are: sample collection tools, measurement methods, and data communication. In this discussion, the author will touch on some of the more important developments in the areas of sampling and measurement methods.

Obtaining accurate data on subsurface soil or water contamination has long posed a difficult challenge to environmental scientists. Obtaining samples without contaminating or otherwise adversely affecting the soil or ground water is exceedingly difficult using conventional techniques. Several approaches to solving this problem have been under development for a number of years. These include development of non-drilling methods for obtaining subsurface samples and development of *in situ* techniques for detecting and measuring soil and water contamination. In the past few years these efforts have borne fruit with the development and commercialization of the cone penetrometer, and the adoption of remote sensors that can be used to identify and measure subsurface contaminants.

The principle behind the cone penetrometer is relatively simple. A truck mounted, hollow lance equipped with a point that can be disengaged or opened, while in the ground, is pushed into the ground reaching depths of 30 m or more depending on soil characteristics. In order to be able to exert the forces needed to push the cone deeply into the ground, the trucks are normally quite heavy (40,000 kg) and can exert greater than 27,000 kg of hydraulic pushing force on a 30–50 mm diameter penetrating lance. The cone penetrometer offers a number of advantages. These include an ability to quickly locate areas of contamination at a site since driving the lance takes only minutes. It gives the scientist the ability to easily collect samples of soil, ground water, or soil gas at any desired depth. And the application with the most potential is its ability to make *in situ* measurements of the soil water or gas. The unit can serve to place one or more sensors at specific points in the subsurface to yield a profile of the soil and ground water contamination.

This last advantage of the cone penetrometer has not yet been fully realized. Among the sensors that have been successfully evaluated and are currently being used in the United States for such *in situ* analysis are optical sensors based on fluorescence and Raman spectroscopy (for location of chlorinated hydrocarbons and other non-aqueous phase liquids), chlorinated compound specific soil gas sensors, electrochemical sensors for detecting metals and other conducting species, as well as conventional geophysical logging devices that can be used to map the subsurface to allow a more accurate assessment of ground water flow pathways.

Two factors have been responsible for the rapid advances that field monitoring has seen take place in the last decade. These are:

1. the development of new measurement techniques or, in some cases, the adoption to environmental problems of techniques that have been used for other applications;
2. the miniaturization and ruggedization of conventional instrumentation to permit its use in a field setting.

One of the more important of the new technologies that have been made available to the environmental analyst have been the immunochemical-based methods. Also contributing important new tools to the analyst's toolbox has been the development of field screening kits, using conventional chemistries, for important environmental pollutants such as polychlorinated biphenyls and other chlorinated organic compounds that are based on conventional chemistry, and the development of solid state chemical sensors.

Immunochemical-based assays have gained widespread acceptance in the medical testing field. They have been found to accurately determine whether or not a woman is pregnant, and can be used with confidence to rapidly identify a number of illnesses. In the later part of the 1980s, a number of researchers began to adapt this technology to solving environmental problems. Among the first of the assays to be made available were kits to determine polychlorinated biphenyl, pentachlorophenol, and polyaromatic hydrocarbon contamination in water and soil. In addition, kits to identify the presence of unacceptable levels of residue pesticide on food and plants were developed.

Immunochemical-based assays offer several important advantages. They are fast, yielding results generally within 30 min. They are sensitive and can determine if contamination is present at the ppm and ppb level. They are selective and generally exhibit a relatively low level of both positive and negative interferences. More importantly, interferences are generally of a positive nature since compounds with a structure similar to that of the target analyte often exhibit a cross-reactivity. It is this relative freedom from negative interference and positive bias that can make these assays attractive to the environmental community. Because of this positive bias, the user has a high degree of confidence that, if the assay indicates an absence of contamination at the indicated level of sensitivity, the area is in fact clean. False positive results are generally of less concern since they can generally be eliminated by subjecting the suspected samples to conventional laboratory analysis.

The chemical and immunochemical-based assays have three primary applications in environmental testing. The largest of these is in site characterization. When contamination is suspected, the test kits can be used to rapidly determine if contamination is present at a level of concern. If it is known that contamination has occurred, then the tests offer a means of determining the extent of contamination in a manner that saves both time and money compared to conventional sampling and laboratory analysis. Using these tests, one can quickly and inexpensively examine areas of suspected contamination and separate the areas that are in need of remediation from those that are clean. The third application is that of process control. During, for example, a site remediation where soil is being removed or a cleanup process is being employed to remove contamination, one often needs to monitor the level of residual contamination to determine if additional soil needs to be removed, or if the treatment process is no longer effective. Here use of field screening tests permits one to answer these questions on a real-time basis. Using the field tests

eliminates delaying the cleanup while awaiting the laboratory results, eliminates lost productivity while the crew waits to find out if additional soil needs to be excavated, and eliminates the expenses of having to reactivate treatment beds or employ redundant processes in order to prevent unexpected exceedances of treatment targets.

The ability to drastically reduce the size and power requirements of conventional analytical instrumentation has led to some of the largest advances in recent years. For example, the development of portable X-ray fluorescence (XRF) instruments brought the benefits that immunoassays gave for organic contaminants to the heavy metals. Use of XRF has been of inestimable value to both the lead in paint cleanup program and to the site remediation efforts. Similarly, the organic arena has seen the commercialization of hand-held organic compound vapor detectors based on the principles of gas chromatography; of field portable gas chromatographs employing both conventional detectors and even mass spectrometers; a wide variety of infrared spectrometers both long path length instruments for air monitoring and conventional Fourier transform infrared (FT-IR) instruments. We have even seen the introduction of portable time of flight mass spectrometers designed to determine the presence of specific, highly toxic organic compounds. Some of these new instruments were originally developed for military applications and have recently been adapted to environmental applications.

IV.1.4. Future trends

The environmental monitoring arena continues to change. New technology continues to be developed that promises both to improve our current ways of monitoring and to open up totally new approaches.

The rapid advances in microminiaturization continue to shrink analytical instrumentation with no end in sight. Research is underway that promises order-of-magnitude reductions in the size of today's instruments. Having a wider variety of instruments available for field analysis will continue and possibly accelerate the trend to on-site analysis. In addition, it opens up the possibility of, for the first time, obtaining real-time information on personal exposure to toxic chemicals. Analytical instruments that can be worn by individuals at home and at work can significantly improve the quality of the exposure information used in assessing risk, which are the basis for regulatory standards.

Remote sensing is another area receiving a great deal of attention on the part of the Agency and the research community. Environmental remote sensing can be subdivided into three major categories based on the distance between the sensor and the area being monitored.

The first category, satellite-based measurement systems are primarily employed to study the Earth and its changing environment. Observations of the oceans, atmosphere, land, and forests enable the study of environmental changes and to distinguish between natural changes and human activity-induced changes. Multispectral and hyperspectral land imaging systems of high and moderate spatial resolution, passive microwave imaging systems, and multispectral thermal imagery are areas of current research interest. Advances in this arena lead to improvements in areas such as land and water management, urban planning, and environmental monitoring.

The second major category of remote sensing encompasses aircraft-borne instruments. Moving the instruments closer to the Earth permits one to more accurately monitor both the atmosphere and the land. Advances in light detection and ranging (LIDAR) systems will permit better monitoring of important atmospheric species such as ozone, carbon monoxide, water vapor, hydrocarbons, and nitrous oxide as well as meteorological parameters such as atmospheric density, pressure, and temperature. Research is currently being sponsored to enable or to significantly expand the capabilities of LIDAR systems to the near ultraviolet through infrared regions of the spectra. In addition, advancing the capabilities of the optical techniques, research to develop radar instruments which are capable of sub-surface probing over soil, wetlands, or water to detect and profile the presence of subsurface minerals, water, and pollutants is being pursued.

The third, but by no means the least important, area is that of ground-based instruments. Here techniques such as long path length FT-IR can serve as valuable tools for monitoring facility and area emissions and for ensuring the safety of site remediation personnel. Advances in this area will be important to Agency efforts to take a more ecosystem and facility wide approach to controlling the release of hazardous pollutants. It will expand our ability to continuously monitor releases and to more accurately assess potential risk. It will also give the facility operator the tools and the information needed to more efficiently and effectively operate the facility.

IV.1.5. Conclusion

In conclusion, the author believes that the next decade will bring major changes to environmental monitoring. The laboratory community will split into two types of organizations. One type of laboratory will specialize in using EPA and other well-accepted, standardized methods to analyze well-characterized matrices (e.g. drinking water, surface waters, routine wastewater effluents, soils). These laboratories will be highly automated with rigid quality control/quality assurance systems in order to offer quality data and low price (similar to today's medical testing laboratory industry). The second type of laboratory organization will deal with non-routine monitoring problems. They will offer the client tailored approaches to monitoring problems. These organizations will use a mixture of conventional laboratory analysis, field screening, and field analysis tailored to the individual clients needs and designed to reduce data gathering costs while ensuring adherence to required data quality objectives.

In any case, the trend toward moving the analysis from the laboratory to the field will not only continue but will also accelerate. We can expect to see less laboratory analyses, more field analysis, more continuous analysis, and more remote sensing.

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IV.2
Identification of unknown solid waste

Tung-ho Chen

IV.2.1. Introduction

In the wake of the terrorist incidents of the World Trade Center Towers and the Pentagon on September 11, 2001 and the recent world-wide anthrax attacks, no place in the entire world is immune to the terrorist attack using chemical, biological, nuclear and other unconventional weapons. This is supported by the newspaper report that the materials left in a compound used by Osama bin Laden's group may have been trying to develop chemical arms and other unconventional weapons. Foul-smelling liquids and charred papers covered with chemical formulas littered a makeshift laboratory in one building used by Al Qaeda (Anonymous, 2001).

The methodologies discussed in this chapter should be directly applicable to the identification of unknown chemical weapons and their residues, both from past wars and armament production, and from the present and future, potentially even more dangerous terrorist activities we have to deal with.

The most important step in the management of unknown solid wastes is the identification of the unknowns. In the course of our solid waste management in recent years, we have encountered numerous unknowns in various containers with illegible labels or without labels in various buildings at US Army Tank-automotive and Armaments Command Armament Research, Development and Engineering Center (TACOM-ARDEC). These unknowns need to be identified prior to their reuse or disposal.

Careful execution of various phases of the analyses of unknowns, which include sampling, sample preparation, identification, confirmation and quantification, is essential to avoid injuries to laboratory personnel and equipment damage. Furthermore, various analytical methodologies need to be carefully selected and applied in a proper sequence to achieve the analysis in an efficient manner. We have therefore developed an analytical scheme that has been utilized in the last decade (Chen et al., 1990a,b, 1991) in the identification of various unknown wastes (Fig. IV.2.1). The key to this performance-based scheme is the categorization of unknowns into energetic and non-energetic materials followed by volatility categorization, which enables proper choice and sequence of instrumentations to be used in the identification. The objective of this chapter is to describe this scheme and present examples of the applications of the scheme developed to the identification and quantification of militarily unique wastes.

Briefly, the scheme consists of initially identifying liquid and solid unknowns as energetic or non-energetic compounds using spot tests. If the tests for energetic materials are positive, their presence is confirmed by infrared spectrometry (IR) or mass spectrometry (MS) or other techniques as needed. Electron spectroscopy for chemical analysis (ESCA) experiments

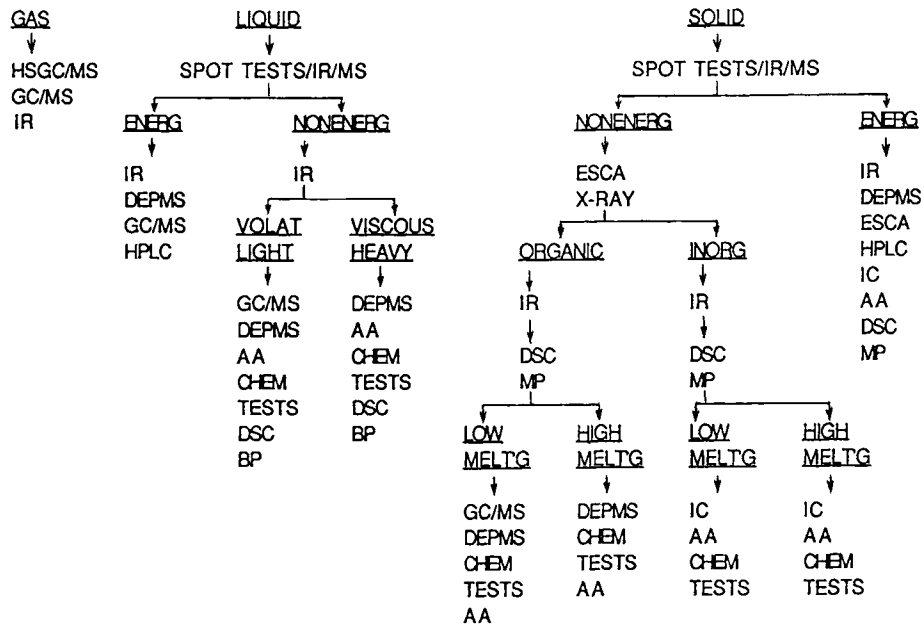


Figure IV.2.1. Analytical scheme for the identification of unknown wastes.

is performed on non-hygroscopic, non-volatile solids for their qualitative elemental composition determination. This is usually followed by X-ray diffraction analysis (XRD) to identify the molecular moieties. XRD is then followed by IR. Very often, the unknown could be identified at this stage. The melting point and boiling point are used as supporting evidence for sample identification as well as for sample selection in gas chromatography/mass spectrometry (GC/MS) and MS analyses. Viscous liquids, high boiling and high melting solids are analyzed by direct exposure mass spectrometry (DEPMS), an excellent technique for the analysis of thermally labile, non-volatile compounds. Headspace gas chromatography/mass spectrometry (HSGC/MS) is used for identifying gaseous specimens and gases liberated from solid samples as will be discussed later.

IV.2.2. Experimental

IV.2.2.1. DEPMS experiment

The specimen was dissolved in acetone or, in other solvent as required, at approximately 1 μg/μl concentration level. About 3–4 μl solutions were deposited, in 1 μl aliquots, on the loop of the direct exposure probe (DEP) heating wire.

The solvent was then allowed to evaporate and the DEP was inserted into the ion source of a Finnigan OWA 1020B Mass Spectrometer. The sample was heated at 10 mA/s to 1 A in the presence of about 3–5 Torr methane gas. The DEPMS experiment, in the positive

ion chemical ionization (PICI) mode using methane as the reagent gas, was completed in approximately 100 s.

In the case of the Unknown 854, labeled as "green pigment" which does not dissolve in any suitable solvent, a small amount of specimen was shaken with a few drops of deionized water to form a suspension. A micro-syringe needle is then inserted into the suspension and with careful manipulation, a small particle of the suspended specimen could be placed on the needle utilizing the surface tension of water. The sample is next carefully transferred to the loop of the DEP heating wire. Upon evaporation of water, the sample is very carefully introduced into the interlock section of the probe and pumped very slowly, especially at the beginning to avoid loss of sample prior to introducing the specimen into the ion source of the mass spectrometer. This technique does not work particularly well and several tries may be needed. The problem is loss of sample during transfer to the heating wire and pumping in the sample interlock section.

IV.2.2.2. Other instruments

These were operated in the usual manner.

IV.2.3. Results and discussion

In the following, the identification of some unknowns selected from our recent work will be described to demonstrate the usefulness of the analytical scheme developed. It should be noted that the background information and knowledge on the possible identity of the specimen could be utilized to choose appropriate analytical strategy for rapid identification of the unknown. It may be further noted that other techniques not listed in the general scheme are utilized as needed. Flexibility in choosing analytical strategies and use of proper methodologies are essential to successful unknown identification.

IV.2.3.1. Unlabeled glass reagent bottles filled with brown fumes and white solid mass

The stoppers of the bottles were frozen and could not be loosened by the usual laboratory techniques for opening such bottles. They had to be broken very carefully behind a barricade and inside a plastic bucket containing crushed ice to quench any possible

acetone and a few drops of the solution were deposited on the sodium chloride IR window. The solvent was allowed to evaporate to form a thin layer of the specimen. This technique will prevent any possible incident that may occur during any laboratory operations involving impact or grinding such as the preparation of KBr pellets for IR studies. From the IR spectra of the prepared specimens, the samples in question were identified to be pure 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) (Chen et al., 1991).

IV.2.3.3. Unknown explosive compositions involved in the suspected fraud investigation

This case was important on two accounts: (1) the fraud will affect the performance of a military item that is in extensive use today and (2) the fraud could affect the sensitivity of the item adversely. Due to possible safety hazards involved in handling the unknowns, this operation was conducted in a room with its relative humidity controlled at 50%. KBr pellets were prepared very carefully for IR analysis of suspected specimens.

Again, the IR proved that most suspected specimens consisted of a mixture of pentaerythritol teranitrate (PETN) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), rather than the pure HMX as specified (Chen et al., 1991).

PETN exhibits five absorption bands distinct from HMX, which enables direct identification of PETN in the mixture of HMX and PETN. The doublet at 1001 and 1034 cm^{-1} is particularly useful in this regard.

IV.2.3.4. Unknown odor from a new composition

The workers processing a new explosive composition at an ammunition plant noticed an odor and became concerned about the possible occupational safety hazards involved in the processing of this new composition.

For rapid identification of this unknown, the method of choice was *in situ* generation of this odor and subsequent analysis of the sample by HSGC/MS (see Figure IV.2.1 – the analytical scheme). This seemingly straightforward experiment turned out to be fairly difficult as the amount of gaseous sample generated was found to be too small for its positive identification. This problem was solved by generating the gas sample at a higher temperature, i.e. 100°C.

The mass spectrum was identified to be that of ethyl acetate, the solvent used in the manufacture of the composition. Ethyl acetate is a relatively safe compound with an oral LD50 for rats of 11 g/kg. Furthermore, the new composition contained only a very small amount of ethyl acetate. Therefore, it was concluded that the odor in question does not constitute any occupational safety hazards at the ammunition plant (Chen et al., 1991).

IV.2.3.5. Unknown residues from diatomaceous earth and granular carbon columns

TACOM-ARDEC has a small-scale facility for demilitarization of obsolete munitions. This facility uses diatomaceous earth and granular carbon columns for removing energetic and related materials from the explosive contaminated wastewater generated at this site.

As part of this program, the unknown energetic materials adsorbed on these columns were analyzed (Chen et al., 1994).

The initial spot tests for screening the presence of explosives and propellants on the acetone extracts of the diatomaceous earth and granular carbon were negative. It is to be noted that in the demilitarization plant, the wastewater passes through the diatomaceous earth column first, then the granular carbon column before being discharged. The degree of the contamination of the adsorption material is, therefore, expected to be greater in the first than in the second column. Indeed, this has been found to be the case as will be shown later.

Subsequent to the initial spot tests, which established that the adsorption materials were not contaminated to any significant degree, the extractions were repeated using a larger amount of sample and a more thorough extraction procedure. In this case, only the diatomaceous earth column material exhibited a positive reaction for nitramine.

Since the spot tests are not very reliable due to lack of adequate selectivity, the positive response needs to be confirmed by fingerprinting techniques, most commonly MS and IR. Our method of choice is DEPMS, which enabled us to identify or confirm a large number of labile and non-volatile unknown compounds in the past (Chen and Campbell, 1989, 1993; Chen et al., 1990a; Chen and White, 1994).

Figures IV.2.2 and IV.2.3 show the DEPMS spectra of the adsorption materials from the diatomaceous earth and granular carbon columns, respectively. The former established

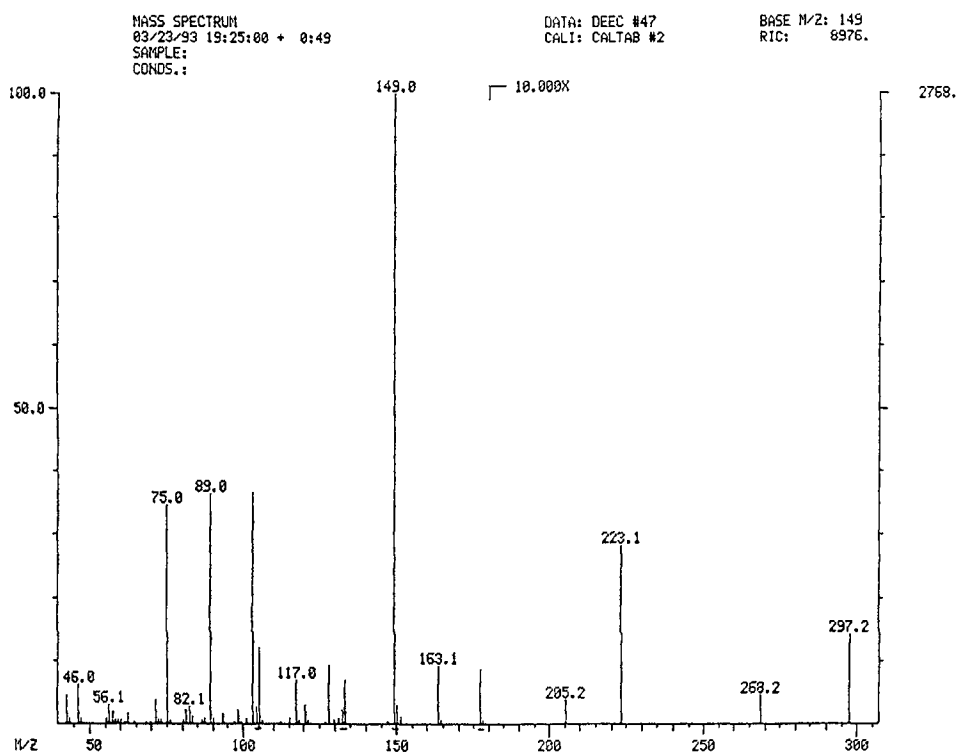


Figure IV.2.2. DEMPS spectrum of the unknown from the diatomaceous earth sample.

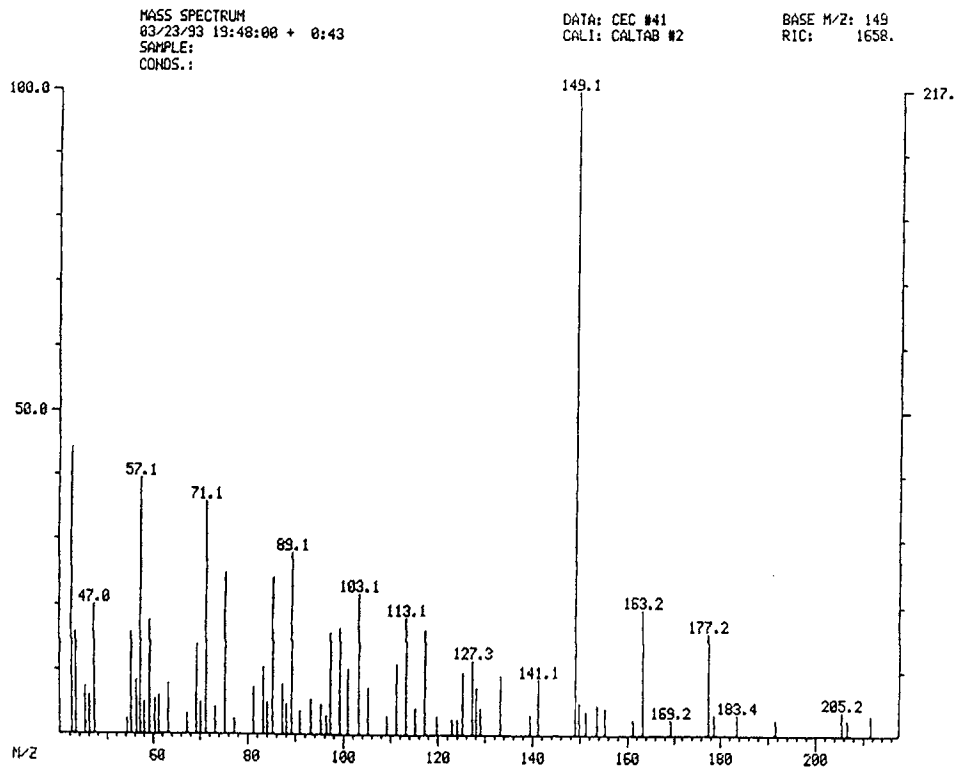


Figure IV.2.3. DEMPS spectrum of the unknown from the granular carbon sample.

the presence of RDX or HMX or both from the diagnostic ions and fragmentation ions discussed in our past work (Chen and Campbell, 1989, 1993) while the latter exhibits the presence of possibly a trace of RDX based on the presence of $[(CH_2NNO_2)_2 + H]^+$, $m/z = 149$ and $[(CH_2NNO_2) + H]^+$, $m/z = 75$. The spectrum in Figure IV.2.3 has low ion intensities and it appears to be contaminated with hydrocarbon(s) as indicated by peaks showing repeated (CH_2) loss patterns in the whole spectrum range.

Figures IV.2.4 and IV.2.5 show the DEPMS spectra of RDX and HMX, respectively. The spectra are quite similar. However, there is one striking difference between the two, i.e. the intensity ratio of the $m/z = 103$ and 105 ions, the ratios being about 3.5 for RDX and about 0.5 for HMX. Based on this, it is concluded that the diatomaceous earth sample is contaminated with mostly RDX and possibly with a small amount of HMX. This is in line with the fact that the RDX manufactured in the US contains some HMX.

Figure IV.2.6 exhibits the HPLC chromatogram of the acetonitrile extract of the diatomaceous earth sample. HMX and RDX appear at the retention times of about 2.02 and 2.49 min, respectively. The unidentified peaks include those with retention times at about 1.02, 4.89 and 5.95 min. The HPLC chromatogram of the acetonitrile extract of the granular carbon sample indicates the presence of trace quantities of HMX and RDX. The amounts of RDX and HMX, in wt%, were determined by HPLC to be 0.65 ± 0.03

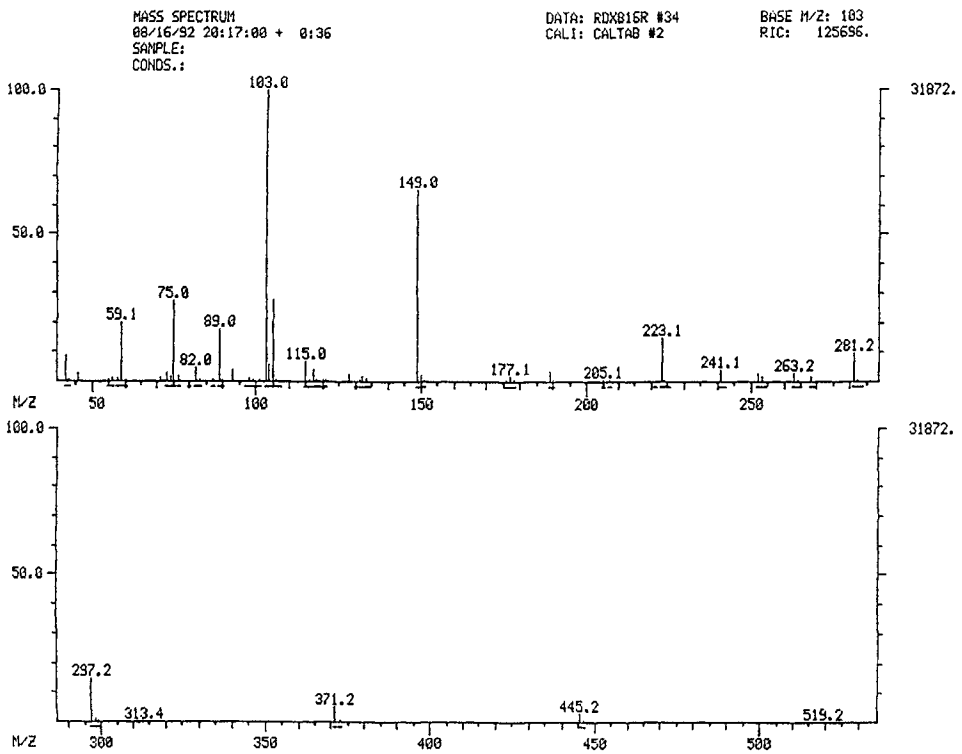


Figure IV.2.4. DEMPS spectrum of RDX.

and 0.08 ± 0.02 for the diatomaceous earth sample and 0.03 ± 0.01 and 0.01 ± 0.00 for the granular carbon sample, respectively. Thus, the adsorption column materials were found to be contaminated with less than 1% energetic materials.

IV.2.3.6. Unknown desert storm sample

The slightly brownish sample was collected after the Persian Gulf War and sent to a location where suspected chemical and biological warfare agents can be safely handled.

In the initial screening for the energetic materials, the spot tests were conducted with great care inside a glove box under a slight vacuum to insure safe testing environment. The results tentatively identified the unknown to be trinitrotoluene. The sample was then shipped to ARDEC for confirmation. IR and DEPMS showed the unknown to be 2,4,6-TNT. Supporting evidences were obtained by HPLC and DSC by matching of the retention time and matching of the melting and decomposition temperatures of the sample with those of the standard 2,4,6-TNT. HPLC also showed the sample to be quite pure (Chen, 1992).

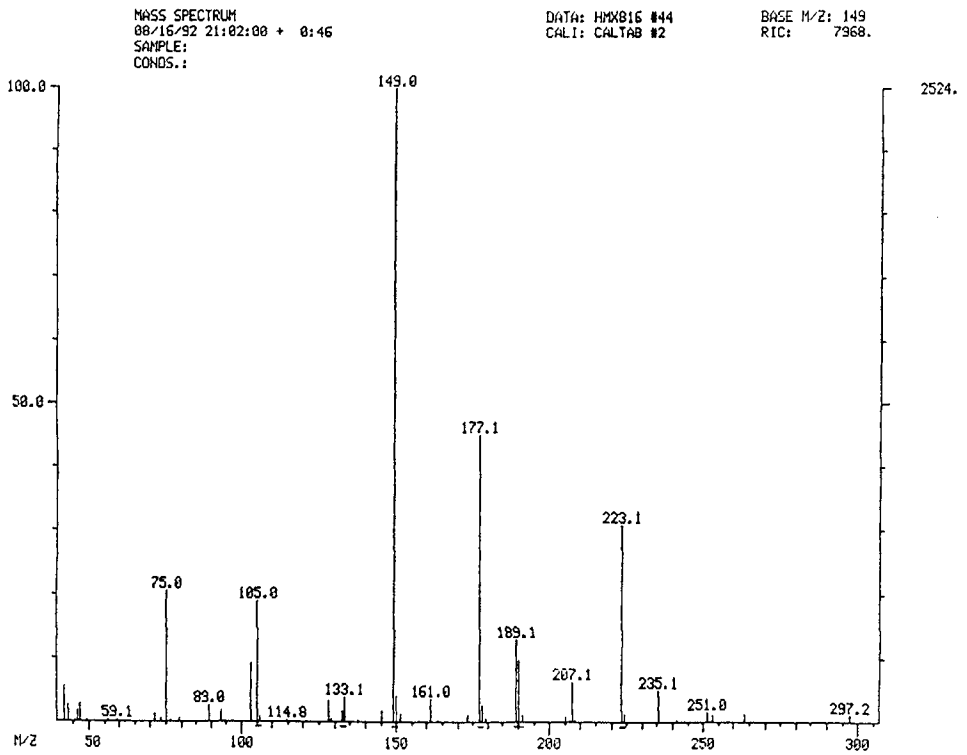


Figure IV.2.5. DEMPS spectrum of HMX.

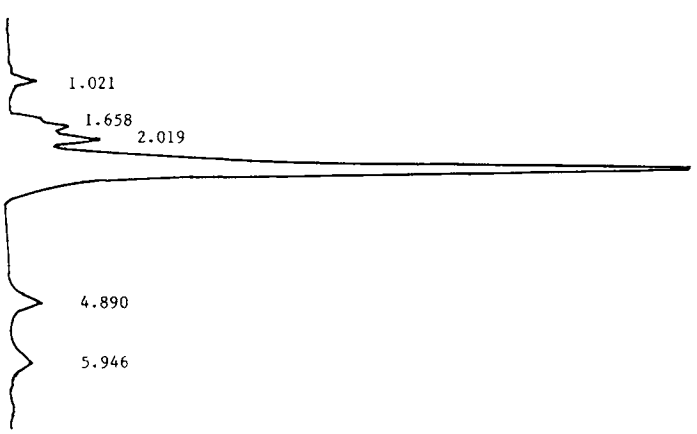


Figure IV.2.6. HPLC spectrum of the unknown from the diatomaceous earth sample.

IV.2.3.7. Explosive residues from explosive-contaminated wastewater filters

Samples of the explosive-contaminated granulated carbon filters and the fiber filters were sent to TACOM-ARDEC from a depot activity that was treating the wastewaters generated by the Army Ammunition Plants. In order to meet the regulations and the deadlines of the environmental regulatory agencies, the depot had to dispose of the accumulated waste filters in a short period. This required the identification and quantification of residues in the shortest time possible. Since the identities of major explosive contaminants in the wastewaters were known, the initial screening tests and other fingerprinting techniques shown in the analytical scheme were not needed in this particular case. Instead, a reversed-phase HPLC was used to quantify the explosive contents of the fibers following the sample extraction with acetonitrile.

The granulated carbon filters were found to contain about 9 wt% each of RDX and 2,4,6-TNT and 1 wt% of HMX apparently derived from the Military Grade RDX. The carbon filters also contained two unidentified unknowns in small quantities amounting to a total integrated area of about 4%. The fiber filters contained essentially only 2,4,6-TNT. They were heavily contaminated with 2,4,6,-TNT in the central areas amounting to as much as 50 wt% in one case. Thus, both carbon and fiber filters were heavily contaminated with explosives. On the average, the carbon filters contained a total of about 22 wt% of RDX and 2,4,6-TNT, while the fiber filters contained about 17 wt% 2,4,6-TNT (Chen, 1992).

IV.2.3.8. Unknown 854

In contrast to previous examples, this unknown, labeled as "green pigment", required considerably more efforts in its identification (Chen et al., 1990a,b) and confirmation.

The spot tests indicated the specimen to be non-energetic and ESCA showed the presence of chlorine and bromine. However, the XRD of the sample powder did not reveal the identity of the sample. The IR spectrum exhibited no absorptions associated with hydrogens, either alkyl or aromatic. But IR enabled tentative identification of the specimen as copper phthalocyanine complex. The atomic absorption spectrophotometry (AA) confirmed the presence of copper (about 3.5 wt%). It should be pointed out that the sample could not be completely brought into solution during the sample preparation for the AA work by an acid digestion procedure. In fact, the specimen did not dissolve in any solvents we tried to a sufficient degree for use in other analyses requiring the sample in solution. Thus, lack of appropriate solvent prevented the use of nuclear magnetic resonance (NMR) technique.

The initial DEPMS, which has a mass range of only up to 800 Da, provided the structural information of the sample establishing that all hydrogens on all four benzene rings are substituted by chlorine or bromine atoms, in agreement with IR studies. This work enabled the formulation of the structure shown in Figure IV.2.7. This structure was essentially confirmed by the near perfect matching of the IR spectra of the unknown and the commercial Pigment Green 36, 3Y-type with a possible formula of $C_{32}H_4N_8Br_6Cl_6Cu$ (Chen et al., 1990a).

The differences in the spectra can be attributed to the halogen contents, i.e. the unknown contains more bromine atoms than the commercial product.

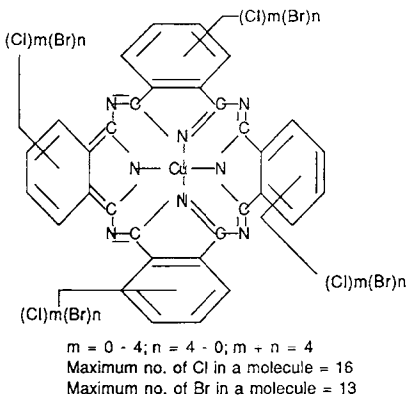
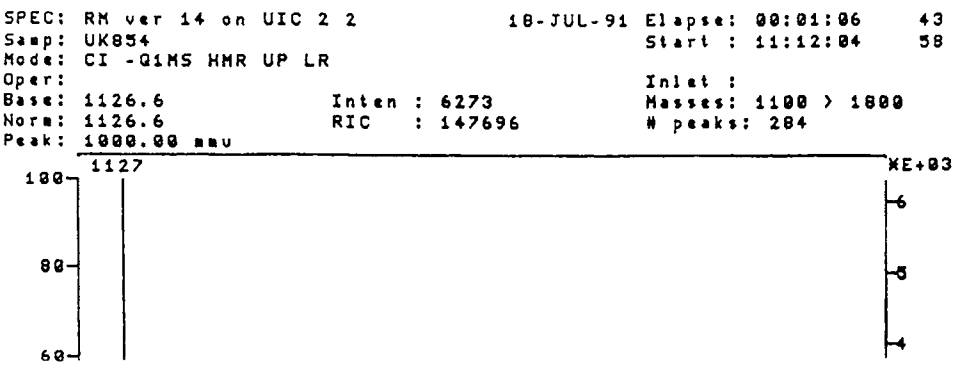


Figure IV.2.7. Structure of Unknown 854.

Subsequently, the DEPMS experiment using an instrument with a mass range of up to 2000 Da confirmed the previous conclusions. Furthermore, as can be seen from the 14 cluster ions in Figure IV.2.8, the specimen was shown to be a mixture of 14 copper phthalocyanine complexes consisting of a completely chlorinated $\{C_{32}N_8(Cl^{35})_{16}Cu^{63}$–$C_{32}N_8(Cl^{37})_{16}Cu^{63}$; M.W. = 1119–1151} complex and 13 complexes with formulas, ranging from $C_{32}N_8(Cl^{35})_{15}Br^{79}Cu^{63}$–$C_{32}N_8(Cl^{37})_{15}Br^{81}Cu^{63}$ (M.W. = 1163–1195) to



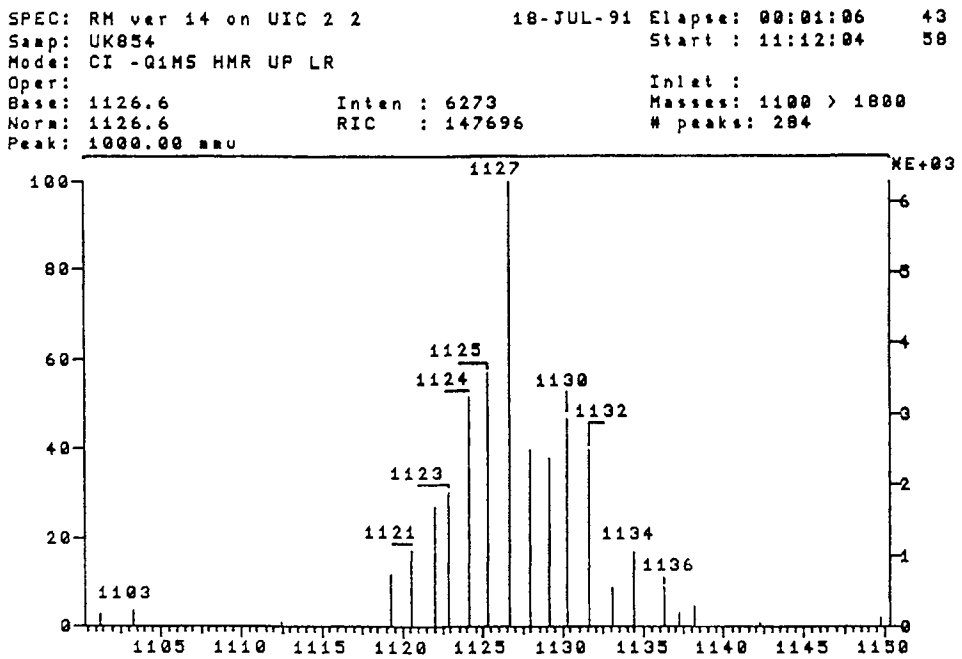


Figure IV.2.9. The expanded DEMPS spectrum of the first cluster ions of Unknown 854.

$C_{32}N_8(Cl^{35})_3(Br^{79})_{13}Cu^{63}$–$C_{32}N_8(Cl^{37})_3(Br^{81})_{13}Cu^{63}$ (M.W. = 1691–1723). The sum of chlorine and bromine atoms in the 13 complexes is 16 and the maximum number of bromine atoms is 13. The only structural feature that still needs to be elucidated is the distribution pattern of halogens in the 13 complexes. Figure IV.2.9 shows the expanded spectrum of the first cluster ions with a computed $(M + H)^+$ ranging from 1120 to 1152 Da (Chen, 1992).

IV.2.3.9. Unknown liquid

This sample is brownish viscous oil with potential application for use as a high temperature lubricant for weapon systems such as guns. We spent considerable effort in the identification, quantification and environmental impact of this material for its potential application (Chen et al., 1998).

The DEPMS spectrum of the unknown (Fig. IV.2.10) exhibited complicated chlorine cluster ion patterns. It may be noted that these ions are protonated ions. This was interpreted to consist of two homologous series of polychlorinated compounds. The overlapping of some chlorine clusters not only made it difficult to interpret the major series but also made it quite difficult to infer the presence of the second less abundant series.

The Fourier transform infrared (FTIR) spectrum of the unknown (Fig. IV.2.11) exhibited the presence of the alkyl group at about 2931 and 2860 cm^{-1}, the ester group at about 1743 cm^{-1} and the dichloro and trichloro carbon radicals at about 1459 and 732 cm^{-1}. Further, the spectrum appears to have a close resemblance to that of the alkyl oxalate ester.

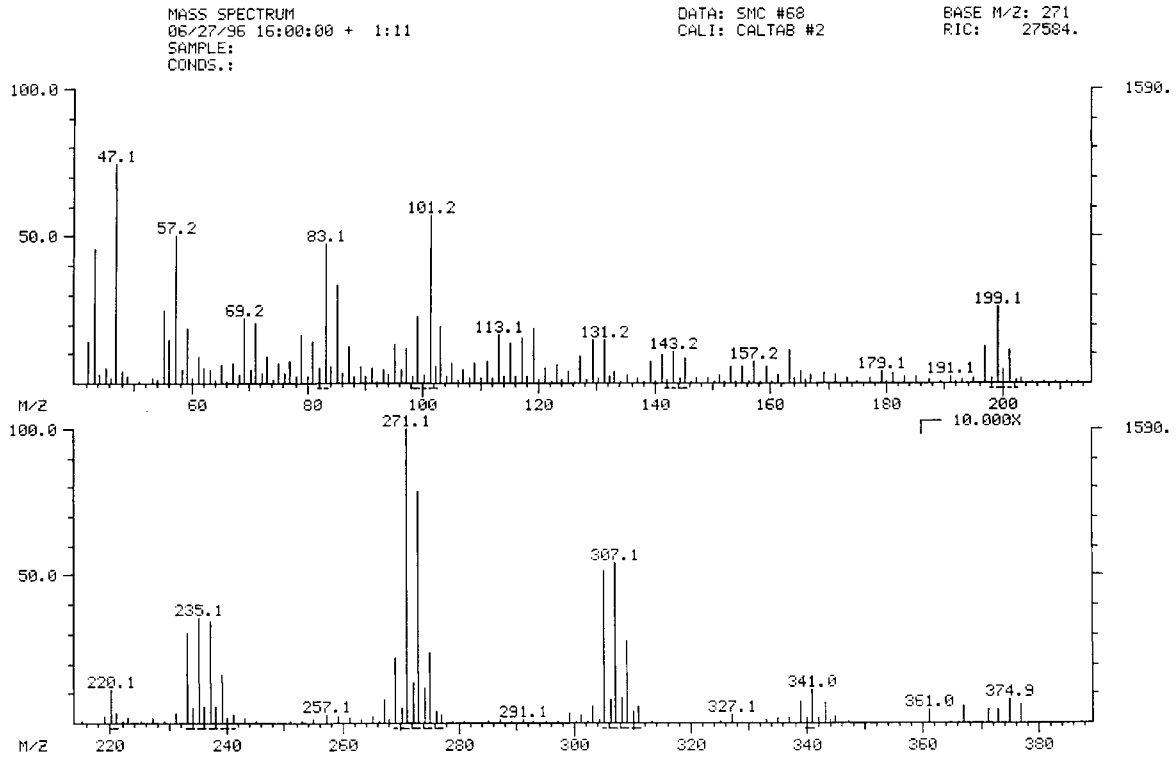


Figure IV.2.10. DEPMS spectrum of the unknown liquid.

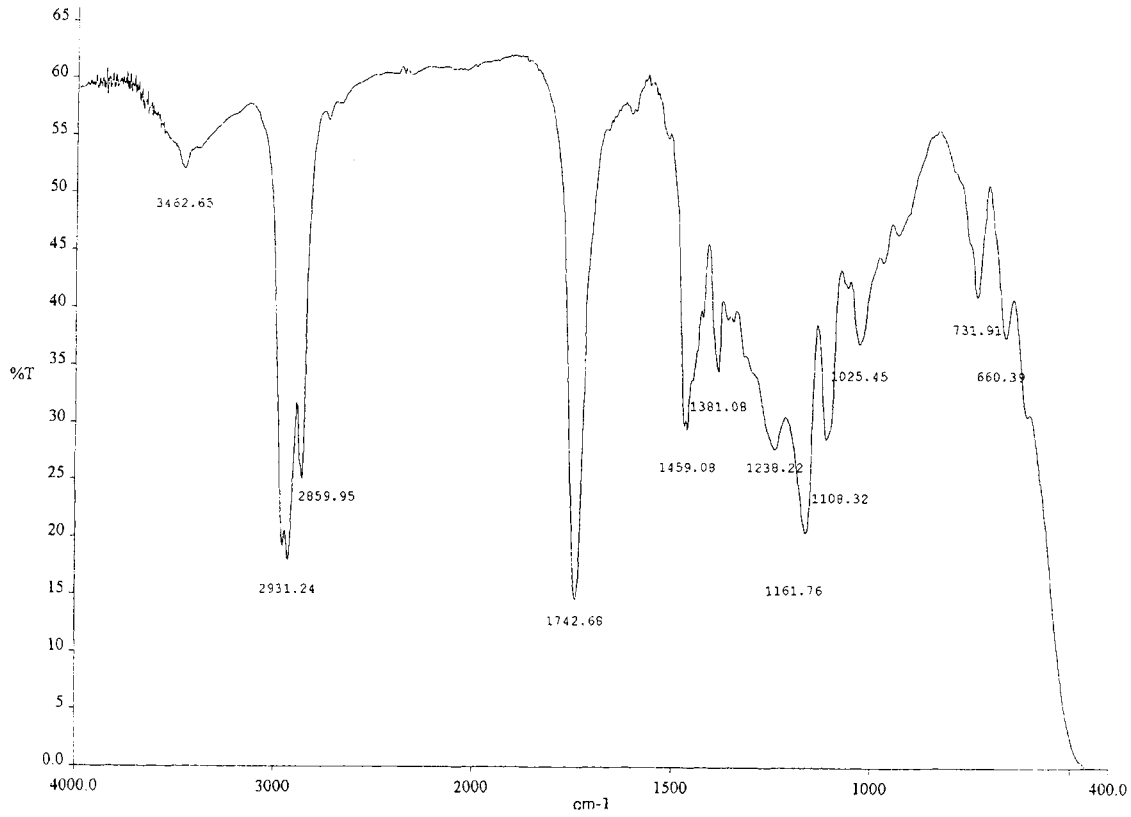


Figure IV.2.11. FTIR spectrum of the unknown liquid.

Incorporating the structural features observed by FTIR, the unknown was inferred to consist of primarily two 5 members each homologous series of polychloroalkyl oxalates and polychlorodihydroxyalkyl oxalates. One series has abundance of approximately two and half times of that of the other. The predominant series consists of, in the decreasing order of abundance, $C_8H_{16}Cl_2(COO)_2$, $C_8H_{15}Cl_3(COO)_2$, $C_8H_{17}Cl(COO)_2$, $C_8H_{14}Cl_4(COO)_2$ and $C_8H_{13}Cl_5(COO)_2$ with the molecular weight of Cl^{35} species ranging from 236 to 372 Da. The intensities of the last cluster ions are very weak. The general formula for this series is $C_8H_{17-13}Cl_{1-5}(COO)_2$. The second less abundant series consists of, in the decreasing order of abundance, $C_3H_4Cl_2(OH)_2(COO)_2$, $C_3H_5Cl(OH)_2(COO)_2$, $C_3H_3Cl_3(OH)_2(COO)_2$, $C_3H_2Cl_4(OH)_2(COO)_2$ and $C_3HCl_5(OH)_2(COO)_2$ with the molecular weight of Cl^{35} species ranging from 198 to 334 Da. The general formula for this series is $C_3H_{5-1}Cl_{1-5}(OH)_2(COO)_2$.

The differential scanning calorimetry (DSC) thermogram of the unknown (Fig. IV.2.12) was interpreted to exhibit a boiling range from about 250 to beyond 410°C of a mixture with some decompositions occurring in the vicinity of 320°C. This indicates that GC/MS may not be an appropriate approach for the identification of this unknown due to the indicated non-volatility and the decomposition of some components at high temperatures. Indeed, in our GC/MS experiments with the column temperature programmed up to 300°C failed to yield any information regarding the identity of this specimen.

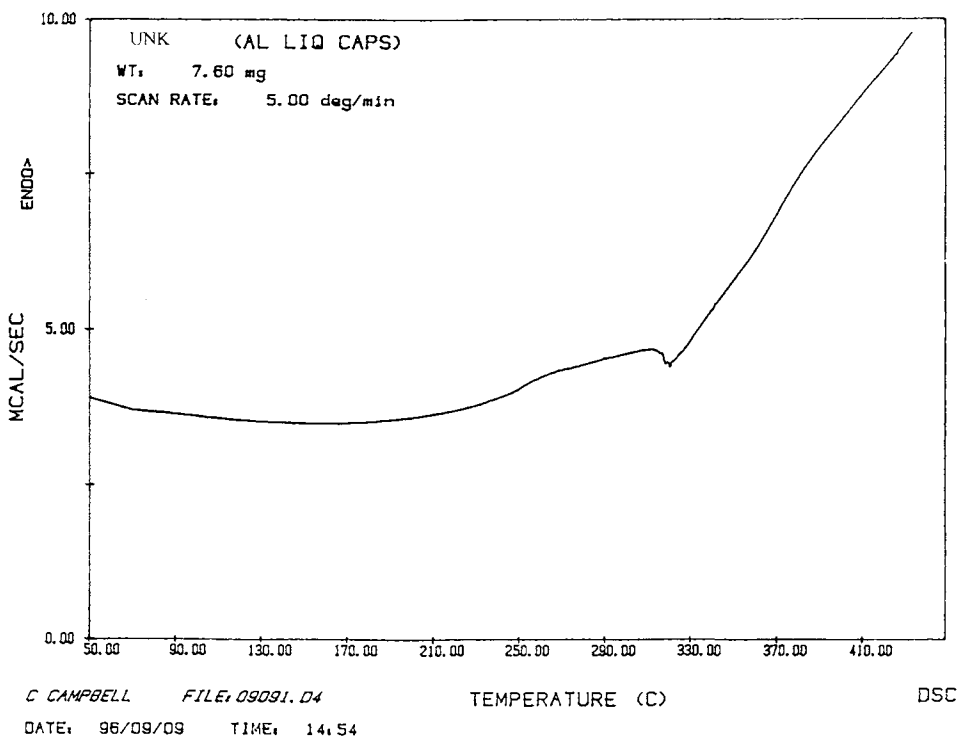


Figure IV.2.12. DCS thermogram of the unknown liquid.

In order to confirm the empirical formulas of the two homologous series of polychloroalkyl and polychlorodihydroxyalkyl oxalates discussed earlier, the accurate mass measurement of one of the more abundant cluster ions was attempted by desorption chemical ionization high resolution mass spectrometry (DCIHRMS). Contrary to expectations, Figure IV.2.13 exhibits complex hydrocarbon-like patterns. The entire features of the spectrum were interpreted to consist of essentially two 13 members each homologous series of high molecular weight dialkyl oxalates and dihydroxyalkyl oxalates. One series predominates the other in abundance by approximately 5–1.

The predominant series consists of 13 members of dialkyl oxalates with carbon numbers ranging from 22 to 34 and molecular weight ranging from 370 to 538. The general formula for this series is $C_{(n+m)}H_{2(n+m)+2}(COO)_2$, where n and m are the carbon numbers of the two alkyl groups attached to the oxalate group. The values of the sum of n and m range from 20 to 32. The accurate mass of the most abundant ion in this series, i.e. $m/z = 427$, was determined to be 427.378470 corresponding to the protonated ion of the inferred species, $[C_{26}H_{50}O_4 + H]^+$ or $[C_{24}H_{50}(COO)_2 + H]^+$. This number agrees very well with the theoretical value of 427.378736, the difference being only about $0.2m$ Da.

The less abundant series consist of 13 members of dihydroxyalkyl oxalates with carbon numbers ranging from 27 to 39 and molecular weight ranging from 472 to 640. The general formula for this series is $C_{(n+m)}H_{2(n+m)+2}(OH)_2(COO)_2$ with the values of the sum of n and m ranging from 25 to 37. The accurate mass of the most abundant ion in this series, i.e. $m/z = 571$, was determined to be 571.493837 corresponding to the protonated ion of the inferred species, $[C_{34}H_{66}O_6 + H]^+$ or $[C_{32}H_{64}(OH)_2(COO)_2 + H]^+$. This number agrees very well with the theoretical value of 571.493766, the difference being only about $0.1m$ Da. It should be noted that both sets of homologous series have identical structural types except that in the first set, the alkyl groups are polychlorinated. Thus, HRMS essentially confirmed the empirical formula assignments for the two 13-member homologous series discussed above.

The apparent discrepancy regarding the identity of the unknown in the DEPMS and DCIHRMS studies was attributed to the loss of most of the more volatile, lower molecular weight polychloroalkyl and polychlorohydroxy oxalates during the DCIHRMS experiment prior to the accurate mass measurements. As a result, only the less volatile, higher molecular weight components of the unknown, i.e. the two homologous series of the alkyl and hydroxyalkyl oxalates were observed.

To assess the environmental impact of the use of the unknown as a potential lubricant candidate for guns in the high temperature environment, the chlorine content of the unknown needs to be determined. Initially, the chlorine content determination by gravimetry as silver chloride was attempted. The procedure consisted of the alkaline hydrolysis of the specimen with sodium hydroxide and precipitation of the resulting chloride ions in the aqueous extract with silver nitrate as silver chloride after acidification of the extract with nitric acid. This was not successful because this unknown was found to be highly resistant to the alkaline hydrolysis. Subsequently, the sodium fusion procedure (Pasto and Johnson, 1969) was employed to decompose the unknown for the determination of the chlorine content. All reactions involved in this procedure are very vigorous and extreme care needs to be exercised to avoid the loss of solution by spattering. The resulting chloride ions were then determined by gravimetry as silver chloride. The chlorine content was determined to be $28.0 \pm 0.2\%$.

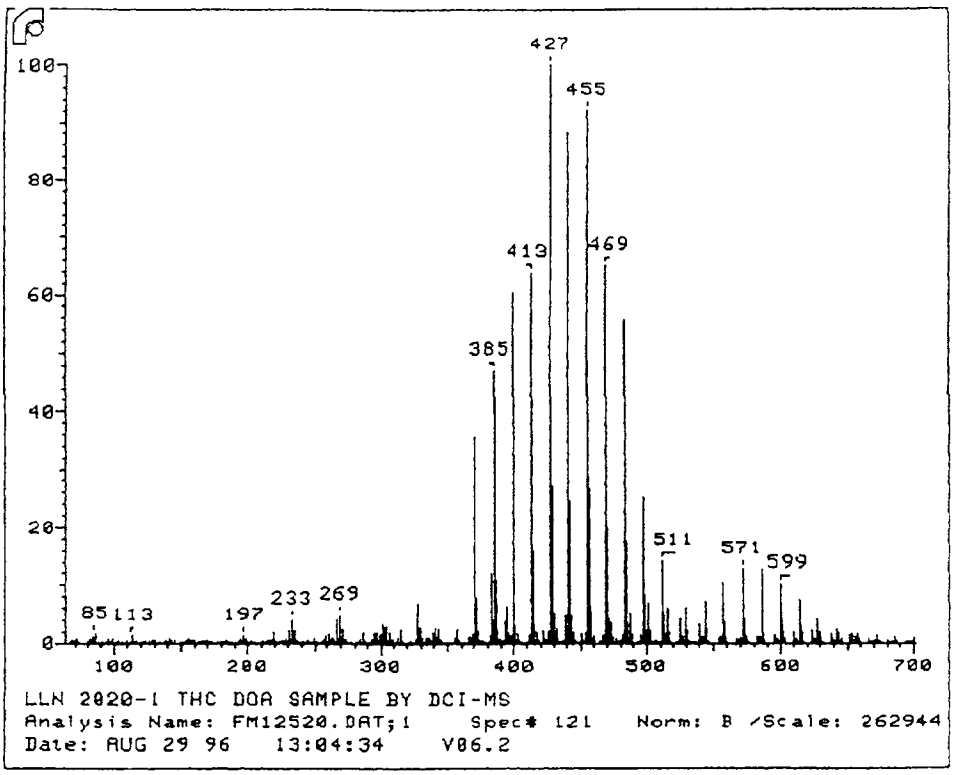


Figure IV.2.13. DCIMS spectrum of the unknown liquid.

The approximate chlorine content and the average molecular weight of the unknown were also computed from the approximate normalized intensity ratios of the two sets of homologous series of Cl^{35} cluster ions (Fig. IV.2.10) and the chlorine contents and the molecular weights of the 10 chlorine species. This yielded approximate chlorine content and the average molecular weight for the unknown of 27% and 262, respectively.

The agreement of the values for the chlorine content obtained by gravimetry and by computation from DEPMS spectrum indicates that the unknown consists of primarily two 5-member homologous series of polychloroalkyl and polychlorodihydroxyalkyl oxalates ranging in molecular weight for the Cl^{35} species from 198 to 334 and 236 to 372 Da, respectively. The minor components of the unknown consist of the two 13-member homologous series of dialkyl and dihydroxyalkyl oxalates ranging in molecular weight for the Cl^{35} species from 370 to 538 and 472 to 640 Da, respectively.

IV.2.4. Some comments on analytical scheme

We have optimized the DEPMS conditions for the identification of non-volatile and labile energetic compounds, especially RDX and HMX. As pointed out earlier, DEPMS enabled us to identify and confirm a large number of labile and non-volatile unknown compounds in the past (Chen and Campbell, 1989, 1993; Chen et al., 1990a; Chen and White, 1994).

It should be pointed out that, DEPMS operated under our conditions provides, in most cases, the molecular weight and the structural information in a single experiment very rapidly. This is the primary reason for our preference and reliance on this particular MS technique in the analytical scheme developed. We have also employed HRMS to confirm the identity of diagnostic ions (Chen and Campbell, 1989), and identify unknown mixtures (Chen, 1983; Chen et al., 1998). Proton nuclear magnetic resonance (p-NMR) was also utilized in the structural elucidation as well as the composition analysis of an unknown liquid explosive mixture (Chen, 1983). Optical microscopy was used in aiding the identification of the unknowns.

Liquid chromatography/mass spectrometry (LC/MS) and related techniques such as the bench-top LC/MS/MS have now been widely employed in the analyses of complex mixtures. These powerful and versatile techniques enable the analyses of complex mixture samples with minimum or no sample preparation. Moreover, the MS/MS capability allows the analysis of unknown mixtures at the trace levels with reliable identification of unknown species. However, in the comparative study of RDX and HMX by DEPMS and thermospray liquid chromatography/mass spectrometry (TSLC/MS), the latter operated in the negative ion mode with discharge provides only limited molecular weight and structural information. Such information for RDX and HMX basically could not be obtained under the conditions of particle-beam LC/MS (PBLC/MS) (Chen, 1993). This study was preliminary in nature, and further work is needed to confirm these initial findings.

Although not included in the scheme, capillary electrophoresis techniques such as capillary zone electrophoresis (CZE), micellar electrokinetic chromatography (MEKC) and capillary electrochromatography (CEC) are now widely applied to the analysis of unknowns. These techniques complement IC and HPLC.

IV.2.5. Further developments

September 11th 2001 terrorist attacks and the subsequent terrorism and bio-terrorism in the USA revealed new monitoring and analytical challenges faced by environmental laboratories around the world. Due to the specific character of the terrorism of the 21st century that uses in full the trumps of extreme mobility, taking by surprise, and unpredictability in choosing the targets of scorching blasts, the laboratories should be no less flexible, mobile and prepared to an instant effective response to the attack, wherever it happens. They have to deal with a new wider range of unknown substances/waste in any compartment of the environment and any place worldwide. The success can be assured by the parallel efforts utilizing the performance-based measurement system (PBMS) approach at the stationary laboratory exemplified above, and further development of field monitoring and field-based analytical methods (FAMs) (see Chapter IV.1). The advantages of these result-oriented approaches in the field of identification of unknown substances/waste are obvious: (i) they address sample- and site specificity, analytical flexibility and freedom in keeping pace with current improvements in analytical chemistry techniques; (ii) they permit on-site identification and preliminary characterization of a hazard, which greatly improve promptness of response, mobility and economic and scientific feasibility in achieving the objectives of public and environmental safety.

Among the variety of FAMs also discussed and referred to in Chapter IV.1, several methods developed recently address directly the objectives of on-site identification of unknown substances/wastes (Davoli et al., 2001), explosives (Carles et al., 2001; Ewing and Miller, 2001; Hewitt et al., 2001), buried objects and landmines (SPIE, 1999) and biological hazards (Denniger and Lee, 2000; Snyder et al., 2000). Besides, the US EPA (2002) provides broad, continuously updated information on currently available FAMs and equipment that can be applied on site for unknown substances/waste identification and sample collection activities. They include methods that can be used outdoors with hand-held equipment, as well as more rigorous methods that require the controlled environments of a mobile laboratory. Some of the most common FAMs addressed in the US EPA document (2002) are fiber optic chemical sensors: rapid optical screening tool (ROST) and laser-induced fluorescence (LIF) coupled with the site characterization and analysis penetrometer system (SCAPS). Other widely used FAMs comprise portable GC, immunoassay test kits (IA), X-ray fluorescence (XRF) and GC/MS.

Besides technical aspects, the principles of analysis are of importance. The American Chemical Society (ACS) Committee on Environmental Improvement is considering an update of the 1983 "Principles of Environmental Analysis". One of the crucial topics this Committee plans to address is establishing criteria for unknown compound identification (Richardson, 2002), which should also provide a valuable assistance in this area.

Many laboratories and their staff – analysts, scientists and managers – were on the front line of response actions to terrorists attacks of September 11, 2001 and of undertaking preventive measures for protection of the next potential targets. The real world analytical challenges faced by these laboratories in responding to these attacks were reflected in the presentations at the Special Session of the 18th Annual Waste Testing and Quality Assurance Symposium (WTQA, 2002).

The awareness of specificity of threat caused by terrorism will undoubtedly give a further strong impulse to the improvement of existing and development of new analytical methods and equipment for faster, more cost-effective and reliable identification and management of hazard posed by terrorism to the public health and environment. Along with these new disasters, the residuals of past, present and future wars and improperly disposed and buried unknown hazardous waste are to be no less adequately identified and managed.

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IV.3
Remote monitors for *in situ* characterization of hazardous wastes

Tuan Vo-Dinh

IV.3.1. Introduction

The development of remote monitors for detection of trace quantities of toxic chemicals is critical to the achievement of environmentally viable and safe technologies. Problems pertaining to the identification of specific compounds at trace levels and the needs to perform *in situ* analysis of complex mixtures continue to present new analytical challenges. An important problem area in chemical sensing is the sensitive identification of trace compounds in complex hazardous waste samples. In order to detect minute amounts of a compound in a complex "real-life" sample, sensors must be able not only to differentiate compounds having different molecular sizes but also to identify specific substituents and/or derivative chemical groups attached to the basic structure. Contaminants in environmental samples frequently encompass a wide variety of chemical species. Due to the generally complex nature of hazardous wastes, several techniques are often required to provide unambiguous identification and accurate quantification of the trace contaminants. The various spectrochemical techniques investigated in the Oak Ridge National Laboratory for use in optical sensing and in trace organic analysis include synchronous luminescence (Vo-Dinh, 1978, 1982), room temperature phosphorescence (Vo-Dinh, 1984; Alak and Vo-Dinh, 1988), surface-enhanced Raman spectroscopy (Vo-Dinh et al., 1984; Moody et al., 1987; Vo-Dinh, 1989, 1995a,b), and fiberoptic laser antibody-based biosensor technology (Vo-Dinh et al., 1987, 1993, 2000). Heavy atoms and cyclodextrins were used to enhance phosphorescence analysis (Alak and Vo-Dinh, 1988) whereas antibodies were developed to improve the specificity and sensitivity of laser-based biochemical sensors (Vo-Dinh et al., 1987, 1993).

This chapter presents an overview of two complementary techniques developed in our laboratory, involving luminescence and Raman spectroscopies used for environmental detection. Molecular fluorescence is often employed for strongly fluorescing contaminants, such as the polycyclic aromatic compounds (PAC), due to the speed and the inherent sensitivity of this technique for PAC. When synchronous fluorescence (Vo-Dinh, 1978, 1982) is used for PAC analysis, the amount of sample pre-treatment can often be reduced due to the greater selectivity of the technique relative to conventional fluorescence emission. An alternative detection method involves Raman and surface-enhanced Raman scattering (SERS) techniques (Vo-Dinh et al., 1984, 1996b; Moody et al., 1987; Vo-Dinh,

1989, 1995a,b), which can be used to detect non-luminescing or weakly luminescing contaminants. The instrumental systems and environmental applications of the luminescence and Raman monitors are discussed in the following sections.

IV.3.2. Laser-based synchronous fluorescence monitors

IV.3.2.1. Synchronous luminescence method

We have developed a unique methodology for enhanced selectivity in luminescence analysis based on the idea of synchronous excitation (Vo-Dinh, 1978, 1982). The SL methodology provides a simple way to measure the luminescence signal and spectral fingerprints for rapid screening of complex chemical samples. Conventional luminescence spectroscopy uses either a fixed-wavelength excitation (λ_{ex}) to produce an emission spectrum or a fixed wavelength emission (λ_{em}) to record an excitation spectrum. With synchronous spectroscopy, the luminescence signal is recorded while both λ_{em} and λ_{ex} are simultaneously scanned. A constant wavelength interval $\Delta\lambda$ is maintained between the excitation and the emission monochromators throughout the spectrum. As a result, the intensity of the synchronous signal I_σ, can be written as a product of the two functions as follows:

$$I_\sigma(\lambda_{ex}),\ (\lambda_{em}) = kcE_x(\lambda_{ex})E_M(\lambda_{ex}),$$

where

k = a constant,
c = concentration of the analyte,
E_x = excitation function, and
E_M = emission function.

For a single molecular species the observed intensity is simplified (often to a single peak), and the bandwidth is narrower than for the conventional emission spectrum. Figure IV.3.1A shows the fluorescence excitation and emission spectra of a strong fluorescent dye, fluorene. In Figure IV.3.1B the synchronous signal of the same sample is given; in this example a 3-nm interval ($\Delta\lambda$) between λ_{em} and λ_{ex} was used. Note the broad structure of both conventional spectra and the narrow peak of the synchronous signal. This feature can significantly reduce spectral overlap in multicomponent mixtures. Correlation of the signal wavelength position with the structure of the compounds becomes easier. For example, the spectrum of a higher ring-number cyclic compound occurs generally at a longer wavelength than the spectrum of a lower ring-number compound. With conventional spectroscopy, this basic rule cannot often be utilized advantageously due to severe spectral overlap. By confining each individual spectrum to a narrow and definite spectral band, the synchronous method offers the possibility of identifying specific compounds or a group of compounds in a mixture (Vo-Dinh, 1982).

The exceptional quality of synchronous luminescence spectrometry can be visualized by using an analogy. The excellent suitability of chromatographic techniques for the analysis of multicomponent mixtures resides in the fact that each component of the mixture provides a simplified signal only (usually one separate "peak"). Synchronous

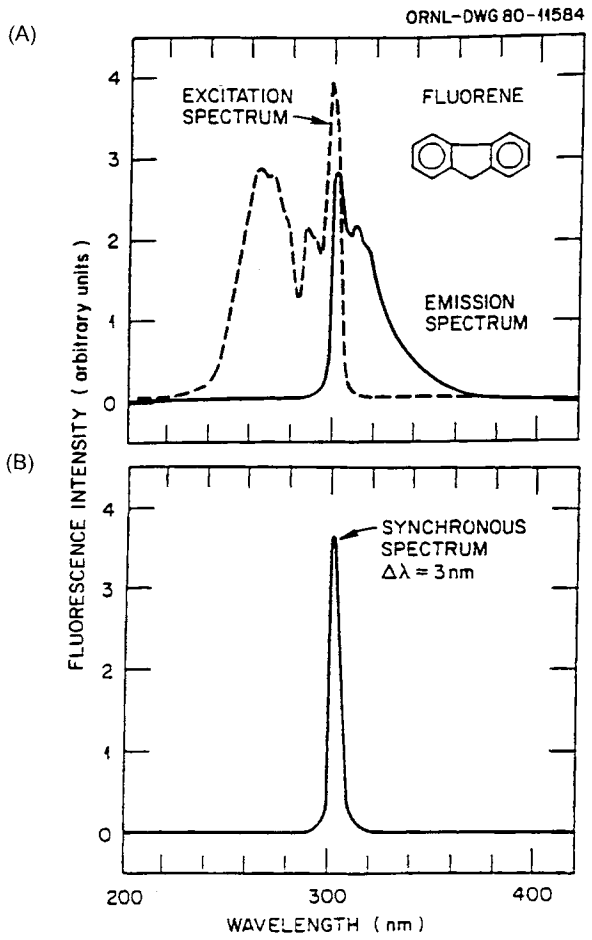


Figure IV.3.1. (A) Excitation and emission fluorescence spectra of fluorene; (B) synchronous luminescence (SL) spectrum of fluorene.

luminescence excitation can be regarded as a unique attempt to apply this property of chromatographic methods to spectroscopy without requiring separation of the components. This can be best demonstrated by a synchronous fluorescence spectrum of a mixture consisting of naphthalene, phenanthrene, anthracene, perylene, and tetracene (Fig. IV.3.2). Each compound gives essentially one signal only and apart from the order of "peaks" of a chromatogram, this mixture would not look much different from a conventional chromatogram.

IV.3.2.2. Instrumental systems

A remote fiberoptic monitor using the laser-based synchronous luminescence (LSL) technique has been developed for detection of PAC contaminants (Vo-Dinh et al., 1996b). The salient features of the device are described here. The source is a small

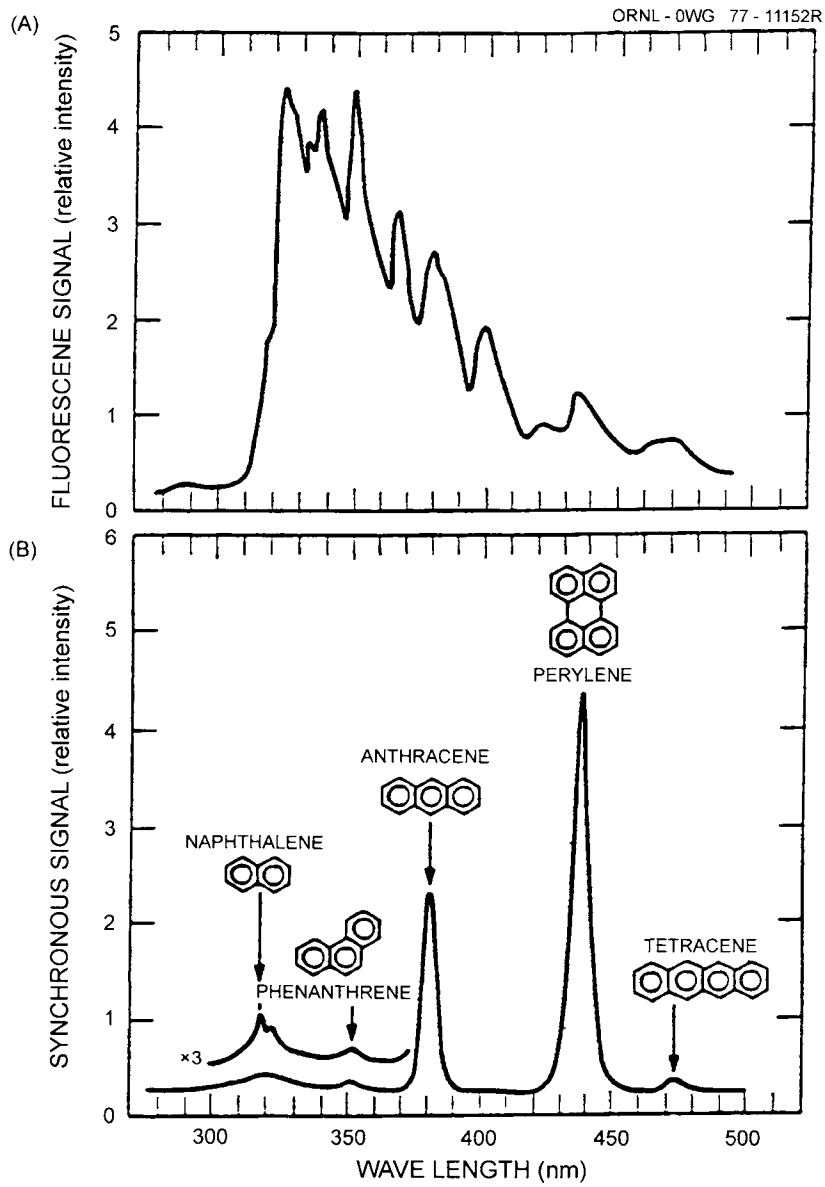


Figure IV.3.2. Advantages of the SL method (after Vo-Dinh, 1978). (A) Fixed-excitation fluorescence spectrum of a five-component mixture; (B) SL spectrum of the same mixture with spectral separation of components.

nitrogen-pumped dye laser (Laser Science VSL-337/VSL-DYE). The entire laser system weighs 7 lb, and can be powered by a battery pack. The dye-laser is extremely simple, consisting of a single oscillator cavity with a grating and an output mirror. Cuvettes containing different dye solutions can be rapidly inserted into the cavity, usually with no re-alignment needed. Typical pulse energies are 5–10 μJ/pulse with the dyes used in these experiments; the repetition rate of the laser was 15 Hz, and the pulse width was 3.0 ns.

Fluorescence from samples was collected at 90° with an *f*/1 lens and focused with an *f*/3.5 lens into a 10-cm focal-length monochromator (ISA model H-10). The output from the photomultiplier (Hamamatsu R928) was amplified (Stanford Research Systems SR445) and input into a gated boxcar averager (Stanford Research Systems SR250). The time constant of the boxcar was 0.2 s. Stepper motors replace the DC motors used previously to control the scanning of both the laser and the monochromator. An analog-to-digital converter (ADC) card (MetraByte DASH-16F) was used for instrument control, timing, and data collection. The software used to control the LSL instrument was developed in-house.

The system was designed to allow several different laser dyes to be used in a single scan (a "multi-dye scan"), thereby extending the wavelength range of the scan. When the laser wavelength reached the edge of the lasing region of one dye, the control program paused to allow a manual insertion of a new dye solution before continuing the scan. The process of dye exchange was rapid; only a few seconds elapsed before scanning was resumed. Due to the simplicity of the dye-laser used, no realignment was necessary when switching between dyes. The wavelength regions scanned by different laser dyes in a multi-dye scan need not be continuous, and can use different wavelength separation ($\Delta\lambda$) values. In the multi-dye scanning mode, the same $\Delta\lambda$ values are used for all laser dyes, and the different dyes "overlap" at the extremes of their scanning ranges.

The LSL monitor could employ standard cuvette sample holders as well as fiberoptic probes for remote sensing. When the fiber probe was used, the cuvette holder was replaced with a flat mirror with a small hole in its center. The end of the 3-m fiber probe was mounted behind the mirror so that the laser light passed through the hole in the mirror and onto the fiber's proximal end (Fig. IV.3.3). The probe consisted of a single fiber, which was used to transmit laser light to the sample and to collect the fluorescence. The fluorescence emitted from the fiber was reflected by the mirror toward the monochromator's collection optics. Only a small fraction (5%) of fluorescence was lost through the hole in the mirror. The position of the lenses was adjusted to optimize for the best laser-to-fiber coupling efficiency (~85%) and fluorescence collection efficiency.

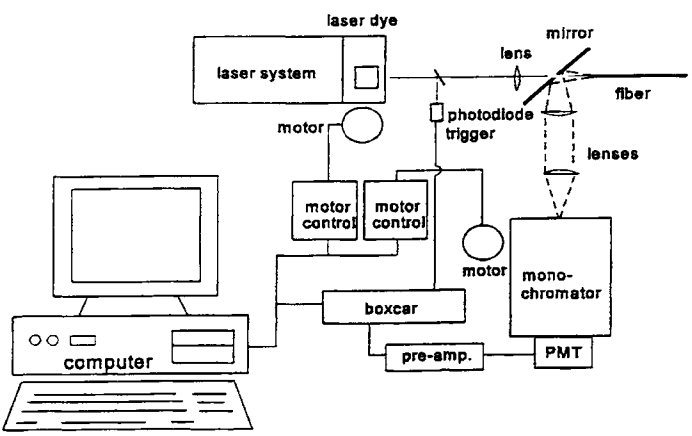


Figure IV.3.3. Block diagram of the laser synchronous fluorescence instrument. Both the monochromator and the dye-laser can be scanned using computer controlled stepping motors (after Vo-Dinh et al., 1996b).

IV.3.2.3. Application: characterization of PAC pollutants

PACs are present in many environmental samples, such as petroleum products, hazardous wastes, coal, tar, creosote, etc. (Vo-Dinh et al., 1987, 1996b). We have demonstrated the improved selectivity of synchronous fluorescence over conventional fluorescence by determining fluoranthene in a contaminated soil sample without previous separation (Stevenson and Vo-Dinh, 1993; Vo-Dinh et al., 1996b). The sample consisted of a reference matrix containing 20 PAC at the ppm level. The conventional emission spectra of fluoranthene and the soil sample extract recorded at the maximum excitation wavelength of the target compound (λ_{ex} = 297 nm) indicated the improved selectivity of the SL method. Two important features of the synchronous technique are noteworthy in complex mixtures such as hazardous wastes: (i) the broadness of synchronous emission bands are considerably narrower than conventional bands; and (ii) usually only one peak per compound is obtained. As a consequence, a lower probability of spectral interference should be expected from various constituents in the sample.

A further demonstration of the usefulness of the LSL method involved analysis of multicomponent mixtures using the fiberoptic probe (Vo-Dinh et al., 1996b). In this analysis, the mixture consisted of 1.8 ppb of benzo[a]pyrene (BaP) and 10 ppb perylene in water. A $\Delta\lambda$ = 25 nm was used to achieve optimal BaP fluorescence; if a smaller $\Delta\lambda$ were used perylene would exhibit only one peak. A boxcar gate delay of 5 ns was used to avoid most of the laser scatter from the ends of the fiber. Three laser dyes were required to scan the range between 385 and 510 nm. The dye cuvettes were rapidly changed after each section of the scan. No dye-laser realignment was required, but the alignment of the laser beam and optical fiber coupling lens was checked after each dye exchange. The current availability of wide-range tuning lasers equipped with optical parametric oscillators will make the operation of LSL instruments simpler. The examples discussed here demonstrate the usefulness of laser-based luminescence monitors for remote sensing of PAC in hazardous wastes.

IV.3.3. Raman and SERS monitors

IV.3.3.1. Raman and surface-enhanced Raman methods

Vibrational spectroscopies are important techniques for chemical and biological analysis due to the wealth of information on molecular structures, surface processes, and interface reactions that can be extracted from experimental data. Raman spectroscopy has recently enjoyed a renewed interest in many fields due to the observations of enormous Raman enhancement for molecules adsorbed on special metallic surfaces (Jeanmaire and Van Duyne, 1977; Chang and Furtak, 1982). This increase in Raman signal, originally attributed to a high surface density produced by the roughening of the electrode surfaces, was later identified as a direct result of a surface enhancement process (Jeanmaire and Van Duyne, 1977), hence the term surface-enhanced Raman scattering (SERS) effect. The observed Raman scattering signals for the adsorbed molecules were found to be more than a million times (10^6) larger than those expected from gas phase molecules or from non-adsorbed compounds.

The experimental observations related to SERS, and the origin of the enormous Raman enhancement are believed to be the result of several mechanisms. There are at least two major types of enhancement mechanisms that contribute to the SERS effect: (a) an electromagnetic effect associated with large local fields caused by electromagnetic resonances occurring near metal surface structures, and (b) a chemical effect involving a scattering process associated with chemical interactions between the molecule and the metal surface. These enormous enhancement factors, which help compensate for the normally weak Raman scattering process, open new horizons to the Raman technique for trace analysis (Vo-Dinh, 1989, 1995a,b; Vo-Dinh and Stokes, 2002).

IV.3.3.2. Raman and SERS monitors and probes

For laboratory analyses, various Raman spectrometers are now commercially available. A portable SERS field spectrometer (Gamma-Metrics, Inc., San Diego, CA) was available for measurements (Bello et al., 1990). We have used both commercial and laboratory-designed systems for our studies. An instrument consisted of a Spex Model 1403 double monochromator with a Spex Datamate DM1 control and data acquisition system. The detection employed the photon counting technique accomplished using a cooled RCA C31034-02 photomultiplier tube. Excitation was provided by a Spectra Physics Model 166 argon ion laser, a Coherent Radiation Model Innova 90K krypton ion laser, or a Liconix Model 4240PS helium–cadmium laser.

The second system was based on a Jobin-Yvon/ISA Ramanor 2000M double-grating monochromator. The data acquisition system was an LSI 11/23 minicomputer purchased from Data Translation Corporation and a DSD/880 Winchester/floppy disk drive. Photon counting was accomplished using a cooled RCA C31034-02 photomultiplier tube. The excitation was provided by a Spectra Physics Model 171 argon ion laser. Scanning electron microscope (SEM) photographs are obtained with an ISI DS-130 scanning electron microscope.

The substrate of the SERS probes preparation involved two steps. The first step was the deposition of microbodies (such as polystyrene latex spheres, fumed silica, titanium oxide, and aluminum oxide particles) on glass plates. This deposition was accomplished by placing a glass slide on a spin-coating device. A few drops of the microparticle/water solution were placed on the glass slide, which was then immediately spun at 2000 rpm for 20 s. Spinning has been found necessary to preclude clumping of the microparticles on the glass surface. The microparticles adhered to the glass providing a uniform coverage. The second step was the coating of the microparticle-covered glass slide with silver (75–100 nm thickness). The glass slide was placed inside a vacuum evaporator. The pressure was less than 5×10^{-6} Torr. The rate of silver deposition was controlled at approximately 1.5–2.0 nm/s. The rate and thickness of silver deposition was measured using a Kronos Model QM-311 quartz crystal thickness monitor. Data from the quartz crystal thickness monitor exhibited a standard deviation of 10%. Following silver evaporation, 2–4 ml of sample solution was spotted on the glass plate substrate. The Raman spectrum was then scanned over the region of interest. For solution measurements, 1 ml of the sample solution was pipetted into a standard quartz cell. The SERS substrate was then inserted directly into the cell and the SERS spectrum was recorded. For *in situ* measurements, the substrates were mounted on a fiberoptic probe and inserted into liquid samples for spectral recording.

The substrate can serve as a probe to collect analyte compounds adsorbed onto its SERS-active surface. In general, microparticles of oxides (alumina, titania, silica) have been used on glass plates, which provide simple, and inexpensive practical supports (Vo-Dinh, 1989, 1995a,b). The size of the surface microstructure can be easily controlled by simply selecting the appropriate microparticle sizes. In most of our studies, silver was used as the coating metal for SERS substrates. Previous research indicates that the type of metal on the surfaces is an important factor affecting the SERS effect. Silver exhibits the strongest enhancement followed by copper and gold. The development of SERS as an analytical technique is relatively recent and many experimental factors require careful optimization in order to obtain the maximum signal enhancement. One of the major difficulties in the development of the SERS technique for analytical applications is the development of surfaces or media that have an easily controlled protrusion size and reproducible structure. In a previous work (Moody et al., 1987) we have shown that the SERS effect depends upon several factors including excitation wavelength, microparticle size, and silver coating thickness. Using 364 nm diameter microspheres, we measured the SERS signal intensity using different excitation frequencies. In this previous study, we investigated this excitation dependence effect for a variety of sphere sizes and silver coating thickness combinations (Moody et al., 1987). Optical fiber-based probes have been developed and used for remote *in situ* measurements (Bello et al., 1990; Alarie et al., 1992; Vo-Dinh, 1995a,b). With these remote systems, the excitation fiber was placed at the back (glass) side of the SERS substrate while the collection fiber was placed at the front (metal) side of the substrate.

IV.3.3.3. Application: fiberoptic remote SERS sensing

The development of SERS-active substrates that allow direct measurements in liquid samples is critical for *in situ* analysis. SERS has been observed using different solid substrates such as metal electrodes, metal islands, films, glass or cellulose coated with silver-covered microparticles. However, with the exception of metal electrodes and colloidal solutions, most of the SERS studies performed with solid substrates to date have been performed in the dry state. Recently, we have developed the technique of measuring SERS in solution using probes covered with silver-coated substrates mounted in fiberoptic sensors.

Figure IV.3.4 shows a schematic diagram of a prototype fiberoptic remote SERS monitor. A preliminary version of a SERS fiberoptic probe has been developed and described previously (Bello et al., 1990; Alarie et al., 1992; Vo-Dinh, 1995a,b; Stokes and Vo-Dinh, 2000; Vo-Dinh and Stokes, 2002). Only the salient features are described here. A single optical fiber was used to transmit the laser excitation into the SERS probe, and a second fiber was used to collect the scattered radiation from the sample. The laser beam transmitted through a bandpass filter was focused into one end of the excitation fiber with the use of a microscope objective lens. This end of the excitation fiber was held by a fiberoptic holder. The terminus end of the excitation fiber was positioned close to the SERS substrate in order to contain the laser beam to a very small spot on the substrate. New SERS-active substrates based on nanoparticles of silver in sol–gel have been developed for use in probes (Volkan et al., 1999).

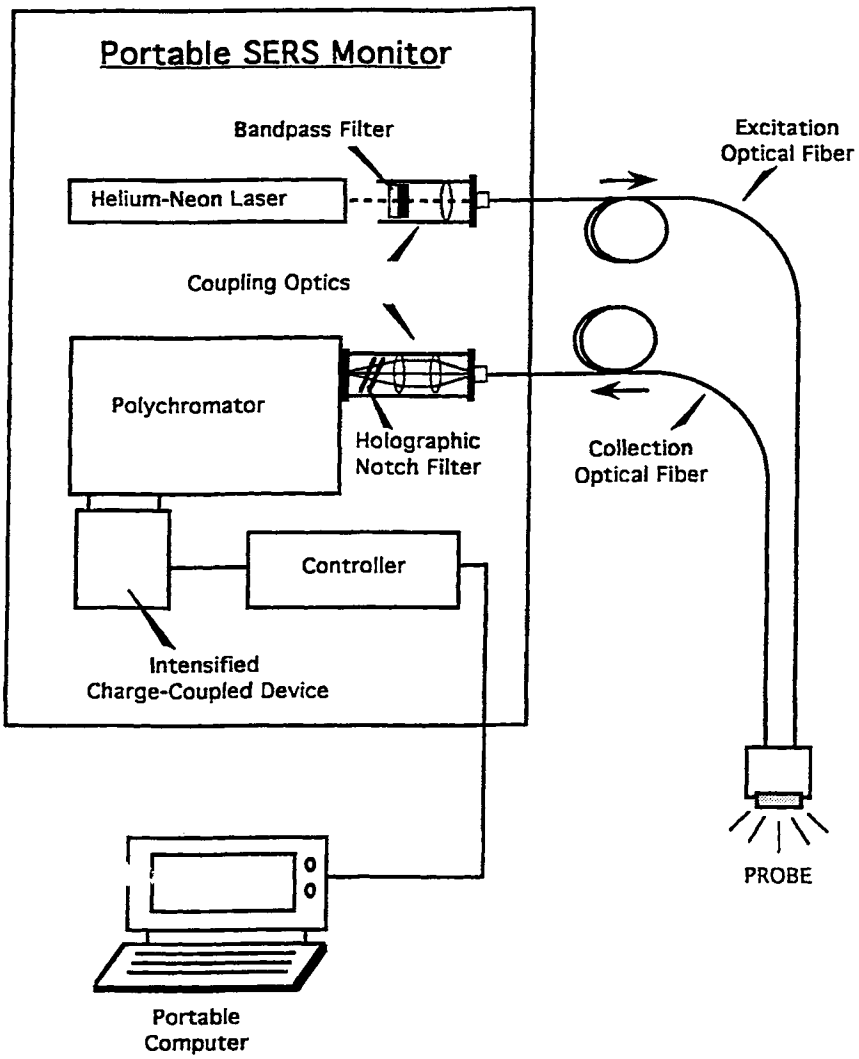


Figure IV.3.4. Schematic diagram of a fiberoptic remote SERS sensor.

The SERS probe was prepared with a glass backing (microscope slide, 1 mm thick) so that the excitation and collection fibers could be positioned either head on, with the fibers positioned on opposite sides of the SERS substrate, or side-by-side, with the two fibers on the same side of the substrate. The terminus end of the collection fiber was positioned next to the entrance slit of a spectrometer. Since the *f*/number of the fiber and that of the spectrometer were different, it was necessary to focus the input radiation from the collection fiber with lenses. An *f*/1 lens was used to collect and collimate the output beam from the collection fiber. A second lens with an *f*/number matching that of the spectrometer (*f*/7) was then used to focus the collected SERS signal into the slit of the spectrometer equipped with a red-enhanced intensified charge-coupled device (ICCD)

from Princeton Instruments, Inc. The length of excitation and collection fibers used was 1–20 m, with minor alteration in the SERS signal. Figure IV.3.5 shows a SERS spectrum of 1-aminobenzoic acid recorded from only 9 ms to 10 s using the fiberoptic remote SERS sensor. The results indicated that the combination of the ICCD sensitivity and the SERS probe effectiveness allowed rapid *in situ* chemical sensing (Alarie et al., 1992). The usefulness of the SERS technique in chemical analysis of a wide variety of species (listed in Table IV.3.1) has been demonstrated (Vo-Dinh, 1989).

IV.3.4. Multispectral imaging and sensing systems

Acousto-optic tunable filters (AOTF) are a relatively new technology used to isolate one or more wavelengths of light. They operate as a tunable optical band pass filter. In contrast to a grating monochromator, an AOTF offers the advantage of having no moving parts and can be scanned at very high rates (millisecond time scale) without the possibility of error due to gear backlash or other mechanical problems. Since AOTFs with high spatial resolution (typically 100 lines/mm) and large optical apertures are available, they can be applied for spectral imaging applications (Hayden et al., 1987; Chao et al., 1990; Cheng et al., 1993).

We have developed several remote spectral imaging systems combining a two-dimensional CCD detector, an AOTF device, and optical imaging fiberoptic probe (IFP) technology (Moreau et al., 1996a,b; Vo-Dinh et al., 1996a). These devices can have useful applications in remote sensing and imaging of hazardous waste samples. The spectral imaging concept combining conventional imaging and spectroscopy is illustrated in Figure IV.3.6.

IV.3.4.1. Operating principle of AOTFs

AOTF devices consist of a piezoelectric transducer bonded to a birefringent crystal. The transducer is excited by a radio frequency (rf) (50–200 MHz) and generates acoustic waves in a birefringent crystal. Those waves establish a periodic modulation of the index of refraction via the elasto-optic effect (Moreau et al., 1996b). Under proper conditions, the AOTF will diffract part of the incident light within a narrow frequency range. This is the basis of an electronically tuned optical filter using the Bragg diffraction of light by periodic modulations in the index of refraction in the crystal established by the acoustic waves. Only light that enters the crystal such that its angle to the normal of the face of the crystal is within a certain range can be diffracted by the Bragg grating. This range is called the acceptance angle of the AOTF. The percentage of light diffracted is the diffraction efficiency of the device. This parameter greatly depends on the incidence angle, the wavelength selected, and the power of the rf signal.

In a non-collinear AOTF, the diffracted beam is separated from the undiffracted beam by a diffraction angle. The undiffracted beam exits the crystal at an angle equal to the incident light beam, while the diffracted beam exits the AOTF at a small angle with respect to the original beam. A detector can be placed at a distance so that the diffracted light can be monitored, while the undiffracted light does not irradiate the detector. In addition, when the incident beam is linearly polarized and aligned with the crystal axis, the polarization of the diffracted beam is rotated 90° with respect to the undiffracted beam. This can provide

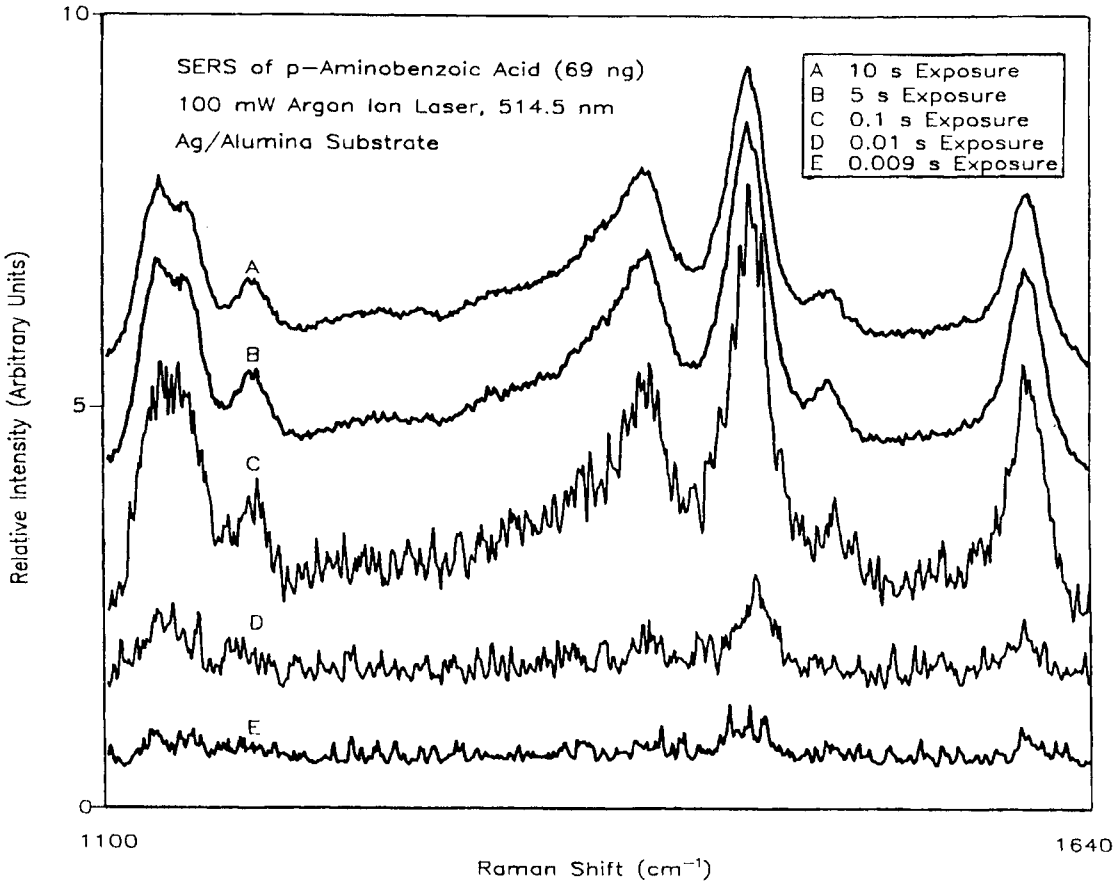


Figure IV.3.5. Schematic SERS monitor for *p*-aminobenzoic acid (1 μl spot of 10^{-3} M solution; excitation = 632.8 nm, 3 mW, 20 m fiberoptic (after Alarie et al., 1992).

Table IV.3.1. Some detection limits using SERS probe (after Vo-Dinh, 1995a,b).

Compounds	Limit of detection (ppm)	Comments[a]
p-Aminobenzoic acid	0.4	Fiberoptic sensor
p-Diacetyl benzene	43	Fiberoptic sensor
Terephthaldehyde	1	Fiberoptic sensor
Terephthalic acid	3	Fiberoptic sensor
p-Cresol	28	Fiberoptic sensor
Benzoic acid	50	Fiberoptic sensor
m-Nitrobenzoic acid	87	Fiberoptic sensor
3-Nitroaniline	36	Fiberoptic sensor
p-Aminobenzoic acid	17	
Benzoic acid	17	
Benzo(a)pyrene-tetrol	8	
Formothion	11	
Pyrene	0.002	
Terephthalic acid	15	
Carbonphenothran	32	Chlorinated pesticide
Bremophos	36	Chlorinated pesticide
Methyl chloropyrifos	32	Chlorinated pesticide
Dichloran	20	Chlorinated pesticide
Linuron	25	Chlorinated pesticide
Chlordane	40	Chlorinated pesticide
1-Hydroxychlorodene	35	Chlorinated pesticide
Methylparathion	<26	Organophosphorus
Fonofoxon	<25	Organophosphorus
Chlorfenvinhos	<36	Organophosphorus
Cyanox	<25	Organophosphorus
Diazinon	<25	Organophosphorus
Formothion	<26	Organophosphorus
Dimethoate	<23	Organophosphorus
Trichlofon	<26	Organophosphorus
Benzo(a)pyrene	0.1	
Carbazole	0.2	
1-Aminopyrene	1.4	
Benzoic acid	0.3	

[a]The limits of detection are given for a complete sample spot although only about 1% of the spot is illuminated by the analyzing laser. The actual limits of detection are therefore 100 times less.

a second means to separate the diffracted and undiffracted beams. One polarizer is placed before the AOTF, and is aligned with the crystal. At the exit of the AOTF, a second polarizer is rotated 90° with respect to the first. The undiffracted light is blocked by the crossed polarizers, while most of the diffracted beam escapes.

IV.3.4.2. Multispectral imaging and sensing systems

A prototype AOTF-based multispectral imaging instrument was developed for fluorescence measurements (Moreau et al., 1996a). The light emitted from the output

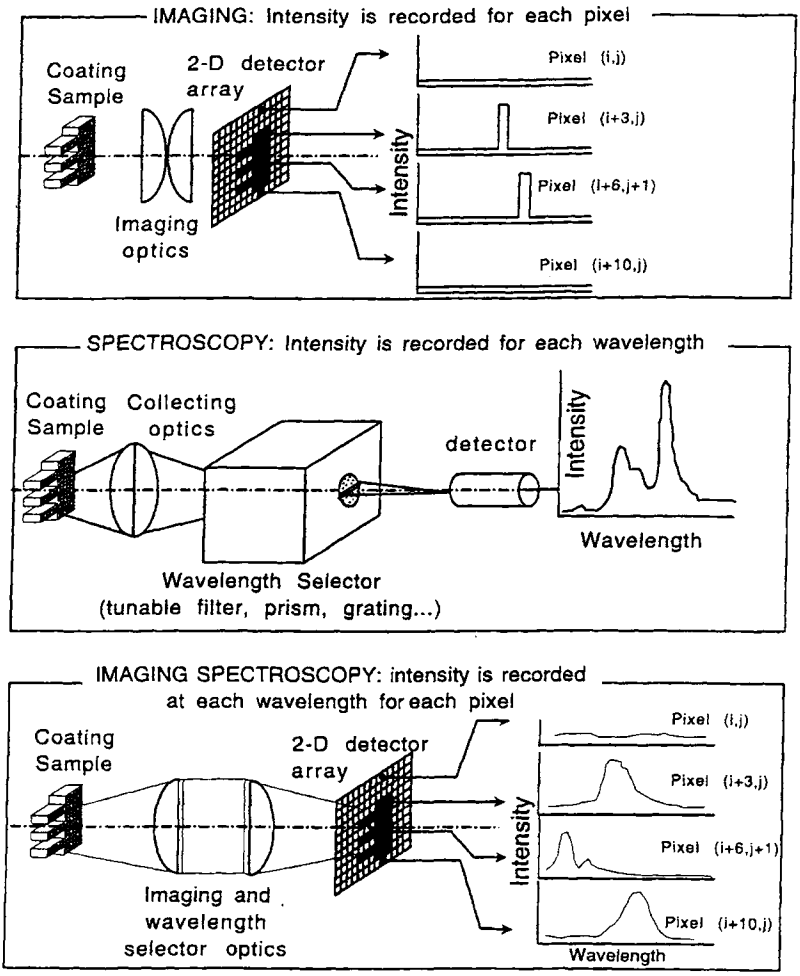


Figure IV.3.6. Principle of imaging spectroscopy (after Moreau et al., 1996a).

end of the IFP was collected by an imaging lens, filtered by the AOTF, and then imaged onto a CCD. By changing the wavelength of the AOTF, a spectrum could be acquired as a series of images (one for each wavelength).

The TeO_2 AOTF used in this work was purchased from Brimrose, Baltimore, MD (model TEAF 10-45-70-S). According to the manufacturer, the AOTF had an effective wavelength range of 450–700 nm (corresponding drive frequency 178–100 MHz). The spectral resolution given by the manufacturer was 20 nm at 633 nm. The diffraction efficiency was 70% at 633 nm. The optical aperture was 10 by 10 mm and the acceptance angle was greater than 30°. The drive power was 1.0–1.5 W.

The rf generator used (Brimrose-model AT) could apply 0–25 W of rf power and was controlled by a DOS-based computer using a 16-bit computer controller board supplied by Brimrose. Custom software was developed at Oak Ridge National Laboratory to control the AOTF, supporting various scanning modes and fixed-frequency operation.

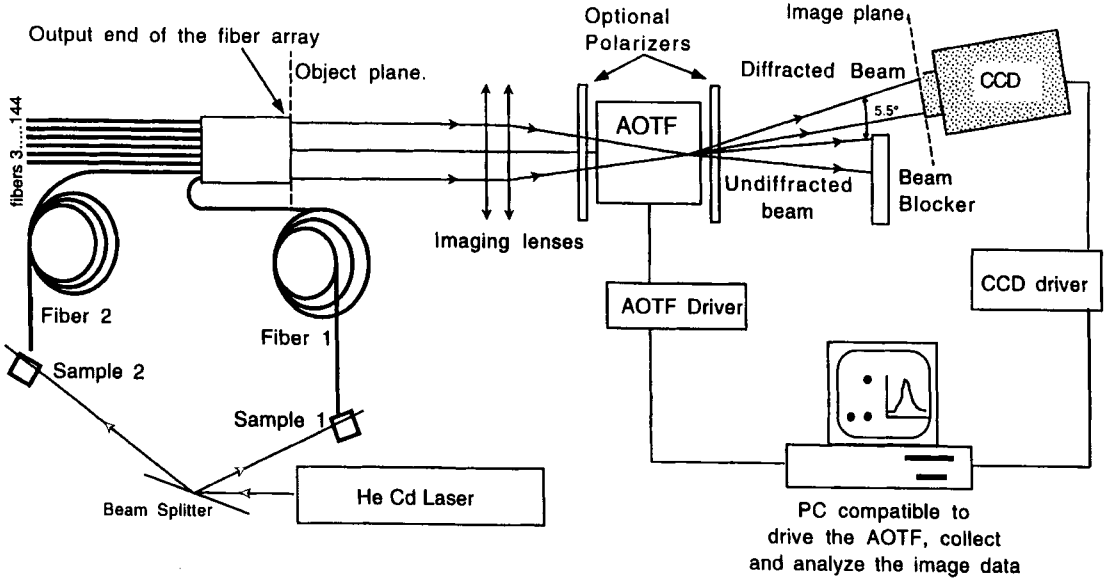


Figure IV.3.7. Diagram of the system used for multichannel sensing (after Moreau et al., 1996b).

The CCD was a model ST-6 purchased from Santa Barbara Instrument Group, Santa Barbara, CA, based on a Texas Instruments TC241 CCD detector. The operating spectral range was 330–1100 nm. The detector was 8.63 × 6.53 mm and had a resolution of 750 × 242 pixels, with a two pixels horizontal binning giving an effective resolution of 375 × 242 pixels. Standard pixel size was 23 × 27 μm. Dark current could be kept as low as 13 electron/pixel/s at −20 °C. The detector was installed on a regulated thermo-electric Peltier effect based cooler. Anti-blooming protection was also included. The analog-to-digital resolution was 16 bits. A mechanical shutter was included in the optical head to facilitate taking dark frames. The CCD controller is based on the IBM 8088 microprocessor and ran at 8 kHz. The interface to the PC compatible computer was accomplished through a regular RS232 cable and baud rate was 115.2 kbaud.

The IFP was purchased from Schott Fiber Optics Inc., South Bridge, MA. It was a rigid image conduit for image transmission made of more than 400,000 individual 12 μm diameter fibers fused together (resolution is twice as much as the CCD resolution). Flat polished ends were 9.5 × 7.0 mm rectangles. Numerical aperture was 0.56 (acceptance half-angle > 30°). Individual fibers were made of glass translucent from 400 nm up to the IR region and transmittance was higher than 0.990/25 mm for the range 480–700 nm. An opaque encapsulation of the IFP provided physical protection as well as light shielding. The excitation source was a HeCd laser from Omnichrome, Chino, CA (Omnichrome-model 3074-6) with a »8 mW output at 325 nm.

Figure IV.3.7 shows a schematic of an instrument designed for remote sensing using multiple probes. The details of the device are described previously (Moreau et al., 1996b). The device has multiple sensor probes that can be used to detect different analytes simultaneously. We have developed several devices that take advantage of recent advances in several technologies, including a two-dimensional CCD detector, imaging fiberoptic, and AOTFs. The integration of these technologies leads to versatile and powerful imaging systems that can remotely detect and analyze fluorescent objects. This imaging system could find useful applications in environmental monitoring areas where the detection of multiple components in complex media is required. The results demonstrate the potential of the AOTF technology to be used for remote imaging spectroscopy and simultaneous spectrum acquisition of different contaminants in hazardous waste samples. For environmental applications, a compact Raman monitor based on AOTF has recently been developed for field monitoring (Cullum et al., 2000).

IV.3.5. Conclusion

Luminescence, Raman, and SERS spectroscopies are spectrochemical techniques that have a number of important advantages to remote sensing of hazardous wastes. The examples shown in this work illustrate the different uses of these techniques for monitoring a wide variety of chemical species. Laser-based luminescence is well known for its high sensitivity for polyaromatic compounds. On the other hand, Raman spectroscopy can be used for weakly luminescing compounds, and can provide an analytical tool having figures of merit that complement luminescence. The Raman technique is well known for its high selectivity. With the advances of fiberoptic technology, the SERS technique, which can amplify the Raman signal by several orders

of magnitude, can provide a remote sensing technique with the added merit of improved sensitivity due to the surface-enhanced effect. Advanced multisensor systems using phosphorescence detection (Campiglia and Vo-Dinh, 1996) and AOTFs (Moreau et al., 1996a,b; Vo-Dinh et al., 1996a) developed in our laboratory further extend the capabilities of remote sensing technologies.

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For further information

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PART IV

4. Advanced biomonitoring of solid waste and waste disposal facilities

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Solid Waste: Assessment, Monitoring and Remediation
Twardowska, Allen, Kettrup and Lacy (Editors)
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IV.4.1
Biomonitors based on immunological principles

Dietmar Knopp and Reinhard Niessner

IV.4.1.1. Introduction

Modern analytical chemistry is playing an increasingly greater role in the field of environmental monitoring, including solid waste, solid waste disposal and contaminated sites. Often critics charge that only a few chemicals are monitored, that the number of samples is inadequate to ensure detection of contamination, and that there is too long a delay between sample collection and communication of results back to the site. This is caused because required methods generally involve sample extraction, cleanup and determination by techniques such as gas chromatography (GC), liquid chromatography (LC), mass spectrometry (MS), thin-layer chromatography (TLC) or other methods. These analyses require well-equipped laboratories and trained personnel, and are often laborious and time consuming. Even with the best analytical methods, problems can arise when hundreds or thousands of samples must be handled. Concern over increasing sample load and rising costs, therefore, motivate the search for rapid, low-cost, simple and reliable tests that could also be automated or carried out on-site (field-portable assays). Besides others such as laser techniques and chemical sensors, attention has focused on the development of immunological techniques. Immunochemical procedures are widely used in clinical chemistry and endocrinology for the routine analysis of hormones, proteins, microorganisms and drugs (Gosling, 1990). In this chapter the basic principle of the immunoassay approach will be outlined and the applicability of this method for environmental monitoring discussed. It includes a general account of efforts to develop immunoassays for identification and quantification of pesticides and industrial chemicals and the development of official guidelines for the adoption of assay kits for contaminant detection in environmental samples, and also describes current commercially available assay kits. For further details on immunoassay methodology, the authors refer to excellent monographs published elsewhere (Tijssen, 1985; Price and Newman, 1991; Masseyeff et al., 1993; Crowther, 1995; Law, 1996) and to a comprehensive review of bioassay/biomarker technology for screening dioxins and dioxin-like compounds by Behnisch et al. (2001).

IV.4.1.2. Immunoassay technology

Immunochemical analytical methods are generally based on the principle of competition between an analyte and a labeled form of the analyte (the tracer) for a limited amount of

a specific binding protein (antibody, immunoglobulin) that was elicited in an animal in response to the injection of a suitable form of the target analyte. The extent of tracer binding will depend on the amount of analyte in the sample. From a calibration graph the amount of analyte can be interpolated.

IV.4.1.2.1. Antibody production

The most important reagent because it determines to a great extent sensitivity and selectivity in an immunoassay is the antibody, which can recognize and bind to the foreign substance. Normally, they are produced only in response to a large molecule (antigen). Small compounds of less than about 1000 Da (haptens) are unable by themselves to elicit an immune response since they are metabolized in the animal. But, after covalent coupling of the hapten to a large carrier protein (the resulting conjugate is termed the immunogen), the immunized animal will produce antibodies also against the attached small molecule. Therefore, the initial task in method development is to prepare an immunogen.

IV.4.1.2.1.1. Immunogen synthesis

If the target analyte contains a suitable group such like a hydroxyl-, sulfhydryl-, amino- or carboxyl function, it can be used for coupling. In the case that these groups should be preserved because they are considered to be of importance for the analyte recognition or if such groups are not present, an analog (analyte derivative) has to be synthesized. For the conjugation to the carrier protein several well-established methods originating from peptide chemistry are available (Hermanson, 1996). With several analytes the introduction of a 4–6-carbon spacer (bridge) between the analyte and the protein was proven to be of advantage for the production of useful antibodies, obviously owing to the better recognition of the attached analytes on the protein surface by the immune competent cells. As carriers a lot of proteins have been described such as serum albumins and gamma-globulins of various species (bovine, human), ovalbumin and thyroglobulin. In accordance with other investigators, we found high immune response using different hemocyanins (keyhole limpet hemocyanine, KLH; helix pomatia hemocyanine, HPH). Optimum coupling density (number of loaded analyte groups) depends on the selected carrier protein, although there is no consensus as to which ratio is best.

Depending on immunoassay format, additional synthesis of a coating antigen which is a heterologous analyte–protein conjugate (different protein compared to the immunogen), or an analyte–enzyme conjugate (the tracer compound in enzyme immunoassays) is required. Both make use of chemical coupling reactions as applied for immunogen synthesis.

IV.4.1.2.1.2. Polyclonal antiserum production

The rabbit is the most commonly used laboratory animal for antiserum production for small analytes. It offers the advantages of being easy to care for, and it produces a moderate amount of serum, often with high antibody amount (titer). However, also

chicken and larger animals such as goats, sheep and horses can be used if available. Only purified and well-characterized immunogens should be applied for the immunization. Together with an immunological adjuvant it is inoculated into the animals' body at reasonable dose and time-scale (immunization schedule) to get an optimum antibody response. While the number of substances with adjuvant activity (from the Latin, *adjuvare*/to help) and the literature describing their use has expanded enormously, their mode of action has remained largely a black box (Werner and Jolles, 1996; Cox and Coulter, 1997). As possible actions are under discussion both immunomodulation, antigen presentation, depot generation, targeting and induction of cytotoxic T-lymphocyte responses. In this laboratory, multiple intradermal injections using Freund's complete and incomplete adjuvants are preferred, similar as described by Vaitukaitis et al. (1971). However, there is no standard protocol, which guarantees success, and most approaches are largely empirical.

The blood is regularly checked for the presence of hapten antibodies and for its specificity and when the titer is satisfactory greater amounts of blood are taken from the ear vein or by cardiac puncture to obtain a stock of antiserum. The serum is separated, divided into small aliquots and in most cases stored at low temperatures (-20, -70°C). Laboratories without access to animal care facilities may provide contracting companies with immunizing conjugate and obtain antisera at specified intervals. Moreover, such companies increasingly provide chemical syntheses, antibody characterization and immunoassays development. However, the "all inclusive" option in most cases is very expensive and further, for the costumer supervision is hardly possible as well as early intervention into the procedure.

However, each polyclonal antiserum will vary in its composition and characteristics both from animal to animal and between the bleedings from the same animal. The characteristics of the antiserum reflect the composite properties of the mixture. Therefore, availability of a polyclonal antiserum is limited thus reducing commercial utilization. Despite these shortcomings in many cases, one animal will supply sufficient antiserum for a very large number of analyses, since the serum can be highly diluted for analysis. Still the majority of commercially available test kits for environmental contaminants is based on polyclonal antibodies.

IV.4.1.2.1.3. Monoclonal antibody production (hybridoma technology)

This technology, introduced by Köhler and Milstein in 1975, makes it possible to cultivate cell lines *in vitro* that can produce a single desired antibody essentially unlimited (Köhler and Milstein, 1975). It is based on the fusion of an antibody-producing cell (a B lymphocyte cell) with a long-lived cancer cell to produce a new hybrid cell with the phenotypic characteristics of both parents. It can grow indefinitely in culture and secrete antibodies uniform in terms of structure and function. Main steps are (1) immunization (generally mice), (2) cell fusion and screening for antibody producing hybridoma cell clones, (3) postfusion cell management and further selection and (4) expansion and scaled-up antibody production. The potentially unlimited supply over a long period of time (as long as the hybridoma cell line is maintained in culture or in storage) of a homogeneous well-characterized antibody reagent especially meets the

demands of regulatory authorities for standardized reagents and methods. The technology is now firmly established and numerous strategies are in use (Peters and Baumgarten, 1989; Stein, 1997). However, because of the high initial labor and costs needed laboratories often hesitate to establish the hybridoma technology.

IV.4.1.2.1.4. Recombinant antibodies (recombinant DNA technology)

In these days a third generation of antibody technology is going to enter the field of environmental immunology. It claims to overcome the disadvantages of hybridoma technology mentioned before by means of methods originating from molecular biology. Basic principle is to isolate genes that encode antibodies from an organism and purifying and reproducing them in another organism. Several different cloning and expression systems have been developed first of all in *E. coli* but also in insect cells, yeast, fungi and plants, all of them constitute easy to grow non-mammalian hosts (Huse et al., 1989; Lee and Morgan, 1993; Hayden et al., 1997). Types of antibody fragments produced are heavy (VH) and light (VL) variable domains, single-chain variable domains (scFv) or Fab fragments. Main advantage of the new technology is that molecular modeling and site-directed mutagenesis of cloned antibodies may provide a more cost-effective and efficient alternative to the tedious synthesis of haptens and accompanied numerous immunizations. It is an exciting new possibility directed on a more efficient manipulation of antibody binding sites to give desirable specificity, binding affinity, tolerance to physical parameters such as pH and temperature, and sensitivity to matrix constituents such as organic solvents and detergents. Type and number of antibodies normally obtained by conventional methods can be extended by several orders of magnitude. First reports on the production of recombinant antibodies, derived mainly from hybridomas, are promising (Karu et al., 1994; Bell et al., 1995; Kramer and Hock, 1996a,b; Hall et al., 1997, Scholthof et al., 1997). Still the method is far from being routine owing to its complexity.

IV.4.1.2.2. Types of immunoassays

Immunoassays can be classified in several directions: (1) type of tracer to quantify the analyte, (2) applied amount of antibodies and (3) separation of bound and free phases is required or not. Table IV.4.1.1 lists possible detection systems. Besides the very early reports on the preparation and characterization of antibodies for environmental contaminants applying hemagglutination (Haas and Guardia, 1968; Centeno et al., 1970), first immunoassays used isotope labels (radioimmunoassay, RIA).

However, practical limitations of RIA, for example, the potential hazards associated with the use of radioisotopes and the requirement of complex instrumentation, are arguments against its application in field test screening. After the introduction of the enzyme immunoassay technique (EIA), it was increasingly used and now is the overwhelming immunoassay type. In these assays an enzyme (most popular are horseradish peroxidase and alkaline phosphatase) is applied for labeling the target analyte or the antibody. If the assay is conducted in solution requiring no separation step the (homogeneous) assay is termed enzyme-multiplied immunoassay (EMIT, but

Table IV.4.1.1. Types of immunoassays classified according to the applied label.

Immunoassay	Marker
Radioimmunoassay	Radioisotope (^{125}I, ^{3}H, ^{14}C, etc.)
Enzyme immunoassay	Enzyme (horseradish peroxidase, alkaline phosphatase, β-D-galactosidase, etc.)
Fluorescence immunoassay	Fluorescein, coumarin derivatives, phycoerythrin, europium^{3+}, samarium^{3+}, terbium^{3+}
Luminescence immunoassay	Isoluminol derivatives, acridinium ester, etc.
Spin immunoassay	Free radical
Viroimmunoassay	Bacteriophages
Metal immunoassay	Metals
Particle immunoassay	Colloids, latex particles
Liposome immunoassay	Liposomes

sometimes also EIA). In contrast to that (heterogeneous) enzyme immunoassays involving the use of a solid phase for separation of bound and free phases before the enzymatic activity (end-point measurement) is determined are known as enzyme-linked immunosorbent assay (ELISA). Both EMIT and ELISA can be run as competitive or non-competitive formats.

IV.4.1.2.2.1. Enzyme-linked immunosorbent assay

Immunoassays for small environmental contaminants rely almost entirely on competitive ELISAs. Usually, plastic tubes, wells of microtiter plates or beads are used as solid phase. The two main principles are demonstrated in Figures IV.4.1.1a and IV.4.1.1b. In the direct competitive ELISA (capture assay) the antibody is immobilized on the solid phase (Fig. IV.4.1.1a). Sample and enzyme tracer (analyte–enzyme conjugate) are co-incubated with the antibody coated surface. Following this step, reagents are washed away and the amount of enzyme tracer bound to the immobilized antibodies is measured by its enzymatic activity after the addition of a chromogenic substrate causing the development of a color. In the indirect competitive format instead of the antibody a coating antigen is immobilized consisting of an analyte or analyte derivative coupled to a protein (this must be different from the protein in the immunogen!) on the solid phase (Fig. IV.4.1.1b). After the addition of sample and antibodies, target analyte from the sample and the coating antigen compete for the antibodies. Antibody binding to the solid phase occurs in inverse proportion to the amount of free analyte present. Quantification of bound antibody fraction by the addition of an enzyme-labeled secondary antibody (raised in a different animal species against the immunoglobulin fraction of the host species that was immunized with the target analyte) provides a measure of the amount of analyte initially present. With both direct and indirect competitive ELISAs, a decrease in

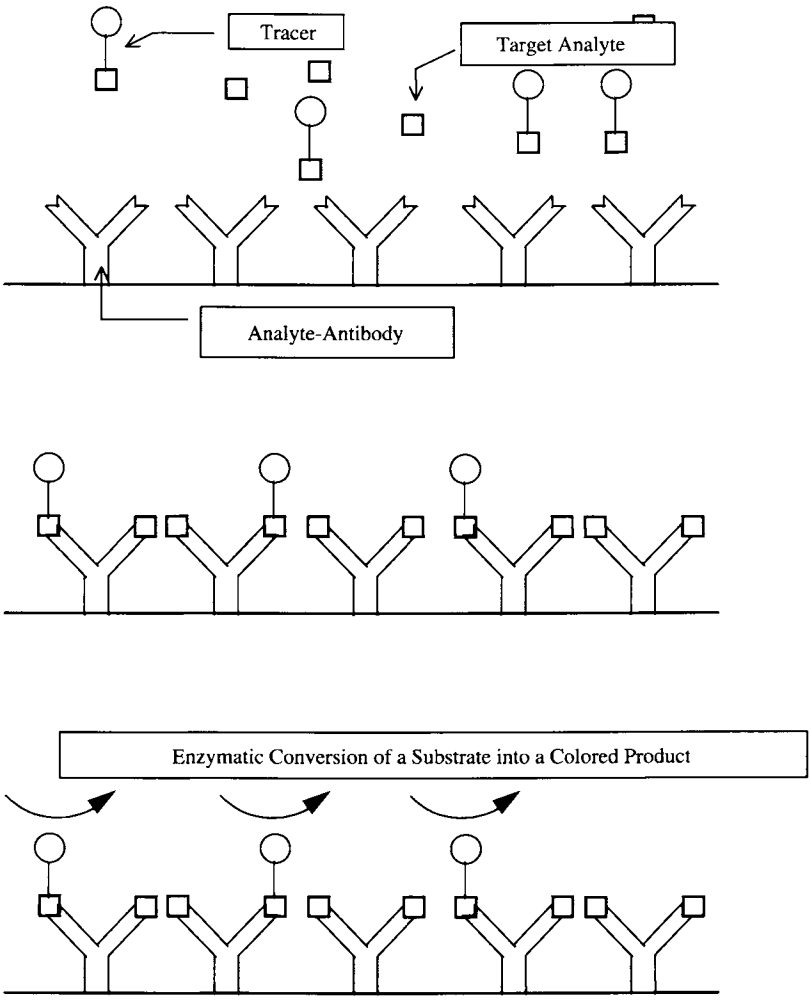


Figure IV.4.1.1a. Principle of a direct competitive ELISA.

enzyme activity is indirect proportional to the amount of analyte in the sample, i.e. the lighter the color produced at the end of the assay the greater is the amount of analyte in the sample. Absorbance can be measured in the laboratory by a special spectrophotometer designed to accommodate a 96-well microtiter plate or in the field by portable equipment or estimated visually.

Both formats have been proven to work with environmental samples. The direct format needs less incubation steps than the indirect one but has the drawback that for each target analyte a new tracer has to be synthesized. Moreover, tracer is exposed to sample matrix that could lead to interferences with enzyme activity by harmful sample components. In contrast, the indirect assay makes use of tracers (enzyme-labeled

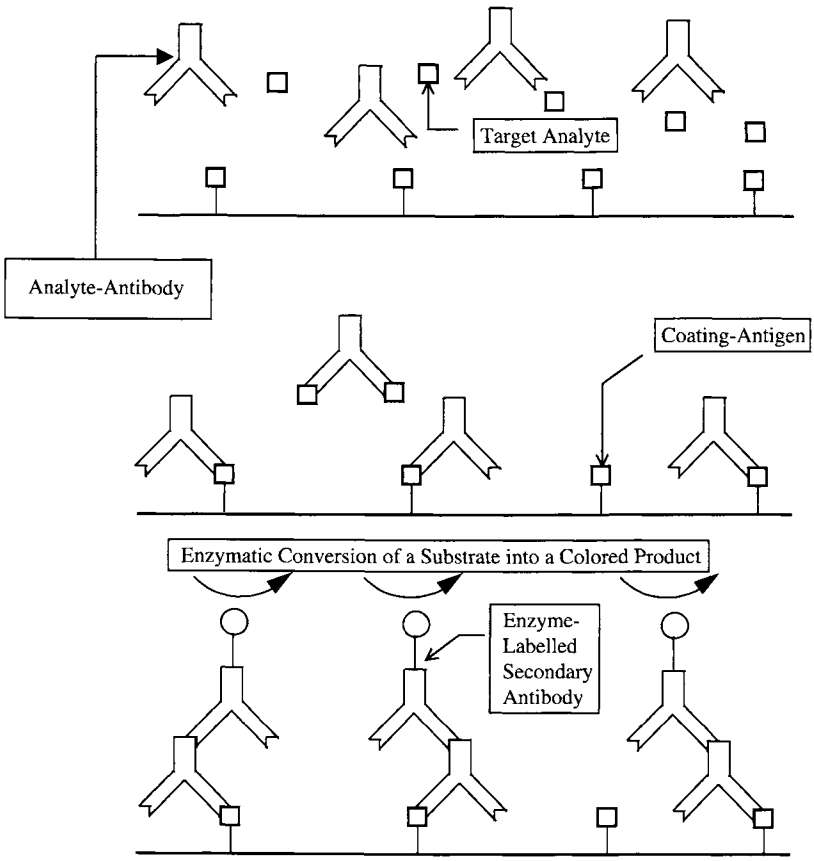


Figure IV.4.1.1b. Principle of a direct competitive ELISA.

secondary antibodies), which are available commercially and will not come into contact with the sample matrix. Although theoretically the indirect format should be more sensitive than its direct counterpart, this seems to be of secondary importance for environmental monitoring if at all.

Analyte amounts in unknown samples are interpolated from an assay calibration curve, which routinely is run on each microtiter plate. The exact shape of this curve is not important, and available curve-fitting programs can approximate this curve using either linearization by logit–log transformation of the data or a sigmoidal shape by four-parameter logistic equations. Mostly, the latter is used plotting logarithmic analyte concentration versus absorbance and taking into consideration only the linear part. In practice, ranges for quantification are most often restricted from 10 to 90% or from 20 to 80% inhibition. Absorbances on the upper or lower asymptotes of the curve can at best be specified as being below or above the corresponding thresholds.

IV.4.1.3. Optimization and validation of an immunoassay

IV.4.1.3.1. Cross-reactivity (CR)

The specificity of an antibody refers to the degree of CR that is the extent to which an antibody reacts with related compounds. For a user it is very important to know which analytes can be trapped in an assay, i.e. which compound could give a positive signal (analyte present!). CR is not limited to polyclonal antisera that constitute a mixture of many different antibodies derived from several lymphocyte clones, but is also an intrinsic property of monoclonal antibodies. Generally, CR is expected as the concentration of a compound needed to displace 50% of the antibody from bound target analyte or target analyte–protein conjugate (Abraham, 1969). It is calculated according to the formula:

$$\%\,\mathrm{CR} = \frac{\text{Target analyte concentration at 50\% antibody binding}}{\text{Concentration of the cross-reacting compound at 50\% antibody binding}} \times 100$$

Data are obtained running the ELISA successively with the target analyte and potential cross-reacting substances. Then, the concentrations at the center point of the calibration curves are compared. In another approach, the percentage CR is defined as the quotient of displacement of the antibody at different points of the calibration curve (DeLauzon et al., 1973). This takes into account that the degree of CR of a compound can vary over the concentration range of the calibration curve. However, at least for environmental immunoassays this approach did not prevail against the calculation of the 50% value. Specificity of antisera may vary strongly and is first of all the consequence of the synthesized immunogen and the applied tracer or coating antigen. In some cases aimed specificity should be as high as possible, for example, when samples should be screened for a single compound. For the determination of sum parameters such as the 16-EPA PAHs, BTX or highly toxic dioxins, lower selectivity is required to use the immunoassay as class specific test. Therefore, an antiserum or antibody should be characterized very early in assay development to find out if it meets the requirements of the assay.

IV.4.1.3.2. Assay sensitivity

Required sensitivity for environmental contaminants is mostly in the ppb or ppt range, depending on target analyte, sample matrix and set threshold limits. According to IUPAC, assays' limit of detection (LOD) is defined as the analyte concentration that will arise after extrapolation to the calibration curve of a zero dose (sample without analyte) minus its threefold standard deviation. For many immunoassays this LOD is still outside the linear part of a sigmoidal calibration curve and therefore is prone to experimental error. As mentioned earlier, the nominal working range should be limited to the linear part that is from 10 to 90% or 20 to 80% of inhibition as concentration estimates in this range are much more reproducible. With constant random error, the precision of an immunoassay increases as the slope of the dose–response curve increases and vice versa. But a steep

calibration curve will cover only a narrow concentration range. Assays' performance characteristics may be quite different in artificial solvents like buffer and highly purified water compared to real matrices. Therefore, performance must strictly be controlled for each matrix type, which is under determination. In those cases where an analyte must be detected close to the LOD, a pre-concentration step can be necessary. Whenever possible, it should be avoided as it interferes with the field-test nature of an immunoassay. Sometimes sensitivity can be tuned up to a point by means of different target analyte derivatives for tracer and coating antigen synthesis, assay formats, pre-incubation of antibodies and analyte, use of fluorogenic enzyme substrates and signal amplification systems (biotin–avidin and biotin–streptavidin auxiliary labels or enzyme cascades) (Avrameas, 1992; Bauer et al., 1995).

IV.4.1.3.3. Matrix effects

The key reagents in immunoassays are proteins (the antibodies) that are sensitive to non-physiological conditions to a different extent. Concluding from this all physical and chemical factors that can interfere with the protein structure can also adversely affect the immunoassay; these are temperature, sample pH, ionic strength and the presence of organic solvents and surfactants (Manclus and Montoya, 1996; Abad and Montoya, 1997). Moreover, dissolved organic matter like humic acids can also interfere with the assay because of specific (recognition of partial structures of the humic acid as antigenic determinants) and non-specific (adsorption of humic acid covering the openings of antibody binding sites or the active center of the enzyme) interactions with the antibodies or the assay detection system (enzyme tracer) (Keuchel et al., 1992; Matuszczyk et al., 1996; Beyer et al., 1997). In addition, the use of antibodies for the identification of non-extractable pesticide residues (bound residues) in humic substances is a new field of immunological analysis (Dosch et al., 1995; Ulrich et al., 1996; Dankwardt et al., 1997). With indirect ELISAs the sample is removed from the microtiter plate before the enzyme-labeled secondary antibody will be added thus excluding interference with the detection system. Such interferences are rare in clinical applications, i.e. for the determination of target analytes in physiological fluids and tissue homogenates making immunological determinations in clinical chemistry much better interpretable. In contrast, detailed investigation of possible matrix effects is an indispensable element of the immunoassay development.

Both positive (overestimation of target analyte) and negative (underestimation of target analyte) interferences are known. This should be demonstrated with results obtained in our laboratory. The effect of different concentrations of water-miscible organic solvents on the antibody–analyte interaction was studied using indirect pyrene- and 1-nitropyrene-ELISAs (Knopp et al., 1997). In that study the effect of solvents on the optical density of a blank (zero analyte) at different concentrations was determined. As outlined in Figures IV.4.1.2 and IV.4.1.3 it was totally different considering the individual solvents and the two antisera. For example, the addition of acetonitrile caused up to sevenfold increase in optical density at 13.3% organic solvent in the 1-nitropyrene-ELISA. In contrast to this, same solvent amount reduced the signal to about 70% in the pyrene-ELISA. Concluding from this, acetonitrile if present at this concentration, could lead to false negative (1-nitropyrene-ELISA) or false positive (pyrene-ELISA) results.

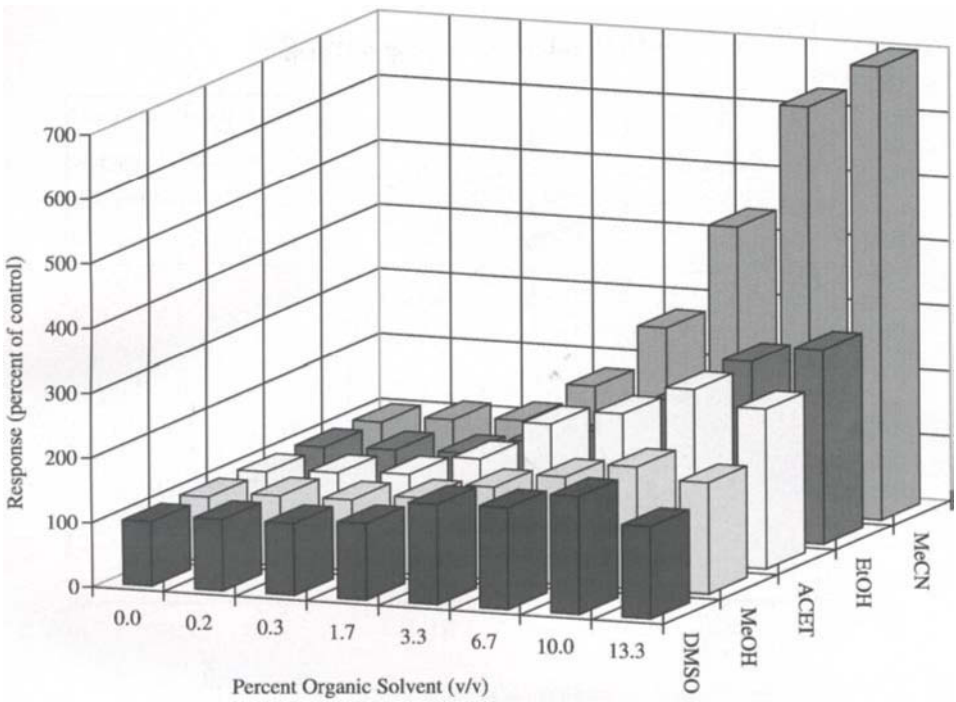


Figure IV.4.1.2. Effect of organic solvents at different concentrations on the optical density of the blank value (1-nitropyrene-ELISA).

In another experiment the effect of humic acid on a direct competitive 2,4-D-ELISA and the indirect pyrene-ELISA was compared (Matuszczyk et al., 1996; Knopp et al., 2000). As shown in Figure IV.4.1.4 with increasing concentration of humic acid, a significant decrease in the maximum optical density was found in the 2,4-D-ELISA. However, the LOD as well as the IC_{50} value changed only slightly to higher concentrations. The same humic acid concentrations had nearly no influence on the signal in the pyrene-ELISA (Fig. IV.4.1.5). Only at the highest concentration (10 mg/l) a small shift of the calibration curve to higher concentrations was observed making this assay much better suited for environmental samples, which contain higher amounts of dissolved organic matter.

IV.4.1.3.4. Sample preparation

As always stated, no or only minimal sample preparation is one of the outstanding properties of immunological methods. However, this depends mainly on the claimed sensitivity and selectivity, the robustness of the assay, the target analyte and on sample matrix type. Generally, a sample preparation can be eliminated with water samples when analyzing groundwater or drinking water, since immunoassays are run predominantly in

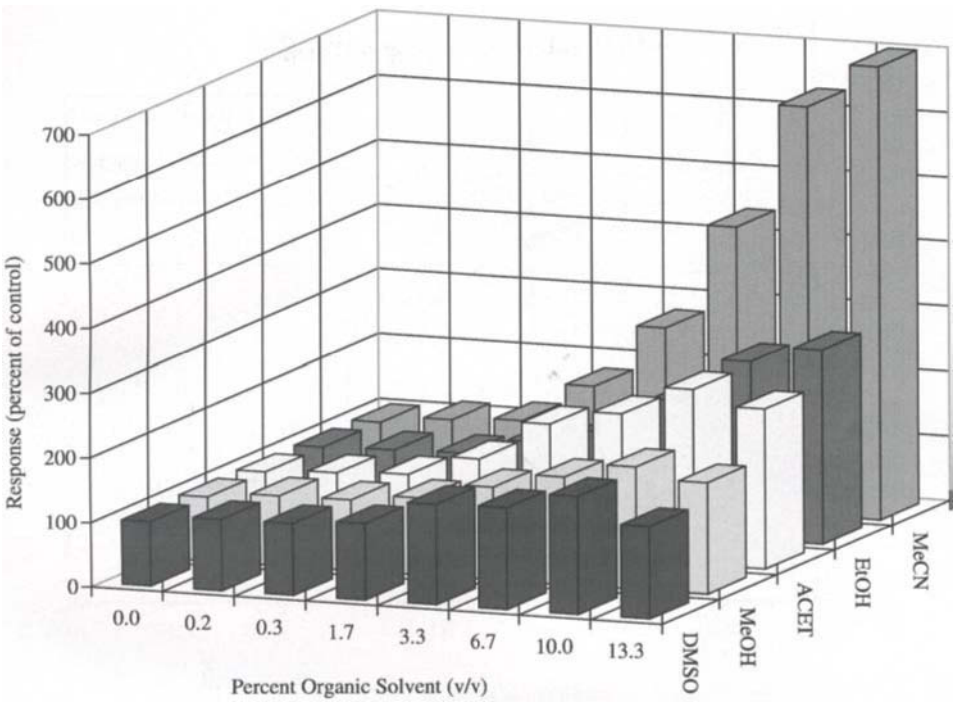


Figure IV.4.1.3. Effect of organic solvents at different concentrations on the optical density of the blank value (1-nitropyrene-ELISA).

aqueous solution. This often comes true also for surface water although with higher cloudiness of the water a filtration step should go ahead. With increasing complexity sample matrix interferences often can be diluted out using purified water or buffer solutions (Knopp et al., 1999). This can only be done with samples that contain higher amounts of target analyte not to get out of the working range of the assay. Solid-phase extraction (SPE) is increasingly used to enrich analytes from aqueous samples (Pollema et al., 1992; Fiehn and Jekel, 1996).

At least for solid samples like solid waste, soils, sediments, plant material and aerosols the sample preparation such as extraction is indispensable. As a rule of thumb with increased enrichment higher reliability and assay sensitivity will be obtained. Therefore, the extent of sample preparation must be in accordance with the later use of the assay. In one case, as for dioxins, a highly sensitive and accurate assay can be aimed at, requiring more extensive sample preparation but still reducing the costs for traditional highly expensive high-resolution GC/MS. In contrast to this, when a great number of samples should be monitored often less sensitive and semiquantitative assays are favored that need only reduced enrichment. Whenever possible, as for polar analytes, sample extraction should be done with aqueous solutions. Anhydrous organic solvents will be necessary to isolate non-polar and lipophilic agents from hydrophobic fractions of environmental samples. After extraction highly volatile solvents can be removed totally or only reduced

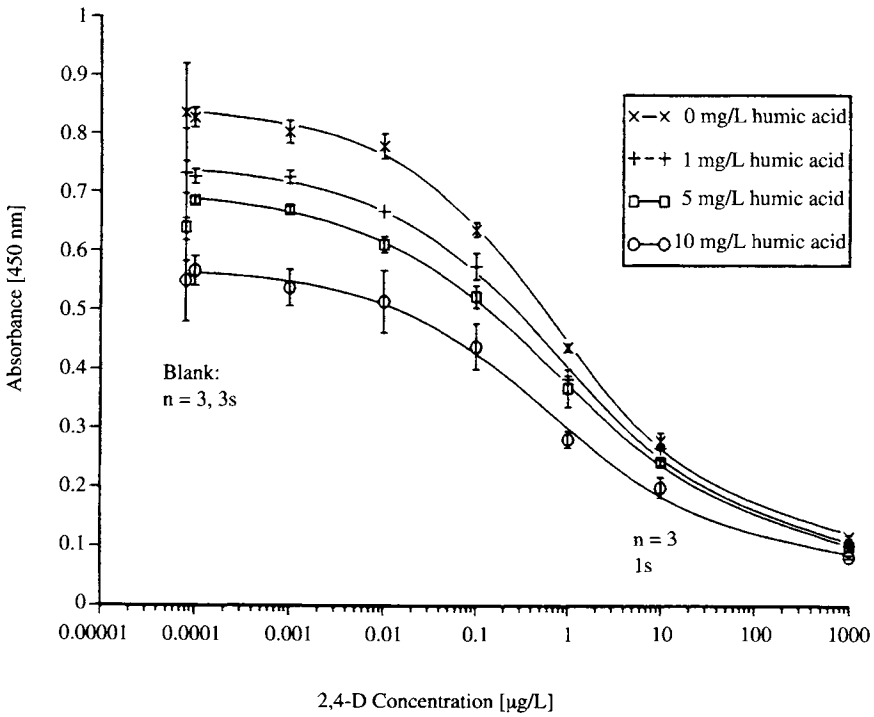


Figure IV.4.1.4. Effect of humic acid on the 2,4-D-ELISA.

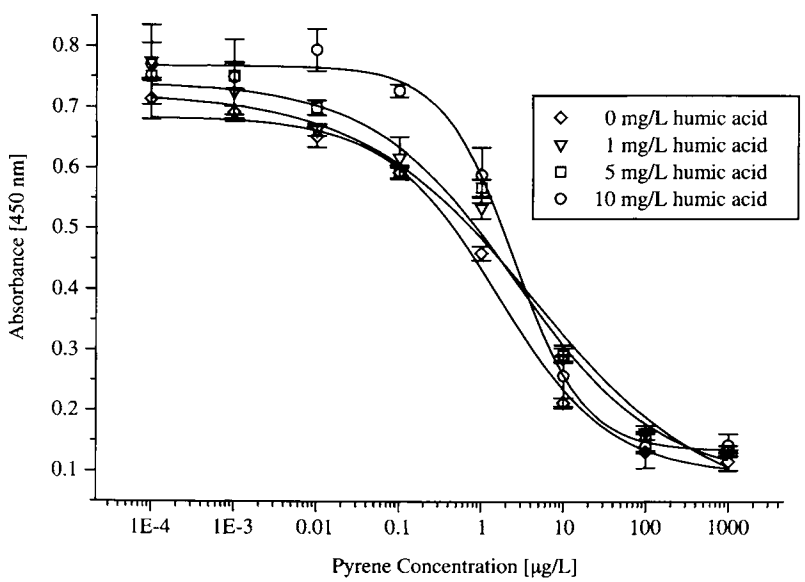


Figure IV.4.1.5. Effect of humic acid on the pyrene-ELISA.

in volume under a stream of nitrogen or under vacuum. In the case of volatile analytes care must be taken to prevent losses. Depending on the solvent compatibility of the assay the dried residue has to be taken up with buffer or another suitable solvent or an aliquot of the extract, mostly a dilution with water or buffer, can be directly transferred to the microtiter plate. Moreover, an organic co-solvent can enhance solubility of the target analyte and therefore prevents wall-adsorption to reaction vessels.

IV.4.1.3.5. Assay validation

Assay validation can be described as a process, which should demonstrate that the analytical method would yield acceptable precise, reproducible and accurate results for a given analyte in a specific matrix. As any other analytical method, immunoassays are prone to several errors. The most important interferences are matrix constituents, which were discussed before. Additional factors are the individual components of the assay system such as hardware (automatic microplate washer and reader), solid-phase material (microtiter plates, tubes, plastic microspheres), pipettes and tips, and the applied reagents (Harrison, 1997). High quality equipments, interfaced with computers to collect and analyze data, are nowadays available from several manufacturers. Microplates, plastic tubes and tips are offered by a vast number of suppliers. Some time is needed to assess the quality and suitability of these materials including monitoring of product lots for lot-wise variability. The same holds true for commercial reagents and chemicals such as enzymes, enzyme-labeled secondary antibodies, blocking agents and substrates; not to forget the quality of in-house reagents like antibodies, coating antigens and buffer solutions. For these substances quality also may vary "lot-wise", i.e. from different preparations and after storage. Whenever possible (sufficient sensitivity, suitable for the matrix of interest...) a critical comparison of an immunoassay with an independent established (non-immunochemical) method should be an inherent part of the immunoassay development. Besides known standards, fortified and unknown samples, different matrices and a sufficient number of field samples of each matrix type from a variety of different locations should be included. Once the results are obtained, the correlation between the methods can be calculated. In addition, any false positives or false negatives generated during the analysis should be noted. False positive results, while not desirable, are not as big a problem, since these samples should be confirmed by means of a reference method. In contrast, falsely identified negative samples, once eliminated from the sample set, are lost to the study. Therefore, a main effort must be directed to exclude as far as possible any tendency to produce false negatives.

IV.4.1.4. Immunoassay standardization

The acceptance of the technology will only be obtained if the same test procedure can be exhibited elsewhere under the same conditions and with identical performance as often as needed. Experience with standardization and quality assurance (QA) from the clinical chemistry can be advantageously transferred to environmental immunochemistry but there are numerous problems, which are unique like the immense variability in composition of environmental matrices and the small size of the environmental market.

Inter-laboratory comparisons (round robin studies) can be performed to assess the applicability of an immunoassay for the analysis of selected matrices. For many years, several federal government and regulatory agencies in the US (FDA, EPA, FSIS, ARS), Canada (Laboratory Service Branch of the Ontario Ministry of the Environment and Energy; Quebec Ministry of the Environment) as well as the Association of Official Analytical Chemists (AOAC), the Immunoassay Group of the Central Committee III of the Division of Water Chemistry in the Association of German Chemists (GDCh) and the IUPAC have been involved in the development of guidelines for the evaluation of immunoassay kits. The Analytical Environmental Immunochemical Consortium (AEIC) was established in 1992 in the USA and is comprised of agrichemical and immunochemical companies, academic institutions and other interested parties that develop, provide or use immunochemical methods and associated equipment for environmental chemical analysis. It was formed to promote the use of immunoassays and to provide a credible but impartial source of information about immunoassays. One of its main tasks is to establish performance standards and quality assurance guidelines.

The primary parameters for evaluating analytical method performance are common to a variety of testing systems. They include precision (variability), specificity, sensitivity (LOD and working range), accuracy and systematic errors (bias). Additional important characteristics are reliability (robustness), defined performance limits, defined quality control and quality assurance, cost-effectiveness, versatility, safety and availability of the test system. An immunoassay test kit as it is commercially available from a manufacturer is a packaged system, which contains the principal components (coated solid phase, enzyme conjugate, antibodies, standards and other reagents). Some kits additionally contain everything needed to perform (in the field) the analysis from beginning to end (disposable sample vessels, spatula, extraction and filtration devices). The *User Directory* added should be unmistakably and comprehensively, adequate to the target group and use of the test kit. Besides a description of the principle of the method, the intended use, sample matrix and claimed performance should be outlined. The analytical procedure should be described very detailed referring also to reagent stability and storage conditions, critical steps and a summary of results from earlier validation experiments.

IV.4.1.5. Environmental applications

Since the development of immunological techniques for pesticide residue analysis was first reviewed by Ercegovich (1971) several very helpful reviews of this application have been published (Hammock and Mumma, 1980; Hemingway, 1984; Newsome, 1986; Hammock et al., 1987; Mumma and Brady, 1987; Vanderlaan et al., 1987, 1988; Hammock, 1988; Harrison et al., 1988; Jung et al., 1989; Gee et al., 1990; Kaufman and Clower, 1991; Sherry, 1992, 1997; Van Emon and Lopez-Avila, 1992; Hock, 1993; Meulenberg et al., 1995; Niessner and Knopp, 2001). Until now, immunoassays for chemical contaminants were mainly developed for screening of aquatic and soil contamination but also for food and crop analysis and the biological monitoring of exposed individuals. The vast majority of these methods was applied for pesticides including herbicides, insecticides and fungicides that are generally hydrophilic, non-volatile and stable in water. However, the spectrum was extended also to other trace

contaminants like polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and BTX (benzene, toluene, xylenes) that are lipophilic and in some cases highly volatile. In Table IV.4.1.2, commercial immunochemical test kits are summarized according to the suppliers' information. If taking into consideration also relevant publications from the scientific literature, then the number of environmental chemicals for which an immunoassay has been developed would be even higher.

As always introduced the advantages of immunoassay techniques lie in their sensitivity, specificity, wide applicability, adaptability to laboratory or field situations, speed and low cost. New insights into small-volume scaled processes are possible, too. Single rain droplets can be analyzed without any further manipulation. In its present configuration required sample volume is on the order of microliters, making immunoassays a true microanalytical tool. Often analyses can be carried out directly in the crude sample or with only minimal sample preparation such as simple dilution thus avoiding extraction and cleanup steps. This is of special importance if a huge number of samples has to be measured as it can be necessary for the monitoring of remediation processes, site mapping and identification of "hot spots". Therefore, the application of immunoassays is highly indicated for screening purposes to separate "negative" samples (no target analyte present or only detectable at levels below a set threshold limit). In order to demonstrate some of the advantages and limitations of environmental immunoassays, some preliminary results of a study are summarized below that was conducted at our laboratory to compare immunochemical and traditional analytical determination (HPLC) of PAHs in real-world environmental samples such as groundwater, soil and leaching water from waste deposits (Knopp et al., 1995, 2000; Seifert, 1996).

IV.4.1.5.1. ELISA for polycyclic aromatic hydrocarbons

PAHs are ubiquitous environmental pollutants of natural or anthropogenic origin. They are formed due to incomplete combustion of various materials particularly fossil fuels. Sources of PAHs are power stations, domestic and industrial heating systems, combustion engines (diesel and petrol) and refuse burning. PAHs present in the atmosphere are distributed between gas and particle phases. They are transported over long distances and can be found in wet and dry deposition. Contamination of soils can differ widely depending on local immission situation. Manufactured gas plant sites and cokery sites are known for significant PAH-release into surrounding soil. The International Agency for Research on Cancer (IARC) stated that there is sufficient evidence that some of these compounds are carcinogenic to experimental animals. The US Environmental Protection Agency (US EPA) has identified 16 unsubstituted PAHs as priority pollutants: naphthalene, acenaphthene, acenaphthylene, phenanthrene, anthracene, fluorene, benz[a]anthracene, chrysene, fluoranthene, pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene. For the analysis of environmental samples, purification and enriching followed by a powerful chromatographic separation and identification are required (Lintelmann et al., 1993; Rose et al., 1993). Most utilized is HPLC with UV (254 nm) or fluorescent detection. Rapid, simpler and more cost-effective methods would facilitate analytical measurements.

Table IV.4.1.2. Commercial immunochemical test kits for priority pollutants (P, plate kit; T, tube kit).

Target analyte	Manufacturer
Acetochlor	Coring-System (P)
Alachlor	Mallinckrodt Baker (T), Coring-System (P,T)
Aldicarb	Mallinckrodt Baker (T), Coring-System (P,T)
Atrazine (triazines)	Mallinckrodt Baker (T), Coring-System (P[a],T), Riedel de Haen (P)
Bioresmethrin	Coring-System (P)
Captan	Mallinckrodt Baker (T)
Carbaryl	Mallinckrodt Baker (T)
Carbendazim/benomyl	Mallinckrodt Baker (T)
Carbendazim/MBC	Coring-System (P,T)
Carbofuran	Mallinckrodt Baker (T), Coring-System (T)
Chlordane	Coring-System (T)
Chlorpyriphos	Mallinckrodt Baker (T), Coring-System (P)
Chlorpyriphos-methyl	Coring-System (T)
Chlorothalonil	Mallinckrodt Baker (T)
Chlorsulfuron	Coring-System (P)
Cyanazin	Mallinckrodt Baker (T), Coring-System (P)
Cyclodiene	Coring-System (T)
2,4-D	Mallinckrodt Baker (T), Coring-System (P,T)
DDT	Coring-System (T)
Endosulfan	Coring-System (P)
Diazinon	Coring-System (P)
Fenitrothion	Coring-System (P,T)
Harnstoffherbizide	Coring-System (P)
Hexazinon	Coring-System (P)
Isoproturon	Coring-System (P)
Lindan	Coring-System (T)
Metalaxyl	Coring-System (P)
Methoprene	Coring-System (P)
Methomyl	Mallinckrodt Baker (T)
Metolachlor	Mallinckrodt Baker (T), Coring-System (P)
Metsulfuron-methyl	Coring-System (P)
Microcystin	Coring-System (P,T)
Molinat	Coring-System (P)
Paraquat	Mallinckrodt Baker (T), Coring-System (P)
Parathion/parathion-methyl	Coring-System (P)
Pirimiphos-methyl	Coring-System (P)
Procymidone	Mallinckrodt Baker (T), Coring-System (P,T)
Silvex	Mallinckrodt Baker (T), Coring-System (T)
Thiabendazol	Coring-System (P)
Toxaphene	Coring-System (T)
Triasulfuron	Coring-System (P)
Triclopyr	Mallinckrodt Baker (T)
Trichlorpyridonol	Mallinckrodt Baker (T)
BTEX	Mallinckrodt Baker (T), Coring-System (T)

(*continued*)

Table IV.4.1.2. (Continued)

Target analyte	Manufacturer
Pentachlorophenol	Mallinckrodt Baker (T), Coring-System (T[a])
Petroleum hydrocarbons	Coring-System (T)
PCB	Mallinckrodt Baker (T), Coring-System (T[a])
PAH	Mallinckrodt Baker (T), Coring-System (T[a]), Quantix (P)
TNT	Mallinckrodt Baker (T)
RDX	Coring-System (T)
Mercury (II) ions	BioNebraska (P[a],T)

Summarized according to the available literature and the suppliers' information. If not signed otherwise the test kits are based on polyclonal antibodies.
[a]Monoclonal antibody-based test kit available.

Commercial immunochemical test kits for the determination of total PAH-content in soil were offered in the past by *Mallinckrodt Baker* (LOD 70 μg/kg, tube kit), *Coring-System* (LOD 100 μg/kg, tube kit), *Quantix* (LOD μg/kg, microtiter plate kit) and *Merck* (600 μg/kg, immunofiltration device). Application of these kits for water analysis is also possible: *Mallinckrodt Baker* (LOD 0.7 μg/l), *Coring-System* (LOD 1 μg/l), *Merck* (8 μg/l) and *Quantix* (LOD 50 μg/l). Moreover, *Mallinckrodt Baker* offered a carcinogenic PAH-ELISA (LOD 0.2 μg/l in water and 20 μg/kg in soil). The PAH-ELISA used in the described study was developed at our laboratory and was based on polyclonal antibodies raised in rabbits against a pyrene–KLH conjugate (Meisenecker et al., 1993). Test format was an indirect competitive ELISA performed in 96-well micotiter plates. The linear dynamic range of the method calibrated with pyrene was 0.05–5 μg/l (from 20 to 80% inhibition) for aqueous standards and 0.25–20 μg/l (from 20 to 80% inhibition) for aqueous standards containing 10% acetonitrile as they were used for the analysis of extracts from soil.

IV.4.1.5.1.1. Groundwater monitoring

Because of building activities in the area of a former gas plant site, a mobilization and wash-out of PAHs from the contaminated soil with the lowered groundwater level were noticed. For purification the water was removed from the quarternary groundwater layer downstream of the contaminated area and cleaned with multilayer filters and activated charcoal. Purification process was controlled routinely by HPLC-analysis of the PAH-content. Including sample preparation throughput was about 15 analyses every 3 days. Supposing the immunochemical results (pyrene-equivalents as calculated from pyrene calibration curve) to be approximate values of the total PAH concentration then these data compare very well ($r = 0.82$) with the sum of 16-EPA PAHs as measured by HPLC (without acenaphthylene which cannot be detected by fluorescence) (Fig. IV.4.1.6). Based on 114 determinations the immunoassay generated an 18% false positive (defined as a positive response for a sample that contains the 16-EPA PAHs below the claimed action level of 0.2 μg/l) and no false negatives (defined as a negative response for a sample that contains the 16-EPA PAHs at the action level of 0.2 μg/l). The majority of the false

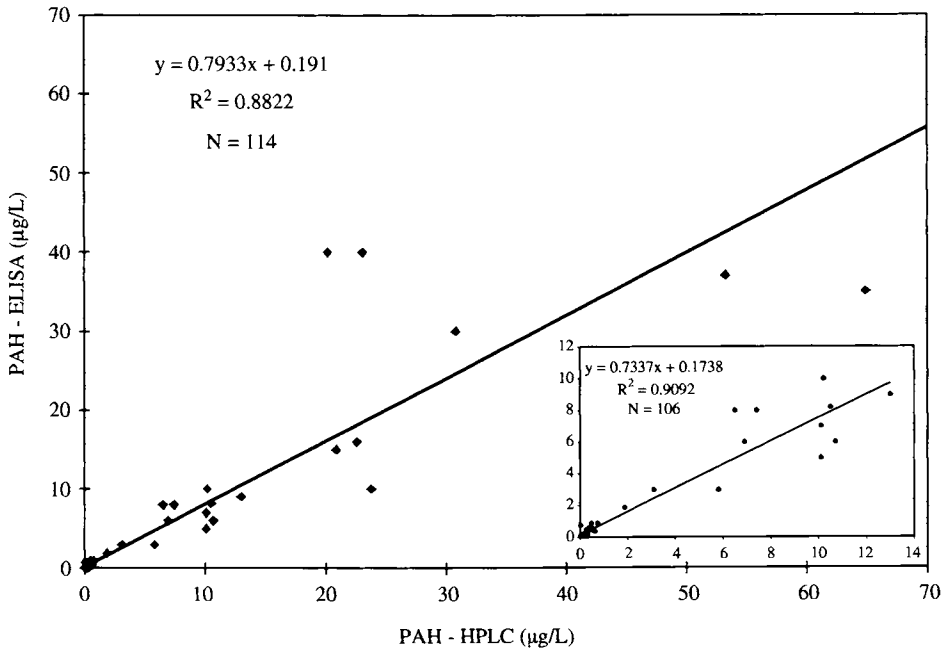


Figure IV.4.1.6. Comparison of HPLC- and ELISA-PAH determination in contaminated groundwater of a former gas plant site. Individual values represent the sum of 16-EPA PAHs as measured by HPLC (without acenaphthylene) and were correlated to the amount of pyrene-equivalents as calculated from the pyrene calibration curve.

positive results were at concentrations near the detection limit. However, as can been seen from the slope of the regression line, ELISA results were on average significantly lower than corresponding summarized PAH concentrations from HPLC. This was not surprising because the antibodies will never exhibit identical binding affinity to each of the single PAH compounds. In this case, only those chemicals, which are structurally most related to pyrene (the immunizing hapten) and which exhibit some higher water solubility could bind to the antibodies to a certain extent. These are first of all fluoranthene and phenanthrene as was found in cross-reactivity studies with calibration standards that were prepared to cover water-soluble concentration ranges. At present, nearly nothing is known whether PAH metabolites can also contribute significantly to the ELISA signal. This is mainly caused by the lack of available metabolite standards to measure cross-reactivity. It is known from the literature that a wide variety of bacteria, fungi and algae have the ability to metabolize PAHs starting with the incorporation of molecular oxygen (Shuttleworth and Cerniglia, 1995). As an example, the cross-reactivity of 1-hydroxypyrene was found to be 180% in this ELISA pointing to the importance of biodegradation products as potential interfering compounds. In accordance with these findings, Li et al. (2000) reported an overestimation of PAHs in water and sediment samples by ELISA over GC–MS which was attributed to, at least in part, PAH metabolites. The presence of 1-hydroxypyrene was confirmed by HPLC-fluorescence in that study. This is of special

interest for those immunoassays that aim at a whole group of target analytes as in the case of PAHs.

IV.4.1.5.1.2. Soil monitoring

In a further study the application of this ELISA for soil samples was investigated. Generally, immunological determination of soil matrices is (1) more complex compared to aqueous samples because the target analyte has to be extracted and (2) interferences by soil constituents such as humic acids are often found. Starting with fortification experiments using well-characterized standard soils and several extractive procedures were compared to study PAH-recovery (Fig. IV.4.1.7).

Efficiency was comparable using ultrasonication (acetonitrile) or soxhlet extraction (tetrahydrofurane) and was on average some lower (about 10%) using agitation (acetonitrile). PAH determination again was performed in parallel with HPLC and ELISA. The same extractive procedures were tested with aged field samples from several sites including forest soil, farmland, grassland, city ground, soil of a former gas plant site, and a reference material that was certified with EPA SW-846 methods 3540 and 8270 by 20 laboratories. As measured with HPLC, PAH concentration ranged between 0.15 and 703 μg/g of soil. As with the spiked samples soxhlet extraction and ultrasonication showed similar efficiency whereas agitation resulted in a loss of recovery of about 10%. In comparison to the previous groundwater samples ELISA determination of soil extracts resulted in a much greater underestimation of PAH concentration when comparing the pyrene-equivalents with the sum of the 16-EPA PAHs (without acenaphthylene) from HPLC (Fig. IV.4.1.8). Again this was not surprising looking at the PAH profile in the soils and taking into consideration the cross-reactivity pattern of the antiserum (Fig. IV.4.1.9).

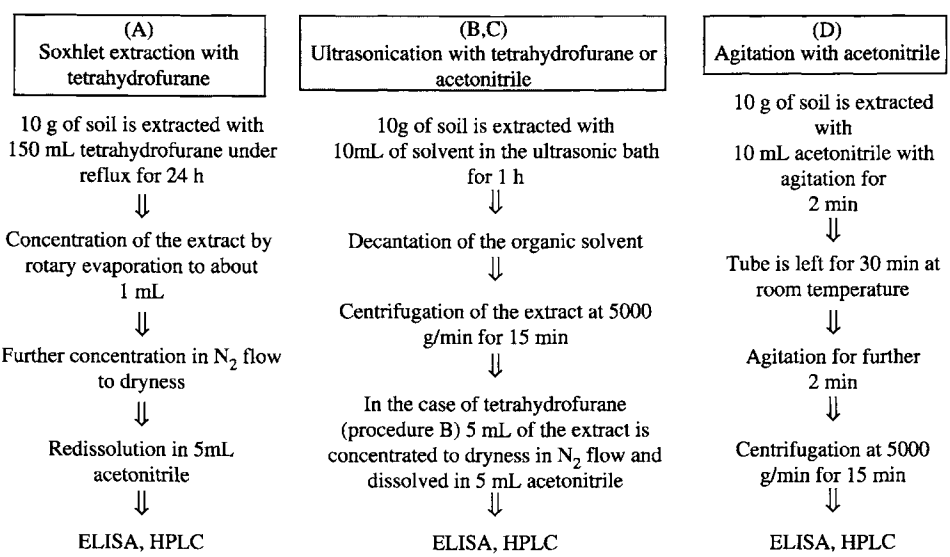


Figure IV.4.1.7. Extraction procedures tested for the recovery of PAHs from soil.

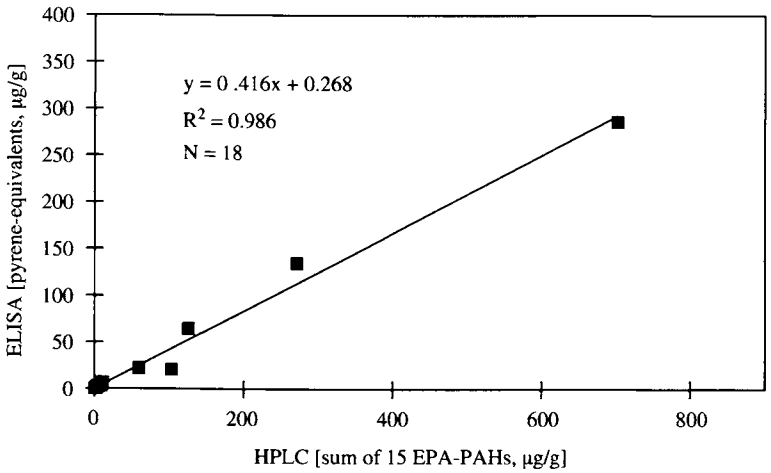


Figure IV.4.1.8. Comparison of HPLC- and ELISA-PAH determination in soil extracts. Individual values represent the sum of 16-EPA PAHs (without acenaphthylene) as measured by HPLC and were correlated to the amount of pyrene-equivalents as calculated from the pyrene calibration curve.

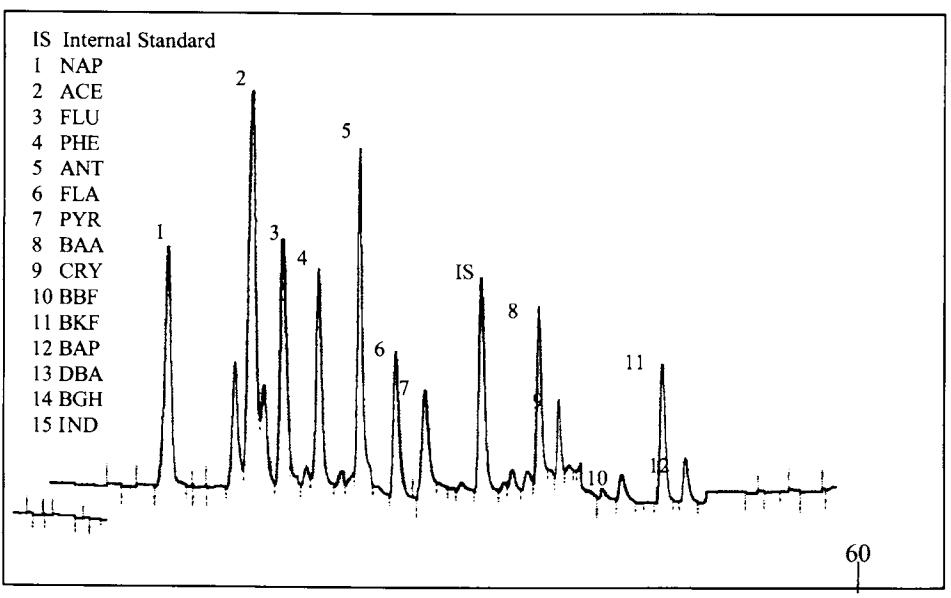


Figure IV.4.1.9. HPLC chromatogram of a highly contaminated soil from a former gas plant site. Extract was diluted 1:500. Used abbreviations of PAH compounds: NAP, naphthalene; ACE, acenaphthene + acenaphthylene; FLU, fluorene; PHE, phenanthrene; ANT, anthracene; FLA, fluoranthene; PYR, pyrene; BAA, benz[a]anthracene; CRY, chrysene; BBF, benzo[b]fluoranthene; BKF, benzo[k]fluoranthene; BAP, benzo[a]pyrene; DBA, dibenz[a,h]anthracene; BGH, benzo[ghi]perylene); IDP, indeno[1,2,3-cd]pyrene.

Table IV.4.1.3. Classification of ELISA results.

Class	Contamination level	ELISA-pyrene equivalents (μg/g)	Estimated PAH-level (sum of the 16-EPA PAHs, μg/g)
1	Very low	<0.35	<1
2	Low	0.35–3.5	1–10
3	High	3.5–35	10–100
4	Very high	>35	>100

The ELISA data were classified according to Table IV.4.1.3 to consider if it can be used for a semiquantitative estimation of the PAH contamination in soils. Applying this for all the data obtained so far with the soil extracts about 5% of the estimated PAH concentration was either false positive or false negative (Table IV.4.1.4) pointing again to the effect of target analyte partition and relative response factors (reactivity of the analytes in the test sample relative to the reference compound in the assay) on the correctness of results in class specific ELISAs. The false negative sample from this study

Table IV.4.1.4. Assessment of the classification set-up.

Soil type	ELISA-pyrene equivalents (μg/g)	Class	HPLC-sum of 16-EPA PAHs (without acenaphthylene) (μg/g)	Estimation of PAH-contamination level with the ELISA
Reference soil	0.02	1	0.26	Correct
Reference soil	0.03	1	0.15	Correct
Reference soil	0.05	1	0.33	Correct
Grassland	0.05	1	0.18	Correct
Reference soil	0.13	1	0.25	Correct
Forrest soil	0.17	1	2.56	False negative
Forrest soil	0.35	2	2.11	Correct
Reference soil	0.54	2	0.57	False positive
Farmland	1.0	2	1.78	Correct
Farmland	2.2	2	4.61	Correct
Grassland	2.94	2	4.22	Correct
City ground	3.1	2	8.9	Correct
City ground	6.6	3	11.2	Correct
EPA-reference soil	20.6	3	98.2	Correct
City ground	22.2	3	59.57	Correct
Gas plant soil	64.22	4	126.09	Correct
Gas plant soil	134.6	4	271.59	Correct
Gas plant soil	286	4	702.92	Correct

contained a phenanthrene proportion greater than 70%. Because this compound shows a cross-reactivity of only about 10%, the extrapolation of the ELISA-"pyrene-equivalents" led to an underestimated PAH-level. Perhaps, it will be possible for this PAH-ELISA as for class specific ELISAs in general that the rate of false negative results can further be reduced and accuracy enhanced by a fairly simple approach: Determination of the target analyte partition of a few random samples from the contaminated site with a traditional technique as the base for the calibration of the ELISA with the known cross-reactivities of the individual compounds (site-specific calibration). However, this has to be proved in the future.

IV.4.1.5.1.3. Leaching water monitoring

Depending on the type of the waste deposit leaching water can constitute an extremely complex matrix difficult to be analyzed by immunochemical techniques. In this study, leaching water from two different waste deposits was analyzed in regard to the PAH contamination. While the water from the municipal waste deposit showed only a weak cloudiness, the sample from the special waste deposit was a dark fluid covered by an oily layer disseminating a strong smell of coal tar. As was found with HPLC, PAH concentration was rather low (28 μg/l) in the sample from the municipal waste deposit but was very high in the aqueous (8.15 mg/l) and oily (540 mg/l) layers of the sample from the special waste deposit. The lower condensed higher water-soluble 2-, 3- and 4-ringed PAHs dominated in both samples with a high excess of naphthalene in the sample from the special waste deposit. Water from the municipal waste deposit as well as the aqueous layer of the special waste deposit could be analyzed with the ELISA after at least 1:100 pre-dilution of the samples, as was found with fortification experiments. Underestimation of the PAHs was in the same order as described for the soil samples, i.e. recovery was 25% (special waste deposit) and 40% (municipal waste deposit) compared to HPLC. For the immunochemical analysis of the oily layer from the special waste deposit it was pre-diluted 1:10,000 with acetonitrile and then applied as acetonitrile/water (10:90, v/v) solution directly in the ELISA. Recovery rate found for PAHs in this sample was only about 2% compared to HPLC, obviously owing to matrix interferences. PAH profile in both layers was very similar but the sum of the 16-EPA PAHs by a factor of about 66 was higher in the oily layer (Figs. IV.4.1.10, IV.4.1.11a and IV.4.1.11b).

To summarize, the PAH-ELISA was proven to be applicable to groundwater samples from a gas plant site for screening out samples of PAH concentration (as the sum of the 16-EPA PAHs) below 0.2 μg/l (threshold limit as set by the German Drinking Water Act) and thus, as the main advantage in this case, leading to reduced sample load for the time-consuming and more costly traditional analytical method. Application to different soil samples ($n = 18$) revealed that 5% of the estimated PAH concentration was either false positive or false negative that was mainly caused by the PAH partition in the sample. ELISA results can be classified to be used for an estimation of the PAH concentration at levels < 1, $1-10$, $10-100$ and > 100 ppm. PAHs can be recovered from soil with high yield using 1-h ultrasonication with acetonitrile (for laboratory ELISA). Extraction efficiency is lower with agitation but is acceptable as part of a first-step on-

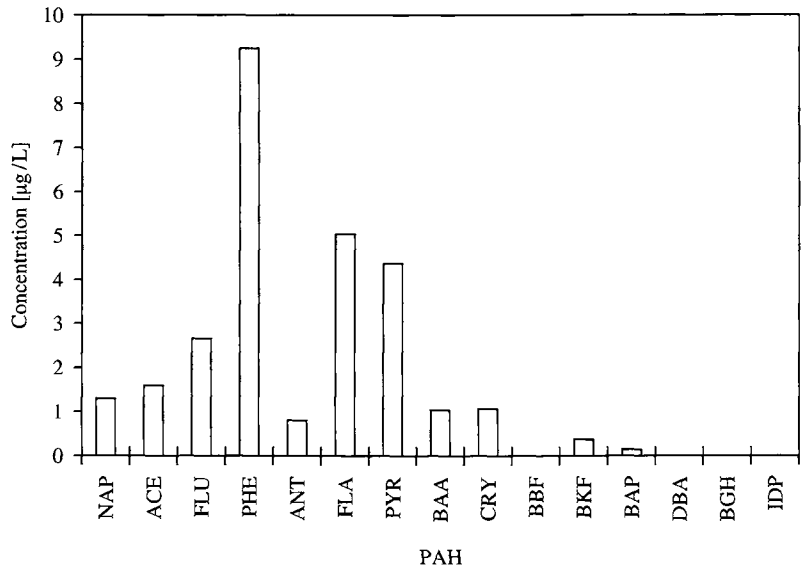


Figure IV.4.1.10. PAH-profile in the leaching water from a municipal waste deposit. PAH order and used abbreviations: as in Figure IV.4.1.9.

site field test to provide rapid, semiquantitative and reliable test results for making environmental decisions. While groundwater samples can be measured directly, soil and leaching water require at least 1:100 dilution prior to immunochemical analysis to remove matrix interferences. The classification set-up proposed for the estimation of the PAH-level in soils was also applicable to the leaching water samples from municipal and special waste deposits as well.

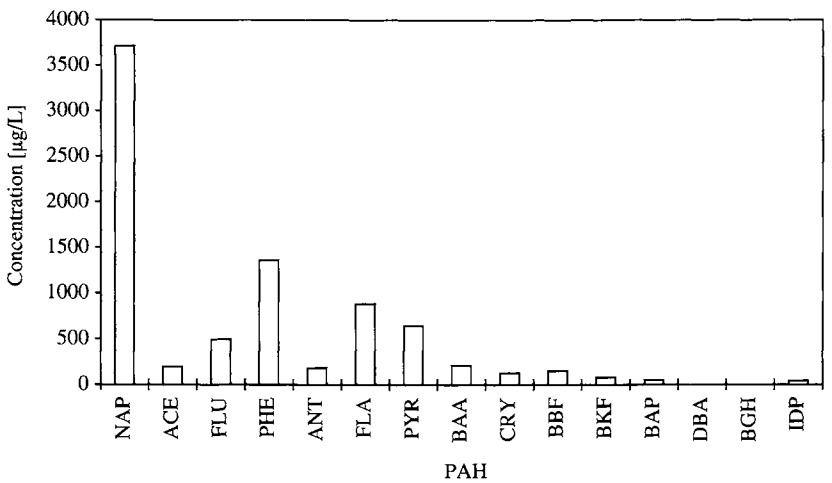


Figure IV.4.1.11a. PAH-profile in the leaching water from a special waste deposit. PAH order and used abbreviations: as in Figures IV.4.1.9 and IV.4.1.10.

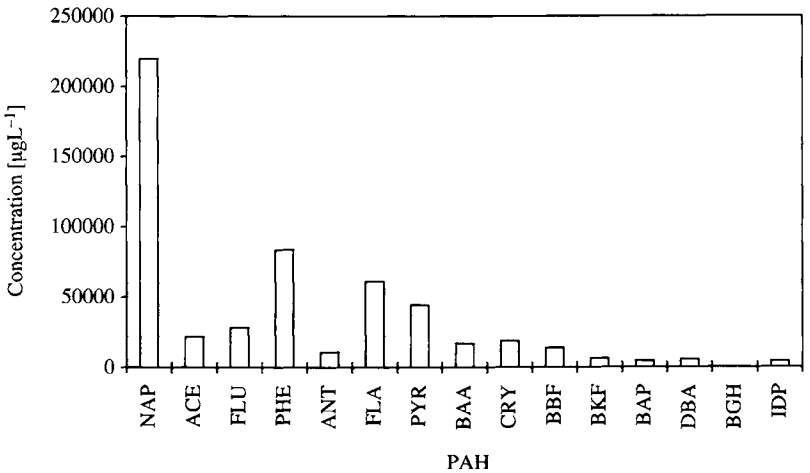


Figure IV.4.1.11b. PAH-profile in the oily layer of the leaching water from a special waste deposit. PAH order and used abbreviations: as in Figures IV.4.1.9, IV.4.1.10 and IV.4.1.11a.

IV.4.1.6. Future immunochemical techniques

There are several emerging concepts of immunoanalysis. Flow injection analysis (FIA) and immunology have been combined to create flow injection immunoanalysis (FIIA; antibody-based flow-through immunosensor) that enables analysis to be carried out in a rapid, on-line and automated way. It has been employed in variety of devices (Liu et al., 1991; Pollema et al., 1992; Gunaratna and Wilson, 1993; Whelan et al., 1993; Ruzicka, 1994; Kumar et al., 1996; Gonzalesz-Martinez et al., 1997; Krämer et al., 1997; Narang et al., 1997; Fránek et al., 2000; Bjarnason et al., 2001; Nistor et al., 2001). Other efforts are directed on the development of test-strips or immunofiltration arrangements based on immunological principles that could be very suitable to perform a semiquantitative, rapid, inexpensive and non-instrumental analysis on-site (Rittenburg et al., 1990; Schneider et al., 1991; Anonymous, 1993; Dankwardt and Hock, 1993; Giersch, 1993; Keuchel and Niessner, 1994; Siebert et al., 1995; Del Carlo et al., 1998; Morais et al., 1999). Evaluation can be done visually or spots can be read out by a pocket reflectometer. Some additional future growth areas are high-performance immunoaffinity chromatography, multianalyte immunoanalysis and molecular imprinting techniques that could be of special interest for the monitoring of solid waste sites and therefore, should be introduced in some more detail below.

IV.4.1.6.1. High-performance immunoaffinity chromatography (HPIAC)

Normally, the initial sample preparation steps where analytes must be purified and enriched from environmental samples are the most time-consuming part of an analytical method. Nowadays, several solid-phase materials (chemical adsorbents) in the format of cartridges or discs are increasingly used for the isolation of target analytes from complex

matrices (El Harrak et al., 1996). However, these adsorbents are not very selective but rather will retain chemical compounds by their non-polar or polar nature. Higher selectivity can be obtained using an immobilized secondary molecule (ligand; that may also be a biomolecule) on the solid-phase material that exhibits higher affinity to the target molecules (affinity chromatography) (Cass and Ligler, 1988). Immunoaffinity chromatography, as the term suggests, exploits the fine specific and reversible interaction between an antibody and its antigen to purify and concentrate the antigen from a crude sample that may include soluble and insoluble impurities. In the opposite manner an immobilized antigen can be used to isolate its antibody from a polyclonal antiserum. Typically, the antibody is immobilized on an insoluble support matrix by simple adsorption or covalent coupling, which mainly depends on matrix type and antibody stability (Schramm et al., 1993). The ideal support material is of high mechanical stability, macroporosity, ease of activation, hydrophilicity and inertness. The most popular support matrices for affinity chromatography are beaded agarose, polyacrylamide gels, azlacton functional copolymer beads and silica-based packings (bonded-phase silicas, glass beads, coated glass beads). There currently exist many methods for activation of the supports that can be divided into those that produce randomly oriented immobilized ligands (attachment of the ligand to the support via primary amino groups on the protein is favored) and those that produce more uniformly oriented species (attachment via the Fc region). A new approach is the physical entrapment of the antibodies in the pores of a silicate glass prepared by the sol–gel technique (Avnir et al., 1994; Dave et al., 1994; Avnir, 1995; Lev et al., 1995; Zühlke et al., 1995; Turniansky et al., 1996; Roux et al., 1997; Cichna et al., 1997a,b; Doody et al., 2000; Lan et al., 2000; Altstein et al., 2001; Pulido-Tofino et al., 2001). This support offers a number of advantages like improved stability and no antibody leaching even under harsh elution conditions. Although there were published first results which were obtained with real samples, the method is still in its infancy (Scharnweber et al., 2000; Spitzer et al., 2000; Cichna et al., 2001).

The principal stages of immunoaffinity separations are loading, washing, elution and regeneration. Following loading, the immunoaffinity support is washed to remove impurities present in the sample as well as those bound non-specifically to the matrix. During the elution step, the captured analyte is removed from the column by using a solvent that reduces the affinity of the analyte to the antibody such like extreme pH, chaotropic agents, organic solvents, low ionic strength and others. A regeneration step should follow to prepare the column for loading again if the affinity support is to be reused. No single schedule seems to work best for all antibodies and is still a trial-and-error procedure (Yarmush et al., 1992a,b).

Complementary features of immunoaffinity chromatography and traditional chromatographic techniques (HPLC, GC, CE) allow them to be combined to produce a highly efficient technology with superior selectivity, speed and sensitivity. This can be realized off-line using cartridges or on-line with a tandem system using an immuno precolumn (high-performance immunoaffinity column) and column switching. Based on the results of numerous applications mainly from residue and pesticide analysis, it can be speculated that this approach will be extended to other classes of environmental pollutants and their degradation products as well in the near future (Farjam et al., 1991; Orthner et al., 1991; Van Ginkel, 1991; De Frutos and Regnier, 1992; Kim et al., 1993; Stanley et al., 1993; Vanderlaan et al., 1993; Kussak et al., 1994; Rule et al., 1994; Thomas et al., 1994; Marx

et al., 1995; Matuszczyk et al., 1995; Pichon et al., 1995, 1996; Wong et al., 1995; Lawrence et al., 1996; Nedved et al., 1996; Rollag et al., 1996; Strong et al., 1996; Van Emon and Lopez-Avila, 1996; Hage et al., 1997; Shelver et al., 1998; Weller, 2000; Delaunay et al., 2000; Bou Carrasco et al., 2001). Whether the principle of immunoaffinity also can be used successfully for routine monitoring of air-borne pollutants such as indoor air studies, workplace monitoring, and studies on air-mediated transport of organic compounds will depend first of all on the development of devices suitable to keep necessary liquid, which is required for the sampling antibodies.

IV.4.1.6.2. Multianalyte immunoassays

A limitation of an immunoassay compared to common chromatographic techniques often specified by environmental analysts consists in its single-compound analysis. However, this is only partly true. Because antibodies target epitopes, not the whole antigen, multiple substances may have the same or similar epitopes. When this is the case the cross-reactivity of antibodies can be used for a multiresidue analysis of structurally related compounds that might be a class of pesticides such as the triazines including a number of metabolites. If there is available a library of antibodies (an antibody array) exhibiting a different pattern of affinity for a series of structurally related compounds, an appropriate statistical analysis (multivariate statistical techniques, parametric models) has the power to turn the problem of cross-reactivity into an advantage. Moreover, the number of antibodies required will typically be less than the number of target analytes. Multiple immunoanalysis using an immunoarray, a panel of less selective antibodies with differing affinity patterns, can proceed in different directions. One is mixture analysis in which samples are assumed to contain mixtures of analytes coming from a known small set of cross-reacting compounds (usually no more than four). In another approach, samples are assumed to contain only one unknown analyte from a class of possible compounds (Jones et al., 1997). The immunoarray responses are used first to identify the analyte and then to estimate the concentration. Further, the application of neuronal networks for pattern recognition has also been applied to the analysis, with the inputs being either the untransformed responses or an estimated concentration of a chosen reference analyte (Wittmann et al., 1997).

In contrast to the above approaches, Ekins and co-workers in a series of publications described a miniaturized microspot multianalyte immunoassay system (microarray-based immunoassays) based on labeled antibodies and permitting the simultaneous determination of many analytes in the same small-volume sample (Ekins and Chu, 1995; Chu et al., 1997). The authors estimate that the technique has the potential to detect hundreds of different analytes in a 1-ml sample or less. Minute amounts of different antibodies are to be located in different microspots forming an array on a solid support such as membranes, glass slides, quartz optical fibres or chips. It reflects the realization that the use of vanishingly small concentration of antibody yields assays that are faster and more sensitive than others. For quantification of occupied or unoccupied capture antibodies fluorescent labeled secondary antibodies can be used together with laser scanning confocal microscope or CCD camera (Weller et al., 1999; Bernard et al., 2001). The breakthrough of this technology will mainly depend on the availability of improved solid supports and antibodies (or antibody fragments), and by the development of more simple instruments,

e.g. a compact disc-based microarray technology (Kido et al., 2000). The same concepts are applicable to assays that rely on the use of oligonucleotide probes for genetic testing (McGown et al., 1995).

IV.4.1.6.3. Artificial antibodies

Biological recognition elements like antibodies and enzymes in some cases lack storage and operational stability. This limits their use in industrial, pharmaceutical and environmental analytical chemistry. For several years, considerable efforts are being made to develop synthetic recognition systems specific for a given molecule (Andersson et al., 1993; Wulff, 1993, 1995; Bartsch and Maeda, 1998; Sellergren, 2001). This technique, referred to as molecular imprinting or as template polymerization, involves arranging polymerizable functional monomers and cross-linkers around an analyte of interest (print molecule, template) by non-covalent or covalent interactions prior to initiation of polymerization. Subsequently, the print molecules are extracted or chemically cleaved leaving recognition sites in the rigid polymer network with specific shape (three-dimensional geometry) and functional group complementarity to the original template. The polymer may then be used as an artificial receptor to selectively rebind the template from a mixture of chemical species. The principal means for exerting specificity are ionic interactions and hydrogen bonding between the analyte and the polymer functional groups. The choice of the functional monomer, or combination of monomers, depends on the chemical properties of the analyte that the molecular imprinted polymer (MIP) is being made for. Other variables in polymer synthesis include type and relative amount of cross-linking reagent used, type of solvent, and the time and temperature at which the polymerization is carried out (Hosoya et al., 1996; Mayes and Mosbach, 1996).

Intended applications of MIPs, which are already partly realized, are as substitutes for biological recognition structures in biosensors, as tailor-made solid-phase material for chromatographic separations and as catalytically active polymers or enzyme mimics (preparation of active centers) in organic synthesis (Kriz et al., 1995, 1997). Further, the use as artificial antibodies in ligand binding assays (molecularly imprinted sorbent assay) was reported (Vlatkis et al., 1993; Muldoon and Stanker, 1995; Andersson, 1996; Haupt et al., 1998).

Most of the work so far has involved the development of MIPs for sugars, amino acids and their derivatives, but also therapeutic drugs and other chemical compounds (Kriz et al., 1994, 1995; Andersson et al., 1995; Kempe, 1996; Matsui et al., 1996; Levi et al., 1997). However, MIP preparation was also reported for pesticides, mainly atrazine, one of the most widely used herbicide in the world. These MIPs were used as solid-phase adsorbents in binding assays, HPLC, sensors and SPE columns (Matsui et al., 1995; Piletsky et al., 1995; Siemann et al., 1996; Muldoon and Stanker, 1995, 1997a,b; Ferrer et al., 2000; Köber et al., 2001). From the present point of view it seems questionable, whether binding affinities with MIPs comparable to natural antibodies can be obtained in the near future. At present, for many analytes there is a gap, which comprises several orders of magnitude. This is, however, an advantage for affinity chromatography as it facilitates regeneration and repeated use of the chemical polymers. The high chemical, solvent and thermal stability, and the low cost of preparation make them a valuable complement to antibodies for use in environmental analysis, especially for poorly water-soluble contaminants.

In this context, there is a desire to perform immunoassays in anhydrous organic solvents (Russell et al., 1989; Wetall, 1991; Francis and Craston, 1994; Abad and Montoya, 1997; Dankwardt et al., 1997; Stöcklein et al., 1997; Horácek and Skládal, 2000). Analysis of crude organic solvent extracts may be possible and this would greatly simplify many current procedures. Still, the applicability for difficult environmental matrices has to be proven.

IV.4.1.7. Conclusions

Immunological techniques are increasingly being recognized as rapid, sensitive and inexpensive methods in environmental analytical chemistry. By screening out negative samples (no target analyte present or only detectable at levels below a set threshold limit) they can constitute a valuable tool to decrease the demand for chemical analyses by more time-consuming and highly sophisticated instrumentation. At present, corresponding tests are available mainly in the microtiter plate and tube format. Still the limited provision of highly affine and well-characterized antibodies for environmental contaminants must be considered as a constraint for further dissemination of these methods. This will change, as growing progress made in molecular biology will be reflected in this area. Some of the main efforts are directed to the development of ready-to-use and easy to perform field tests, which can be used on-site for monitoring remediation processes, site mapping and identification of "hot-spots". Increasing activities in validation and standardization of immunochemical tests as were initiated by federal government and regulatory agencies of several countries and well-recognized national and international organizations will lead to more transparency and uniformity in method development and evaluation and therefore, will contribute that the assays get rid of their smack as "dubious biological tests", sometimes found in discussions with analytical chemists. Immunological methods cannot be assessed, dependent from the view, simply as "good" or "bad" but rather as suitable for an application or not.

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IV.4.2

A simple cleanup procedure and bioassay for determining TCDD – toxicity equivalents of environmental samples

Karl-Werner Schramm and Antonius A.F. Kettrup

IV.4.2.1. Introduction

Polyhalogenated aromatic hydrocarbons (PHAH), such as polychlorinated dibenzo-*p*-dioxins (PCDD), dibenzofurans (PCDF) or biphenyls (PCB), are ubiquitous environmental contaminants. PHAH cause a multitude of effects such as hepatotoxicity, teratogenesis, immunotoxicity and tumorigenesis (DeVito and Birnbaum, 1994; Safe, 1994). The determination of the potential toxicity of PHAH in environmental samples is very difficult, as these invariably contain complex mixtures of PHAH. To standardize and simplify the risk assessment of PHAH matrices, the concept of TCDD toxicity equivalents (TEQ) was developed (NATO/CCMS, 1988; Safe, 1990; Ahlborg et al., 1992, 1994). This concept is based on defining toxicity equivalent factors (TEF) for individual compounds by comparison with 2,3,7,8-TCDD, the most toxic PHAH. TEQ values represent the sum amounts of individual congeners multiplied by their TEF.

At present, chemical analysis of the 17 toxic 2,3,7,8-substituted PCDD/F congeners by HRGC/HRMS (high resolution gas chromatography/high resolution mass spectroscopy) is the standard method for determining TEQ of environmental samples. However, this analysis is laborious and time consuming and thus unsuited for analysing large numbers of environmental samples. By limiting analysis to 17 PCDD/F and 13 PCB, the risk assessment does not include the potential toxic effects of other toxic PHAH such as fluorinated, brominated and mixed halogenated PXDD/F, as well as other compounds, e.g. azo and azoxy compounds, biphenylethers, naphthalenes, sulfur-analogue dioxins and alkylated dioxins. Potential synergistic or antagonistic effects of the PHAH are not taken into consideration.

To circumvent these shortcomings, several attempts have been made to develop a biological assay for determining the total toxic potential of PHAH mixtures in environmental samples (Bosveld and van den Berg, 1994). PHAH have in common that they bind to a cytosolic receptor protein and subsequently induce the synthesis of several gene products, including cytochrome P4501A1 (CYP1A1) (Poland and Knutson, 1982; Landers and Bunce, 1991) (Fig. IV.4.2.1). On this basis, a bioassay has been established measuring the induction of CYP1A1-mediated aryl hydrocarbon hydroxylase (AHH) or ethoxyresorufin O-deethylase (EROD) activity, predominantly using rat hepatoma cells

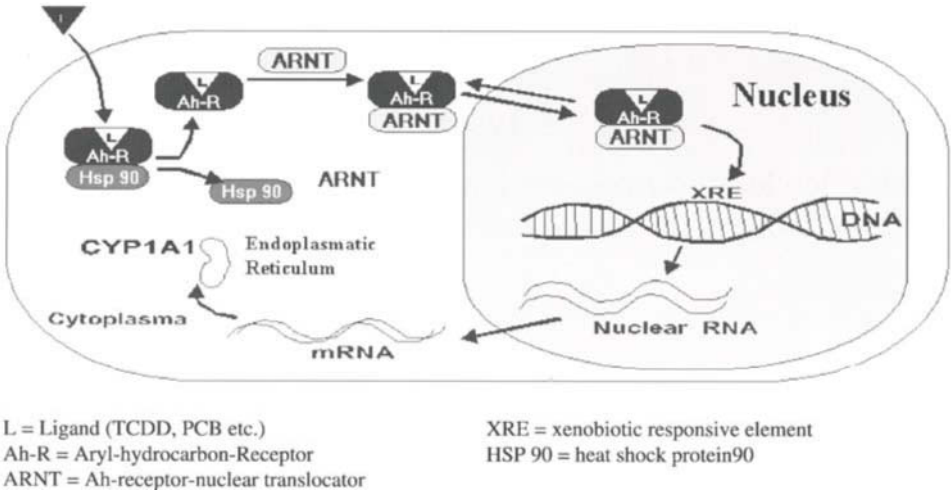


Figure IV.4.2.1. Mechanism of the induction of CYP1A1.

H4IIE for the determination of TEQ in environmental samples (Bradlaw and Casterline, 1979; Zacharewski et al., 1989; Hanberg et al., 1991; Tillitt et al., 1991; Safe, 1993).

Applying a target specific (persistent bioaccumulating toxicants (PBT)) approach, we are employing an extraction and cleanup that separates persistent compounds (P), which are bioaccumulating (B).

- Persistence is achieved by column chromatography on acidified silica gel;
- Bioaccumulation potential is addressed by extraction with lipophilic solvents (toluene, acetone/hexane).

Testing on toxicity (T) such as on dioxin-like response is reported.

IV.4.2.2. Technical details

IV.4.2.2.1. Test materials

Samples were collected from the following sources: fly ash and tissue filter dust from a municipal waste incinerator; sludge from a sewage treatment plant in Northern Bavaria, FRG; soil and sediment from Ya-Er Lake, China; combustion residues from residential fireplaces in Bavaria, FRG; biowaste compost from a compost plant, Institute of Agriculture, Technical University of Munich, Weihenstephan, FRG (Table IV.4.2.1).

IV.4.2.2.1.1. Sample preparation and extraction

Samples of compost were pulverized in a liquid nitrogen cooled Retsch mill. Soil, sludge and sediment samples were freeze-dried. Aliquots of 2–20 g were quantitatively extracted

Table IV.4.2.1. Matrices expected and/or investigated to be analysed with the micro-bioassay.

Matrix	Investigated	Expected to be processable
Environmental	Soil, water, sediment, vegetables	Grass, house dust
Human		Mother's milk
Animals		Tissues (liver, muscles) of fish
Technosphere	Fly ash, tissue filter dust, flue gas deposition, emission combustion residue, compost, sewage sludge, chemicals, products	

in a Soxhlet apparatus using toluene for 24 h. For chemical analysis, samples were spiked with 17 $^{13}C_{12}$-labelled-PCDD/F prior to extraction (Henkelmann et al., 1996).

IV.4.2.2.1.2. Determination of TEQ of PCDD/F by chemical analysis

Cleanup of samples and quantification of PCDD/F using capillary HRGC/HRMS were carried out as described elsewhere (Schramm et al., 1995; Henkelmann et al., 1996). MS measurements were conducted using a Finnigan MAT 95 ($R = 10,000$) instrument for isomer-specific measurement.

IV.4.2.2.1.3. Cleanup for bioassay

Samples of concentrated crude extract were applied to a column wet-filled from bottom to top with 10 g silica (active, mesh 63–200 μm), 20 g silica (44% concentrated sulfuric acid w/w), 40 g silica (4% water w/w). The column was topped with Na_2SO_4. Samples were eluted with 870 ml *n*-hexane and the eluate reduced by evaporation (550 mbar, 333 K) to 2–3 ml. The extract was transferred stepwise into a vial and evaporated to dryness under a stream of nitrogen. Samples were re-dissolved in 500 μl of DMSO/iso-propanol (4:1 v/v).

IV.4.2.2.2. Cell culture

IV.4.2.2.2.1. Macro-EROD assay

Rat hepatoma cells H4IIEC3/T (H4IIE) were grown as described previously (Roscher and Wiebel, 1992). Cells were seeded at a density of 1×10^5/60 mm culture plate. Upon attaining a density of about 70%, cells were exposed to environmental samples or known amounts of 2,3,7,8-TCDD (0.5–40 pg TCDD/plate). All TCDD standards or samples were dissolved in DMSO/iso-propanol (4:1 v/v) and were added to the cell cultures in triplicate. The final concentration of solvent in the medium was 0.5%. After 72 h of exposure, the medium was removed and cells were harvested by scraping with a rubber spatula. Cell suspensions were transferred with 1 ml phosphate buffered saline (PBS) into Eppendorf vials and kept at −80°C until use.

IV.4.2.2.2.2. Micro-EROD assay

EROD activity of intact cells grown in 96-well microtiter plates was determined according to Donato et al. (1993) (Fig. IV.4.2.2). The following modifications were used. Cells were seeded at a density of 1×10^4 per well. After 3 days of growth, the medium was replaced by 100 µl medium containing the test materials, and the cells were exposed for another 3 days. Then, the medium was removed and 100 µl fresh medium containing 8 µM 7-ethoxyresorufin and 10 µM dicumarol were added. After incubation at 310 K for 60 min, the medium was transferred to another 96-well plate containing 130 µl methanol. Resorufin-associated fluorescence was measured at 550 nm excitation and 585 nm emission using a multiwell fluorescence reader.

After measurement of EROD activity, cell cultures were used for determining the cytotoxicity of the test materials employing the neutral red assay described by Borenfreund and Puerner (1985). Finally, protein amounts were assayed according to Smith et al. (1985). Standard deviations of triplicate-measured samples varied by less than 10% of the mean.

IV.4.2.2.2.3. Calculation of biological TEQ (Micro-EROD)

Biological TEQ values were determined according to Hanberg et al. (1991) by comparing the induction of EROD activity caused by environmental samples with that caused by authentic TCDD standards (0–40 pg TCDD/plate). The range of TEQ values determined in duplicate experiments (including extraction and cleanup) was ± 25%.

IV.4.2.3. Results and fields of application

A cleanup has to be used to remove the cytotoxic substances. Therefore, a single sandwich column was tested for its applicability using 28 samples derived from several matrices, such as sewage sludge, compost, soil, sediment, fly ash, tissue filter dust and combustion residue. Provided the samples applied to the column do not exceed 10 g (see below), the cleanup removed all potentially cytotoxic components from the samples (Table IV.4.2.2).

No cytotoxicity could be detected in the final eluates. Also, the isolated material interfered with neither the induction nor the assay of EROD activity. The results show a good correlation between TEQ determined by bioassay and chemical analysis (Tables IV.4.2.3–IV.4.2.6).

The new cleanup procedure is advantageous: it eliminates a host of substances that might interfere with the bioassay, but does not remove compounds, such as coplanar biphenyls, which are frequently associated with PCDD/F (Tillitt et al., 1991; Kopponen et al., 1992). Another advantage of the procedure is its simplicity. The single column chromatography is considerably less laborious than the chemical purification methods used by others (Hanberg et al., 1991; Kopponen et al., 1994).

At present, the sandwich column readily handles extracts derived from up to 10 g of test material. Larger amounts of test material, particularly if heavily contaminated, can overload the column, allowing cytotoxic compounds to pass through. This limits the sensitivity of the bioassay to approximately 1 ng TEQ/kg test material.

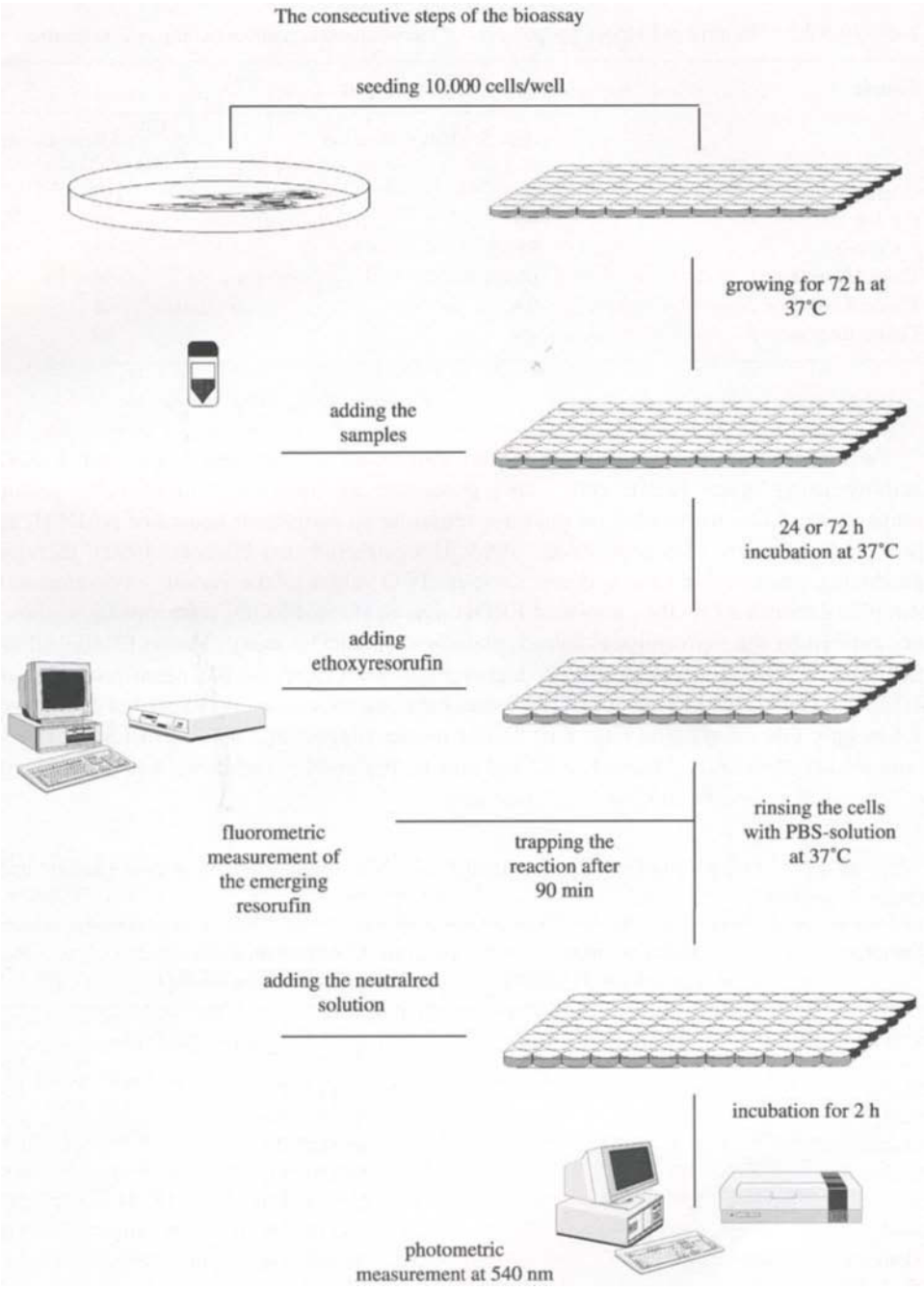

The consecutive steps of the bioassay
seeding 10.000 cells/well
growing for 72 h at 37°C
adding the samples
24 or 72 h incubation at 37°C
adding ethoxyresorufin
rinsing the cells with PBS-solution at 37°C
trapping the reaction after 90 min
fluorometric measurement of the emerging resorufin
adding the neutralred solution
incubation for 2 h
photometric measurement at 540 nm

Table IV.4.2.2. Neutral-red values (in percent) of environmental matrices compared to control.

Sample	Neutral-red value (%)	
	After Soxhlet extraction	After cleanup
Control	100	100
Fly ash 1	94	95
Fly ash 2	88	95
Tissue filter dust 1	68	95
Tissue filter dust 2	93	98
Tissue filter dust 3	19	93

To simplify the bioassay for TEQ, a 96-well assay was adapted to measure EROD activity using intact H4IIE cells. This procedure avoids collection of cells and/or preparation of *in vitro* incubation mixtures requiring an exogenous source of NADPH, as practiced by others (Kennedy et al., 1993; Hoogenboom and Hamers, 1995), thereby producing considerable time and cost savings. TEQ values of the various environmental samples determined by the simplified EROD assay (Micro-EROD) were similar to those determined by the conventional culture plate/*in vitro* EROD assay (Macro-EROD) (data not shown). The latter were slightly higher than the former, on the mean biofactor of 1.1 ± 0.2 (SD). The difference of TEQ values between the two assays exceeded a factor of 1.4 in only one case, tissue filter dust 2. The results suggest that the Micro-EROD assay may readily replace the Macro-EROD and may be preferable to other 96-well plate-based

Table IV.4.2.3. TEQ values of sewage sludge samples: comparison of micro-bioassay and chemical analysis.

Samples[a]	Micro-bioassay (ng 2,3,7,8-TCDD/kg)	Chemical analysis (ng 2,3,7,8-TCDD/kg)	R_{ba}
Sludge 1	137[b]	50 (14; 36)[c]	2.7
Sludge 2	118	47 (21; 26)	2.5
Sludge 3	106	32 (13; 19)	3.3
Sludge 4	152	50 (22; 28)	3.0
Sludge 5	114	68 (28; 40)	1.7
Sludge 6	147	59 (20; 39)	2.5
Sludge 7	157	58 (23; 35)	2.7
Sludge 8	189	62 (25; 37)	3.0
Sludge 9	144	54 (22; 31)	2.7
Sludge 10	198	64 (24; 40)	3.0

[a]Sludges 1–3: raw sludges from Selblitztal; sludges 4 and 5: activated sludges from Selblitztal; sludges 6–10: activated sludges from Eisleben.

[b]Mean of four replicates.

[c]TEQ = amount of PCDD/F and PCB; in brackets, left: PCDD/F (NATO/CCMS); right: PCB (WHO).

Table IV.4.2.4. TEQ values of compost samples: comparison of micro-bioassay and chemical analysis.

Sample	Micro-bioassay (ng 2,3,7,8-TCDD/kg)	Chemical analysis (ng 2,3,7,8-TCDD/kg)	R_{ba}
Compost 1	11[a]	6 (3; 3)[b]	1.9
Compost 2	16	9 (5; 4)	1.8
Compost 3	13	8 (5; 3)	1.7

[a]Mean of four replicates.
[b]TEQ = amount of PCDD/F and PCB; in brackets, left: PCDD/F (NATO/CCMS); right: PCB (WHO).

procedures involving the use of frozen/thawed cells. The use of intact cells in the present EROD assay is also advantageous in that it allows additional tests to be conducted, e.g. on the cytotoxicity of the test material, in the same set of microcultures.

In the following, Micro-EROD values were used for comparing TEQ values derived from bioassay and chemical analysis. The comparison for the 17 toxic 2,3,7,8-substituted dioxins and furans shows that biological TEQ values are markedly higher than chemical-analytical TEQ values (Tables IV.4.2.3–IV.4.2.6). However, the observed difference decreases considerably if TEQ attributable to toxic PCB is included in the chemical-analytical evaluation. For sewage sludge, a PCB-part of 1.15–1.7-fold of the PCDD/F value has to be added. For compost, there is a PCB-part that is 0.9-fold.

The difference between biological and chemical TEQ values is relatively consistent for a specific matrix. The biological TEQ of sludge is about 3 times higher than that of the chemical TEQ. For soil, the values vary from 4 to 9 (Table IV.4.2.5), for emission from 3 to 8.5 (Table IV.4.2.7) and for flue gas deposition the ratio is 9.6 (Table IV.4.2.8). In contrast, TEQ values of samples of tissue filter dust or fire residue differ by a factor of about 1.6. Similar values are obtained for compost (Table IV.4.2.4). Large discrepancies between biological and chemical TEQ, exceeding a factor of 6, were sometimes observed in those samples that contained low amounts of PCDD/F and PCB, i.e. less than 5 ng TEQ/

Table IV.4.2.5. TEQ values of soil- and sediment samples: comparison of micro-bioassay and chemical analysis.

Samples	Micro-bioassay (ng 2,3,7,8-TCDD/kg)	Chemical analysis (ng 2,3,7,8-TCDD/kg)	R_{ba}
Soil 1	1.8[a]	0.2 (0.1; 0.1)[b]	9.0
Soil 2	3.8	1.0 (0.4; 0.6)	3.8
Soil 3	1.4	0.3 (0.2; 0.1)	4.6
Sediment 1	1200	861 (797; 64)	1.3
Sediment 2	13.6	7.2 (6.9; 0.3)	1.8

[a]Mean of four replicates.
[b]TEQ = amount of PCDD/F and PCB; in brackets, left: PCDD/F (NATO/CCMS); right: PCB (WHO).

Table IV.4.2.6. TEQ values of samples of fly ashes and tissue filter dusts: comparison of micro-bioassay and chemical analysis.

Samples	Micro-bioassay (ng 2,3,7,8-TCDD/kg)	Chemical analysis (ng 2,3,7,8-TCDD/kg)	R_{ba}
Fly ash 1	450[a]	264 (263; 1)[b]	1.7
Fly ash 2	705	416[c]	1.7
Tissue filter dust 1	1460	1168 (1,168; 0.2)[b]	1.2
Tissue filter dust 2	735	638 (625; 13)[b]	1.2
Tissue filter dust 3	2015	1645 (1,640; 5)[b]	1.2

[a]Mean of four replicates.
[b]TEQ = amount of PCDD/F and PCB; in brackets, left: PCDD/F (NATO/CCMS); right: PCB (WHO).
[c]TEQ = amount of PCDD/F.

kg (cf. soil samples 1 and 3 in Table IV.4.2.5). A few samples of hazardous wastes, e.g. special waste or seed growing waste, exhibit even ratios up to a factor of 1000. These samples probably contain a complex mixture of chemical compounds additionally to PCDD/F and PCB congeners. These substances, which cannot be eliminated by the conventional clean up procedure, obviously have a high affinity to the Ah receptor. They also can act as a P450 1A1 inductor. In this special case, it may be that the chemicals disturb irreversibly the Ah receptor mechanism.

Biological TEQ values of environmental samples are higher than values derived from chemical analysis. The apparent discrepancy may largely be due to the fact that the bioassay (Table IV.4.2.9) measures the response to all potential toxic compounds that induce CYP1A1, such as polyhalogenated azo- and azoxy compounds, biphenylethers, naphthalenes, sulfur-analogue dioxins/furans and alkylated, brominated or mixed halogenated dibenzodioxins/furans. None of these substances are detected by current routine chemical analysis. Even if these compounds were identified and quantified in

Table IV.4.2.7. TEQ values of emission samples: comparison of micro-bioassay and chemical analysis.

Samples	Micro-bioassay (ng 2,3,7,8-TCDD/m^3)	Chemical analysis (ng 2,3,7,8-TCDD/m^3)	R_{ba}
Emission sample 1	35 ± 7[a]	11.9[b]	2.9
Emission sample 2	1.6 ± 0.3	0.3	5.3
Emission sample 3	0.1 ± 0.01	0.02	5.0
Emission sample 4	2.1 ± 0.3	0.4	5.3
Emission sample 5	20.9	6.4	3.3
Emission sample 6	14.4	1.7	8.5
Emission sample 7	12.3	2.3	5.3

[a]Mean of four replicates.
[b]TEQ = PCDD/F (NATO/CCMS).

Table IV.4.2.8. TEQ values of a flue gas deposition sample: comparison of micro-bioassay and chemical analysis.

Samples	Micro-bioassay (ng 2,3,7,8-TCDD/kg)	Chemical analysis (ng 2,3,7,8-TCDD/kg)	R_{ba}
Deposition 1	52 ± 6[a]	5.4 (5.1; 0.3)[b]	9.6

[a]Mean of four replicates.
[b]TEQ = amount of PCDD/F and PCB; in brackets, left: PCDD/F (NATO/CCMS); right: PCB (WHO).

environmental samples, their TEQ values could not be estimated as little is known about their TEF values. This relates also to some extent to the TEF values of PCB. If bioassays are used, the sum of dioxin-like activity in complex mixtures is expressed as dioxin induction equivalents (IEQ; Schecter et al., 1999), bioassay-TEQs (e.g. CALUX-TEQs; Pauwels et al., 2000) or bio-TEQs (Engwall et al., 1999). The ratio R_{ba} (Schramm and Rehmann, 2000) describes the comparison between the bioanalytical (*B*) (bio-TEQ, bioassay-TEQ or IEQ) and the chemoanalytical (*A*) (TEQ) response.

We define the ratio (R_{ba}) between the bioanalytical (*B*) and the chemoanalytical (*A*) response as:

$$R_{ba} = \frac{B}{A}.$$

TEF values of PCDD/F established from *in vivo* experiments show good correlation with those determined by *in vitro* EROD induction in H4IIE cells (Safe, 1994). This was not true for TEF of PCB (Kennedy et al., 1996). Thus TEF values commonly used for calculating TEQ possibly underestimate the impact of PCB on CYP1A1 induction.

The occasional large difference in TEQ values observed, e.g. in soil contaminated with less than 5.0 ng TEQ/kg (Table IV.4.2.5), could be explained by finding that the bioassay reaches its limit of detection at this concentration. The bioassay consistently yields higher TEQ values than the chemical analysis and it is highly unlikely to produce false negative results.

Table IV.4.2.9. Effectiveness of the cleanup procedure and test duration to remove non-persistent PHAH analysed with the macro-bioassay.

Plant analysed	24 h	72 h	Chemical analysis
Broccoli without cleanup	762	163	
Broccoli with cleanup	4.9	< dl	0.04
Cauliflower without cleanup	100	50	
Cauliflower with cleanup	15.4	< dl	
Radish without cleanup	54	5	
Radish with cleanup	21	< dl	

Only single determination; < dl, below detection limit.

Another bioassay for measuring the TEQ values of environmental samples is the so-called CALUX assay (chemical activated luciferase expression) (Murk et al., 1996; Sandersson et al., 1996). A rat hepatoma (H4IIE) cell line, stable transfected with a construct containing the dioxin-responsive element (DRE) sequence and a luciferase reporter gene (H4IIE-luc), is used to determine the relative potency or the total activities of AhR-active compounds in sediments and pore water extracts. The main difference between the CALUX assay and the EROD assay is that the induction of luciferase activity seems to be dose-dependent and insensitive to substrate inhibition. Regarding the whole procedure, the H4IIE-luc cells are of similar sensitivity as H4IIE cells (Behnisch et al., 2001).

IV.4.2.4. Conclusions

The present study was aimed at establishing a rapid and simple bioassay for measuring TEQ of PBT in environmental samples. A cleanup procedure was tailored to the needs of the bioassay and simplified by measuring EROD activity in intact H4IIE cells grown and exposed to the test material in 96-well plates. To validate the new procedures, TEQ values of 28 diverse environmental samples determined by either chemical analysis or the new cleanup-aided bioassay were compared. The results showed very good agreement between the two sets of TEQ values. The new 96-well-plate EROD assay was also compared with the original, widely practiced bioassay, involving growth and exposure of cells in 60 mm dishes followed by an *in vitro* EROD assay. Again, the two assay procedures yielded similar TEQ values in all the environmental samples tested.

Taken together, the results indicate that the bioassay with its special cleanup offers a time and cost-effective alternative to chemical analysis. In particular, this pertains to the screening of large numbers of samples for PBT with dioxin-like response that arises when monitoring the environment for PHAH contamination. Clearly, this will be a major domain of the bioassay. Chemical analysis will have its place in quantifying individual PHAH congeners or identifying yet unknown toxic PHAH. Ideally, chemical analysis and bioassay are combined for making a risk assessment of environmental PHAH mixtures.

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IV.5

Principles of vadose and saturated zones monitoring in solid waste sites exemplified in mining waste dumps

Jadwiga Szczepańska and Irena Twardowska

IV.5.1. Introduction

IV.5.1.1. Approach to vadose zone monitoring

Waste disposal sites (landfills) can be classified as potential non-point small-area sources of aquatic environmental contamination, though the area occupied by such facilities can range from several tens of square meters to several hundred hectares. They may be formed either as waste dumps on the land surface, or onto the land as impoundments. In both cases waste is exposed to atmospheric conditions and partakes in the natural (climatic) circulation of water. Atmospheric precipitation that infiltrates through the waste layer washes the soluble compounds out of the landfill and carries them through the vadose zone to the groundwater (Fig. IV.5.1). This may affect groundwater quality adversely.

The amount of atmospheric precipitation that percolates through the vadose zone depends upon the infiltration rate I. In the average conditions in Poland, infiltration rate accounts for $I \approx 100$ mm/year $= 0.1$ m/year, thus through 1 ha of land surface percolates annually about 1000 m^3 of water. Average infiltration rate in the vadose zone formed from anthropogenic materials (e.g. coal mining waste in Upper Silesia coal basin in Poland) accounts for $I \approx 400$ mm/year $= 0.4$ m/year, hence about 4000 m^3 of water percolates annually through 1 ha of waste dump.

These data show that at solid waste disposal facilities, particular attention should be paid to the conditions of contaminant migration in the anthropogenic vadose zone of a landfill and in the natural vadose zone beneath the landfill base. The need for vadose zone monitoring is a logical consequence of a failure for preventing contamination by means of saturated zone monitoring. It is well known that the alert provided by groundwater monitoring in the saturated zone is often too late to prevent significant degradation of recoverable groundwater resources, as the contaminant should occur in groundwater in the detectable levels to be noticed.

Vadose zone research was initiated more than two decades ago in the USA and since then has been recognized as an essential element of groundwater protection. The concept

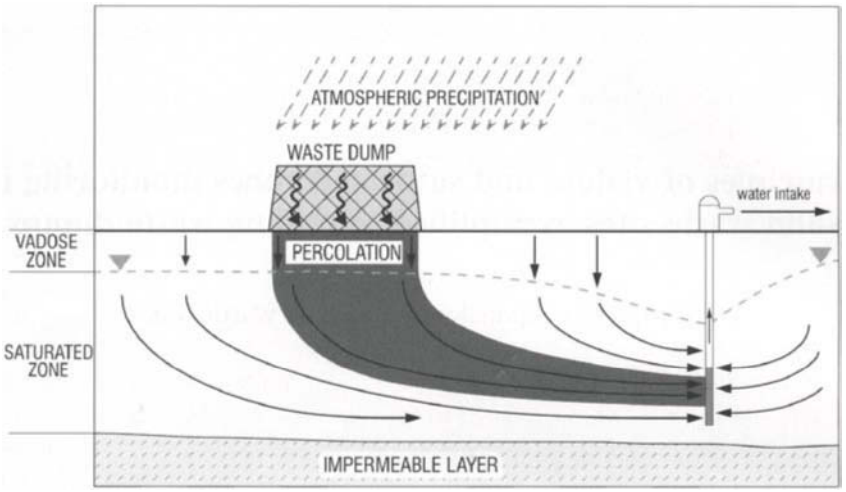


Figure IV.5.1. Scheme of water and contaminant flow in the porous aquifer with free water table (after Griffin, 1991).

behind developing vadose zone monitoring was to provide an early means to detect, and subsequently, intercept or remediate contaminants release from waste disposal facilities before they infiltrate into the saturated zone and degrade recoverable groundwater resources. By providing an early warning for taking instant remedial actions, the potential costs, and the potential for loss of recoverable groundwater resources can be greatly reduced.

U.S. EPA actions concerning vadose zone monitoring in the Resource Conservation and Recovery Act (RCRA) program started in 1978, when EPA proposed to require vadose zone monitoring for all RCRA hazardous waste landfills, surface impoundments, and land treatment facilities. The proposal was based on the research conducted at the EPA Environmental Systems Monitoring Laboratory in Las Vegas (EMSL-LV), in co-operation with the American Society for Testing and Materials (ASTM). After a decade of developing vadose zone monitoring techniques and significant advancements of this technology, the EPA proposed in 1988 to require vadose zone monitoring on a site-specific basis at RCRA hazardous waste landfills, surface impoundments, and waste piles, where the perennial water table is relatively deep and such system can provide effective early alert (U.S. EPA, 1988). In particular, it has been concluded that vadose zone monitoring equipment can be installed effectively at new facilities prior to the construction, or at the periphery of the unit to detect the contaminants migrating horizontally in the subsurface, or at the unlined solid waste management units (SWMUs), or even for many facilities equipped with liners and leachate collection systems that are prone to failure (Durant and Myers, 1995). In general, the EPA considers vadose zone monitoring to be used in conjunction with saturated zone monitoring. In sites where vadose zone monitoring system sufficiently meets the goal of early detection of contaminant release to the subsurface, it was found appropriate to eventually reduce the scope of saturated zone monitoring.

To facilitate implementing vadose zone monitoring at RCRA and other SWMUs facilities on a case-by-case basis, the EPA has developed a two-volume guidance manual on subsurface characterization and monitoring techniques (Boulding, 1993), which contains summary descriptions of more than 280 specific field methods that explain sampling procedures, frequency and sample analysis for adequate techniques. The comprehensive EPA policy directives and guidance manuals provide detailed criteria for selecting, designing and implementing site-specific vadose zone monitoring programs and response remedial actions. The methods and criteria are closely related to the standard methods developed in 1980–1994 by the ASTM, mostly by Committee D18 on Soil and Rock, and published in the recent Volumes 4.08 and 4.09 of ASTM's annual books of standards continuously updated (since 1994–2003).

The most comprehensive guidelines to vadose zone characterization and monitoring representing the synthesis of basic concepts, principles, and limitations of available routine monitoring techniques, QA/QC, as well as remediation and control of contaminants from hazardous sites, with a guide to major references including U.S. EPA and ASTM guidelines are addressed in excellent handbooks by Boulding (1995), Wilson (1995), Wilson et al. (1995) and Looney and Falta (2000).

Both EPA manuals and the aforementioned publications consider monitoring of the natural vadose zone directly beneath or at the periphery of the unit. In hydrogeologic environments where the water table of the saturated zone is too near the land surface and hence the vadose zone is too thin to ensure early detection of contaminant release to the subsurface, vadose zone monitoring may be considered inappropriate. At the same time, unlined SW landfills are in general the most problematic, as a rule being sited in areas with both a thin and permeable vadose zone, such as abandoned sand and gravel pits, or old strip mines. This means that the groundwater in these sites is the most vulnerable to contamination, which is though not adequately considered by the monitoring requirements and regulations.

The basic difference in the approach represented by the EPA and reflected in guidelines (Boulding, 1993, 1995; Wilson et al., 1995, Boulding and Ginn, 2003) and our approach is that according to our experience, the vadose zone screening/monitoring in the SW landfills, in particular in unlined ones, should comprise not just the natural vadose zone beneath the landfill, but also the anthropogenic vadose zone, i.e. the waste layer and pore solutions in the landfill. This would definitely provide an early alert in the case when the chemical composition of pore solution percolating downward in the waste profile shows unfavorable transformations, which indicates an excessive contaminant load-approaching groundwater. Typical examples of vertical redistribution of contaminant loads in non-hazardous waste dumps or landfills are presented in Chapters III.6 (coal mining waste dumps, USCB, Poland: Figs. III.6.20–III.6.22) and III.7 (power plant fly ash pond after closure, USCB, Poland: Figs. III.7.7–III.7.8 a–e). In general, the contaminant loads in pore solutions of non-hazardous waste comprise macro-components, e.g. sulfates, chlorides, nitrates, alkalis, etc. or inorganics (heavy metals), though toxic organic constituents may also occur in considerable amounts in the deeper parts of the vertical profile of a dump due to the vertical redistribution, as was found for steel and iron furnace slag and foundry waste (Twardowska et al., 2000). In any event, the contamination of groundwater by these constituents may make it unfit for any use (e.g. Twardowska et al., 1999; Twardowska and Szczepańska, 2002).

IV.5.1.2. Vadose and saturated zones monitoring technologies

The widely practiced vadose zone monitoring methods comprise direct soil-core and soil-pore liquid techniques as well as soil gas methods. For reconnaissance of vadose and saturated zones contamination from hazardous and non-hazardous disposal waste facilities, very useful methods might be fast developing, non-intrusive geophysical methods (e.g. electrical resistivity, conductivity, electromagnetic induction (EMI), active microwave, thermal infrared, electro-optical sensors, dielectric sensors, gamma–gamma, computer assisted tomography (CAT) scan, induced polarization (IP), time domain reflectometry (TDR, also called TDEM—time domain electromagnetics), ground-penetrating radar (GPR), very low frequency (VLF) electromagnetic resistivity measuring the ratio of electric to magnetic fields, neutron moderation, etc.). These methods can provide indirect evidence of contamination in the anthropogenic and natural vadose and saturated zones of a disposal site, and should be used in conjunction with the direct techniques. Their comprehensive overview is presented in the handbooks on soil, vadose zone and groundwater characterization and monitoring (Wilson et al., 1995; Looney and Falta, 2000; Boulding and Ginn, 2003). Geophysical and remote sensing techniques have for a long time been successfully used for screening and monitoring mining sites, and are particularly helpful in evaluation of the vulnerability of waste rock to acidification, and contaminant migration in the vadose and saturated zones. Reported applications of geophysics for characterizing mine waste include GPR and geoelectrical methods such as direct current (DC) resistivity, EMI, IP, magnetometry (MAG) (Conyers and Goodman, 1997; Campbell et al., 1999; Campbell, 2000; Campbell and Fitterman, 2000), or using imaging spectroscopy for mapping acidic mine waste (Swayze et al., 2000). In general, geophysical methods in mine waste contamination studies can be applied in several fields such as: (i) for characterizing natural stratigraphic conditions (GPR, EM, DC, and seismic methods); (ii) characterizing direction of flow of a contaminant plume, e.g. acid rock drainage (ARD), (EM, DC); (iii) detecting subsurface anthropogenic materials and preferential flow (MAG, EMI, GPR, VLF, metal detection); and (iv) locating buried waste (EMI, MAG, metal detection).

Examples of using EM, VLF and magnetics to locate preferential flow, trace edges of coal mine backfill, and find buried refuse that was a source of ARD (Schuek, 2000) and integration of airborne magnetic, electromagnetic and radiometric methods to survey abandoned mine lands (Smith et al., 2000; McDougal et al., 2000; Painter et al., 2000) illustrate particular usefulness of geophysics to trace ARD plumes and investigate active contaminant leach at mine waste piles.

A number of recent innovative emerging techniques for monitoring and measuring the chemical and physical characteristics of the vadose zone are particularly promising for vadose zone monitoring with respect to time, cost and accuracy, and amenability to generate data and information in near-real time. These techniques comprise chemical sensors, miniaturized or field-portable laboratory instrumentation, non-invasive characterization techniques, and minimally invasive techniques, as well as data and information management tools. Chemical sensors (mass, fiber optical, electrochemical, radiochemical, and thermal) are emerging techniques that can be used for field screening/monitoring mainly for organics, but also for inorganics, metals and radionuclides. Of these sensors, remote fiber-optic monitors appear to be the fastest developing and the most promising

technique for detection of hazardous waste contaminants in environmentally viable and safe way. In this book, the fiber-optic monitoring techniques developed in Oak Ridge National Laboratory for this purpose, have been presented in Chapter IV.3.

A new emerging class of field kits is based on immunoassay techniques, which use antibodies that have a high degree of affinity to target organic analytes. The recognition by U.S. EPA of the utility of immunoassay kits for field screening and field analytical applications resulted in proposal to include BTEX, PCBs and pentachlorophenol immunoassay-based screening method into the RCRA manual for field screening and analytical methods SW-846 (U.S. EPA, 1986–2003), which is periodically updated. Use of biomonitors based on immunological principles and bioassays for environmental applications that can be particularly useful for monitoring of both anthropogenic and natural vadose zone in the hazardous and solid waste sites are summarized in Chapters IV.4.1 and IV.4.2.

Other innovative directions in the vadose zone monitoring and evaluation of hazardous waste site cleanup efficiency is miniaturization of laboratory instrumentation, in particular, development of field portable gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS) and ion mobility spectrometry (IMS) for different organic contaminants (e.g. PAH, PCB, VOCs, etc.) (Meuzelaar, 1993, 2001). Both immunoassay kits and wearable instruments require samples to be brought to the surface, though their great advantage is amenability for providing qualitative and quantitative data in a near-real time.

Particular difficulties in characterization of chemical contamination in the subsurface by volatile and semi-volatile organic contaminants (VOCs and SVOCs) and soil gas due to their extreme instability directed the efforts toward developing sampling technologies that prevent or minimize the loss of volatiles. These technologies, in particular different enhanced sorbent devices, are discussed by Koglin et al. (1995) in the review of the emerging technologies for monitoring of the vadose zone.

One of the most developed new technologies for disposal sites characterization and analysis is the cone penetrometer integrated with real-time, downhole sensing devices (e.g. site characterization and analysis penetrometer system (SCAPS)) (CMST, 2000; Knowlton et al., 1995; Koglin et al., 1995; U.S. Army Corps of Engineers, 1998; U.S. DOE, 1998). The cone penetrometer consists of: (i) a steel cone that is hydraulically pushed into the ground while *in situ* measurements are continuously collected and transported to the surface for data interpretation and visualization; (ii) a 20–40 t truck equipped with vertical hydraulic rams that are used to force a sensor probe 25.4–50.8 mm into the ground with a penetration rate typically 12–15 m/h (Fig. IV.5.2).

Standard cone penetrometers collect stratigraphic information and are equipped with strain gages used for determination of soil type; for this purpose acoustic cones are also used. Other sensors available include measurements of temperature, pH, γ-radioactivity, pressure (P) and shear (S) waves. Time domain reflectometry (TDR) sensors use an electromagnetic pulse to measure the dielectric constant of the soil and to calculate the volumetric soil moisture content. Fiber-optic RH sensors measure relative humidity, which can be used to calculate capillary pore pressure in unsaturated soils. The SCAPS penetrometers are equipped with several other types of sensors; inorganic contaminants are assessed with use of an electrical resistivity sensor, electrochemical sensors have been developed to detect explosives such as TNT in soils. Active and passive radiation probes have been developed to detect radionuclides (U.S. DOE, 1998). Other measurement

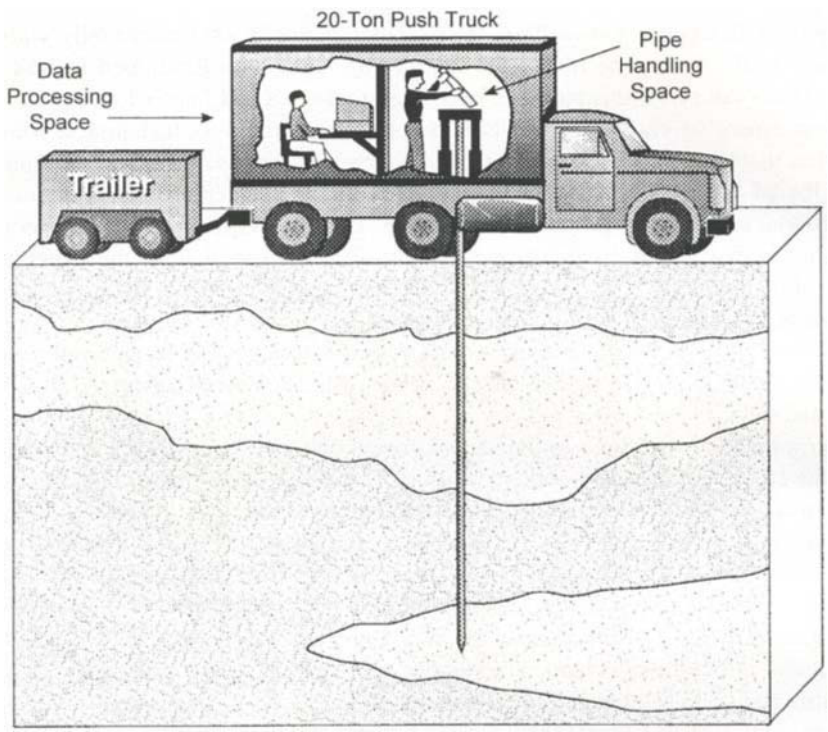


Figure IV.5.2. Site characterization and analysis penetrometer system (SCAPS) technology (after U.S. DOE, 1998).

capabilities include IR fiber-optic chemical sensors (Ewing et al., 1995; Nau et al., 1995) or fiber-optic laser-induced breakdown spectroscopy (FOLIBS) system for detection of heavy metal contamination (Thierault and Lieberman, 1995) and other fiber-optic heavy metals detection systems (e.g. SEA, Inc.), and integration of a fast gas chromatograph into the cone penetrometer system. A fiber-optic-based laser-induced fluorescence (LIF) system is used for detection of heavy fuel fractions. The research efforts in the last decade have been focused on the development and improvement of LIF sensors for cone penetrometers of different types, e.g. a laser-induced fluorescence excitation–emission matrix probe (LIF-EEM) (Lin et al., 1995), other fiber-optic LIF sensors (Knowles and Lieberman, 1995; Nielsen et al., 1995), or the single-wavelength fluorescence and multi-channel sensor (Haas and Forney, 1995) for evaluation of organic contaminants. The rapid optical screening tool system (ROST) can be used to screen the subsurface for petroleum hydrocarbons. An LIF method has also been demonstrated to characterize PAH contamination (Stepan, 1999). One of the last developments comprise the dense non-aqueous phase liquid (DNAPL) toolbox that includes the following technologies: standard sensors for lithologic delineation, LIF probes, ribbon non-aqueous phase liquid (NAPL) sampler, field Raman spectrograph, GeoVis™ Soil video imaging system, Cone Permeameter™, Geoprobe™ membrane interface probe, and various sediment and groundwater samplers (CMST, 2000). An example of a SCAPS-LIF probe is given in Figure IV.5.3.

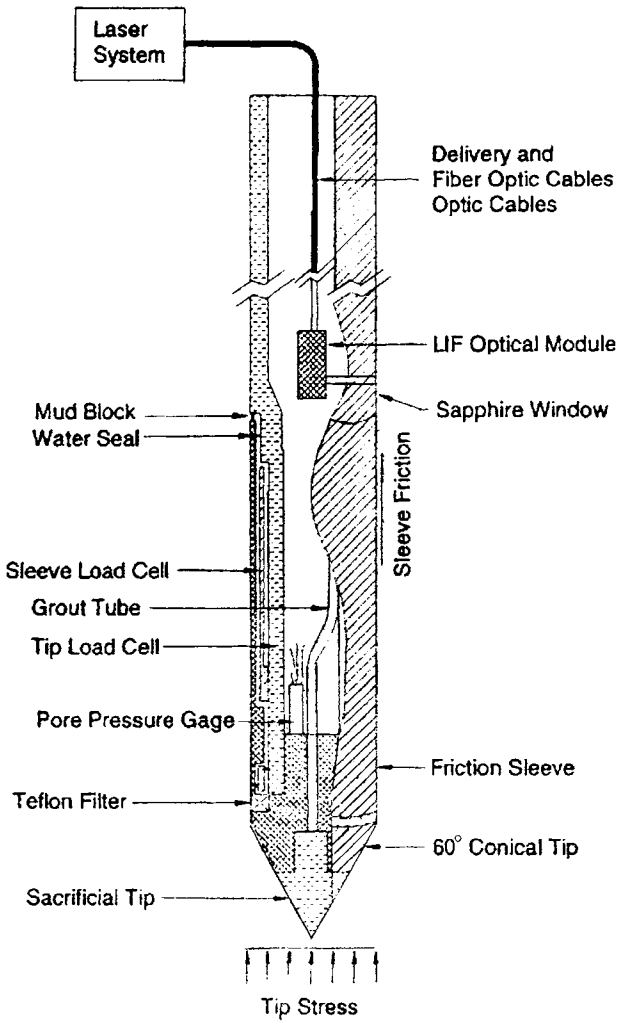


Figure IV.5.3. SCAPS-LIF probe (NaRaD, S. Lieberman, 619-553-2778), after U.S. DOE (1998).

Cone penetrometer technology can be adapted for other new sensors to measure various types of contaminants and other chemical characteristics of the subsurface; it can be used to install piezometers for soil vapor and groundwater measurements and to collect soil and water samples and is claimed to be less expensive when compared to drilling and sampling. Some limitations of use at all lithologic formations have been recently overcome by further advances in technology, e.g. by developing a vibratory assist device to allow penetration through hard rock zones. The most advanced currently available LIF sensors are though still too expensive to be applied commonly.

Therefore, conventional vadose zone monitoring methods such as direct soil-core and soil-pore liquid techniques as well as soil gas methods are still widely in use. Below, alternative invasive techniques for generating qualitative and quantitative information

about contaminants in the vadose zone and some basic principles of vadose and saturated zone monitoring in the waste disposal facilities are presented.

IV.5.2. Basic principles of vadose and saturated zone monitoring in the SWMU sites

IV.5.2.1. Basic concepts

Migration of contaminants in the SWMU site occurs in two zones (Fig. IV.5.1):

- Vertical migration in the vadose zone (non-vertical movement in the layers of different permeability can also occur);
- Horizontal migration in the aquifer (in the saturated zone).

The vadose zone therefore plays a role of a retardation barrier against contaminant migration to the aquifer (saturated zone). The basic parameter to be considered in risk assessment to groundwater from waste disposal facilities is the mean time of water migration from the land surface to the aquifer (t_a):

$$t_a = \frac{x}{U_a} \qquad (a - \text{years}) \tag{IV.5.1}$$

where x is the thickness of the vadose zone (m) and U_a, the actual velocity of vertical migration of water in the vadose zone (m/year).

Classification of a risk for water quality in the saturated zone as a function of a vertical migration time (t_a) is presented in Table IV.5.1.

Mean time of horizontal flow in the aquifer (t) is evaluated from the equation:

$$t = \frac{L}{U} \qquad (\text{years}) \tag{IV.5.2}$$

where L is the migration distance (m) and U, the actual velocity of water flow (m/year).

Actual velocity of water flow U in the aquifer:

$$U = \frac{V}{n_0} \qquad (\text{m/year}) \tag{IV.5.3}$$

Table IV.5.1. Classification of a risk for aquifer water quality based on the time of water migration (t_a) through vadose zone (after Kleczkowski, 1991a).

Class of risk	Extent of risk	Mean time of water migration from the land surface to aquifer t_a (years)
A	High	<5
B	Moderate	5–25
C	Low	25–100
D	Practically no risk	>100

where V is the mean filtration velocity (m/year) and n_0, the active porosity (dimensionless).

As

$$V = kJ \quad \text{(m/year)} \tag{IV.5.4}$$

where k is the hydraulic conductivity (m/year) and J, the hydraulic gradient (dimensionless), the actual velocity of water flow is:

$$U = \frac{kJ}{n_0} \quad \text{(m/year)} \tag{IV.5.5}$$

Velocity of a horizontal water flow can be classified in accordance with the principles applied in mapping major aquifers (Kleczkowski, 1991a,b) (Table IV.5.2).

Data presented above show that velocity of water flow in aquifers is generally low, scarcely tens or hundreds of meters per year.

Time of migration of conservative contaminants (that do not react with the ambient water–soil environment, $R = 1$) is equal to the time of water migration t_a and t, estimated from Equations (IV.5.1) and (IV.5.2) on the basis of actual water flow velocity in the vadose zone (U_a) and in the saturated zone (U).

For the contaminants amenable to sorption ($R > 1$) the migration time (t_a^*) is R times longer than that of conservative contaminants (t, t_a):

$$t_a^* = Rt \tag{IV.5.6}$$

where R is the retardation coefficient evaluated from the sorption isotherms.

For prediction of contaminant flow and transport in the vadose zone in space and time, numerous 2D and 3D computer models have been developed, and new ones suitable for a variety of vadose zone applications continuously appear in the market (e.g. GMS 4.0 or WHI UnSat Suite Plus packages). Nevertheless, the present state of the art still does not provide reliable computer-modeled simulations that may be used alone, but are considered to be the most useful in iterative monitoring/modeling combination with expert opinion for predicting and quantifying environmental risk from contaminated sites (Fogg et al., 1995; Cramer and Cullen, 1995).

Due to long-term impact of mining activity on the ground and surfacewater quality, lasting for decades, geochemical modeling of mine drainage formation in time and space

Table IV.5.2. Classification of water flow velocity (U) in the major aquifers (after Kleczkowski, 1991a,b).

Mean actual velocity of water flow U (m/year)	Character of flow
<10	Very slow
10–30	Slow
30–100	Moderately fast
100–300	Fast
>300	Very fast

with consideration of kinetics of sulfide oxidation and buffering capacity of a material is an integral part of predictive models that are still under development (Foos, 1997; Szczepańska and Kmiecik, 2001), along with commercially available geochemical computer programs, e.g. AquaChem having a direct interface to the popular PHREEQC model (SSG, 2003; Waterloo Hydrogeologic, 2003).

IV.5.2.2. Factors affecting quality of hydrogeochemical data

High economic value and commonly occurring risk to the shallow unprotected aquifers constrains the necessity of continuous water quality observations in the specially established monitoring network in the SWMUs and hazardous waste sites under RCRA. Monitoring of old sites should be preceded by site screening and analysis of site history and construction details if available. Water monitoring can be defined as repeated (with a defined frequency) analysis of water quality in permanent points, data processing and prognosis of trends to support actions focused on interception and remediation of adverse anthropogenic impact on the aquatic environment.

Sampling frequency of water quality monitoring in the vadose zone (pore solutions) and in the saturated zone (groundwater) is designed site-specifically, depending upon the velocity of water flow in these zones.

Sampling procedure is the first particularly important stage in the screening/monitoring of anthropogenic (waste layer) and natural vadose zone (pore solutions), as well as saturated zone (groundwater). To assure satisfactory analytical quality of data reported in the monitoring protocol (required level of precision and accuracy), proper procedures in a whole monitoring process should be used, starting from site selection, sampling technique, sample collection, processing and preparation for analysis, analytical methods, and data handling. Errors occurring in these stages should be summarized and will affect the final data given in the report (hydrogeochemical data – water physico-chemical characteristics). According to estimates, about 30% of the total error originates from sample collection and transport, 60% is due to sample processing and preparation for analysis, and barely 10% are analytical errors (Nielsen, 1991). QA/QC should not be limited just to the testing stage, but should comprise all the stages where errors can occur, with particular respect to the first stage, i.e. sampling (Fig. IV.5.4).

One of the major objectives of monitoring is evaluation of water quality changes in time or space. In the first case, the trends in water quality changes in time are assessed in the selected points of the monitoring network. In the second case, the extension of the contaminated zone from the contamination source is evaluated on the basis of measurements conducted in the local monitoring network. Thus, water sampling should be adequately time- and spatially representative. The time representativity depends on the sampling frequency that should enable assessment of the changes of water chemical composition resulting from the impact of the different sources of contamination. The frequency of sampling is assessed on the basis of hydrogeological premises depending upon the sampling depth and actual water flow velocity.

The spatial representativity is connected with sampling in the monitoring network (from permanent points), from the defined aquifer, constant depth and in the defined time intervals. Below, the general principles of representative sampling of the vadose and

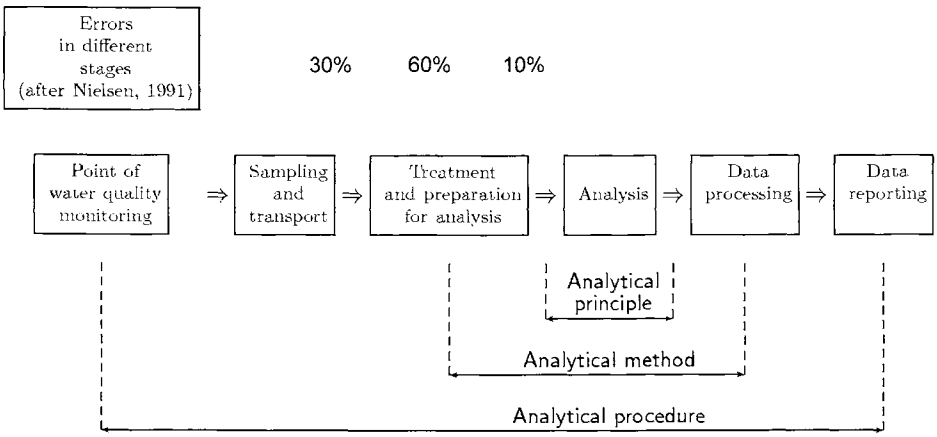


Figure IV.5.4. Monitoring of water quality. Phases of water quality monitoring procedures and relative error rates occurring in the subsequent phases.

saturated zones by invasive methods and QA/QC programs for assessment of errors occurring in the different phases of water quality monitoring (Fig. IV.5.4) will be discussed.

IV.5.2.3. Vadose and saturated zones sampling

Measurements of geochemical profiles of mine and other waste dumps have become a routine part of geoenvironmental investigations (Robertson et al., 1998; Twardowska et al., 1999, 2000; Helgen et al., 2000; Twardowska and Szczepańska, 2002).

Assessment of contaminant migration in the natural or anthropogenic vadose zone by invasive methods comprises the following procedure:

- Drilling of monitoring boreholes.
- Sampling of natural and anthropogenic soils from the defined depth intervals.
- Extraction of pore solutions from the soil samples (pressure methods, water extracts, solvent extracts).
- Analysis of constituent concentrations characteristic for the given source of contamination (indicator analysis) with use of adequate analytical methods.

Changes of chemical composition of pore solutions in the vadose zone in conjunction with the vertical redistribution of contaminant loads and transformations of chemical composition of pore solutions are observed in adequate depth and time intervals defined on the basis of the mean vertical infiltration velocity of precipitation waters U_a and conservative constituents, which migrate with the same velocity $R = 1$. This parameter can be assessed approximately from the mean infiltration rate and volumetric moisture content of soils in the vadose zone:

$$U_a = \frac{I}{W_0} \quad \text{(m/year)} \tag{IV.5.7}$$

where I is the mean infiltration rate of precipitation waters in the vadose zone (m/year) and W_0, the volumetric moisture content of soils in the vadose zone (dimensionless).

In the natural conditions of Poland mean infiltration rate I accounts for about 17% of atmospheric precipitation H (Pazdro and Kozerski, 1990), i.e. about 100 mm/year (0.1 m/year).

In Table IV.5.3 are given mean migration velocities assessed from Equation (IV.5.7) for typical natural soils of the vadose zone (loess) of several major groundwater basins (MGWB) in Poland. The mean volumetric moisture content of loess $W_0 = 0.30$ (Fig. IV.5.5A), hence the mean vertical migration velocity $U_a = 0.33$ m/year.

In the anthropogenic soils (e.g. coal mining waste of USCB, Poland) the infiltration rate is much higher compared to the mean values for natural soils. Infiltration rates for coal mining waste assessed from long-term lyzimetric studies in the natural hydrologic cycle (Fig. IV.5.6) account for $I = 0.68H$, i.e. about 400 mm/year (0.4 m/year). For volumetric moisture content of coal mining waste $W_0 = 0.12$ (Fig. IV.5.7), the mean vertical velocity of water migration U_a in the vadose zone of waste dump accounts for 3.33 m/year.

The vertical migration velocities U_a estimated from Equation (IV.5.7) on the basis of infiltration rate and volumetric moisture content of soils in the vadose zone appeared to be consistent with the data obtained from the field studies on conservative tracer (Cl^- ion) migration. Migration velocity evaluated from the Cl^- ion breakthrough curves (Fig. IV.5.5B) with use of the CXTFIT program (Parker and Van Genuchten, 1984) accounted for 0.31 m/year for loess, and 4.45–2.04 m/year for coal mining waste depending on the extent of weathering disintegration of waste at the dumping site (Table IV.5.4).

Therefore, for assessment of the depth and frequency of the vadose zone sampling, the actual vertical migration velocity U_a estimated from mean infiltration rate I and volumetric moisture content W_0 may be used. Volumetric moisture content W_0 may be assessed from the natural moisture content W_n and volumetric density of soil ρ_d:

$$W_0 = \frac{W_n \rho_d}{100} \tag{IV.5.8}$$

where W_n is the natural moisture content (wt%); ρ_d, the volumetric density of soil (g/cm^3); $\rho_d = \rho/(100 + W_n)100$, and ρ, the volumetric density of soil (g/cm^3).

Table IV.5.3. Mean vertical migration velocities U_a in the vadose zone formed from natural and anthropogenic soils.

Soil type		Atmospheric precipitation H (m/year)	Infiltration I (m/year)	Volumetric moisture content W_0 (m/year)	$U_a = \frac{I}{W_0}$ (m/year)
Natural	Loess	0.60	$0.60 \times 0.17 = 0.10$	0.30	0.33
Anthropogenic	Coal mining waste, USCB	0.60	$0.60 \times 0.68 = 0.40$	0.12	3.33

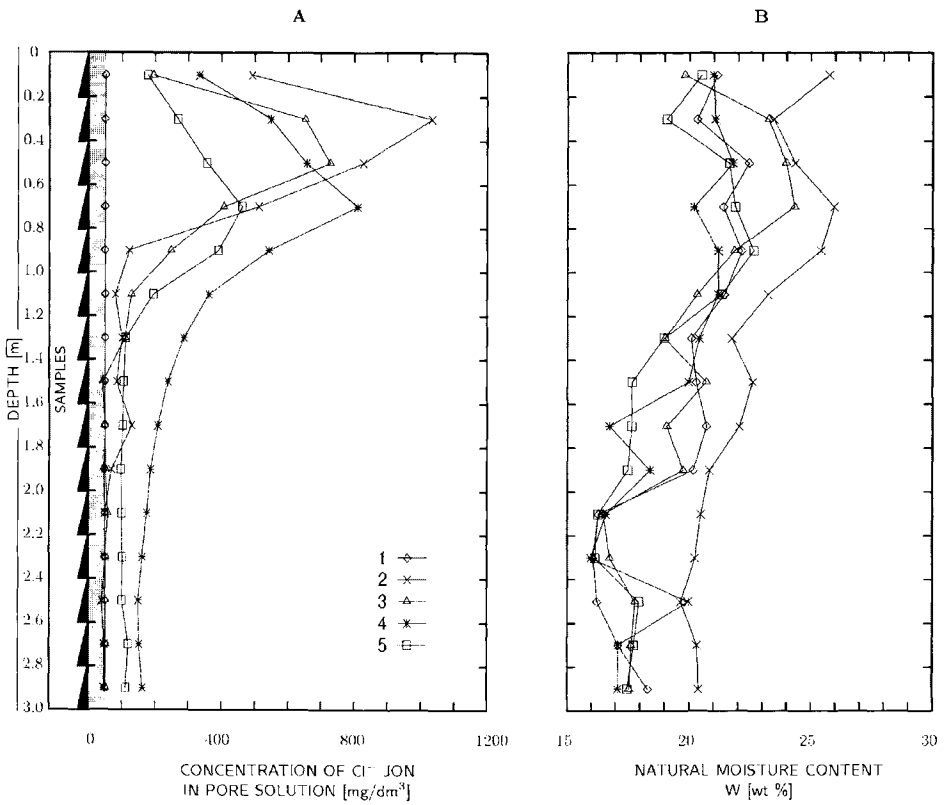


Figure IV.5.5. Conditions of contaminant migration in the vadose zone formed from natural soils. Loess insulating Major Groundwater Basin MGWB 459 in the Krakow area, Poland (after Bury (1994)). A – Scheme of soil-core sampling for observation of Cl^- ion migration. 1 – natural hydrogeochemical background of Cl^- ion preceding tracer injection ($t = 0$), 2–5 – Cl^- breakthrough curves for different time periods from the moment of tracer injection: 2 – after 7 months ($t = 7$), 3 – after 12 months ($t = 12$), 4 – after 24 months ($t = 24$), 5 – after 60 months ($t = 60$). B – Scheme of pore water sampling for evaluation of loess moisture content in the vadose zone.

Location of samples in the vertical profile of the vadose zone and frequency of sampling should be assessed on the basis of the actual migration velocity U_a. For loess, samples have been taken every 0.3 m along the vertical profile (Fig. IV.5.5A,B), while coal mining waste were sampled in 1.0 m intervals (Fig. IV.5.7) with sampling frequency ≥ 1 year.

Sampling frequency should be estimated individually, depending upon the time of water percolation through analyzed vadose zone (t_a). As can be concluded from Equation (IV.5.1), time t_a depends on the vadose zone thickness (x) and actual velocity of vertical migration (U_a).

Water percolation t_a through an analyzed loess layer 3 m thick will last approximately 10 years, hence the frequency of sampling should be no higher than once a year, except the initial period of monitoring, when the sampling should be more frequent due to the need of

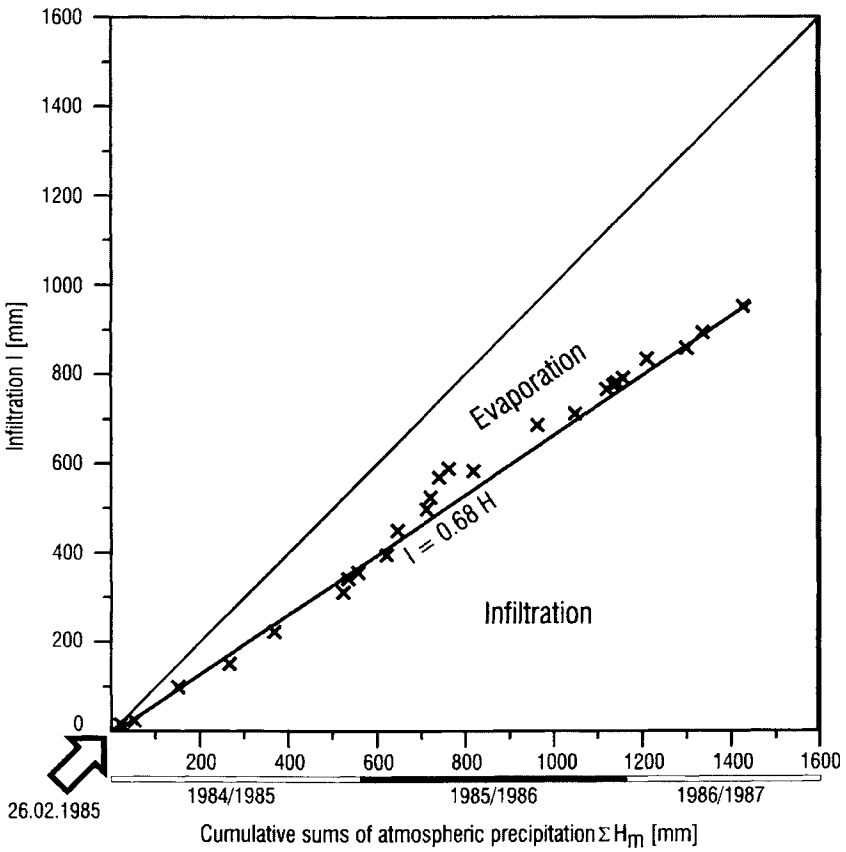


Figure IV.5.6. Infiltration rate *I* vs. precipitation *H* in coal mining waste of USCB, Poland. Lyzimetric studies in the natural hydrologic cycle.

estimation of possible changes in the uppermost layer resulting from the variability of infiltration rate in dry and wet periods.

IV.5.2.4. Monitoring of groundwater quality in the vicinity of waste disposal site

For evaluation of the natural hydrogeochemical background and observation of disposal site (SWMU) impact on groundwater quality (both in operational and post-closure periods) monitoring of groundwater is being conducted. It is classified as a local monitoring (LMGW). Its design, realization and operation in Poland follow the guidelines of the State Inspectorate of Environmental Protection (Staniewicz-Dubois, 1995) and European Union (EU, 1996; EEA, The European Environment Agency, 1999).

The number of observation boreholes and their location depends on the SWMU size and the hydrodynamic field of ambient groundwater. The approximate density of the local monitoring network should be about 1 LMGW borehole/ha. Monitoring wells should be located in three zones (Fig. IV.5.8A,B):

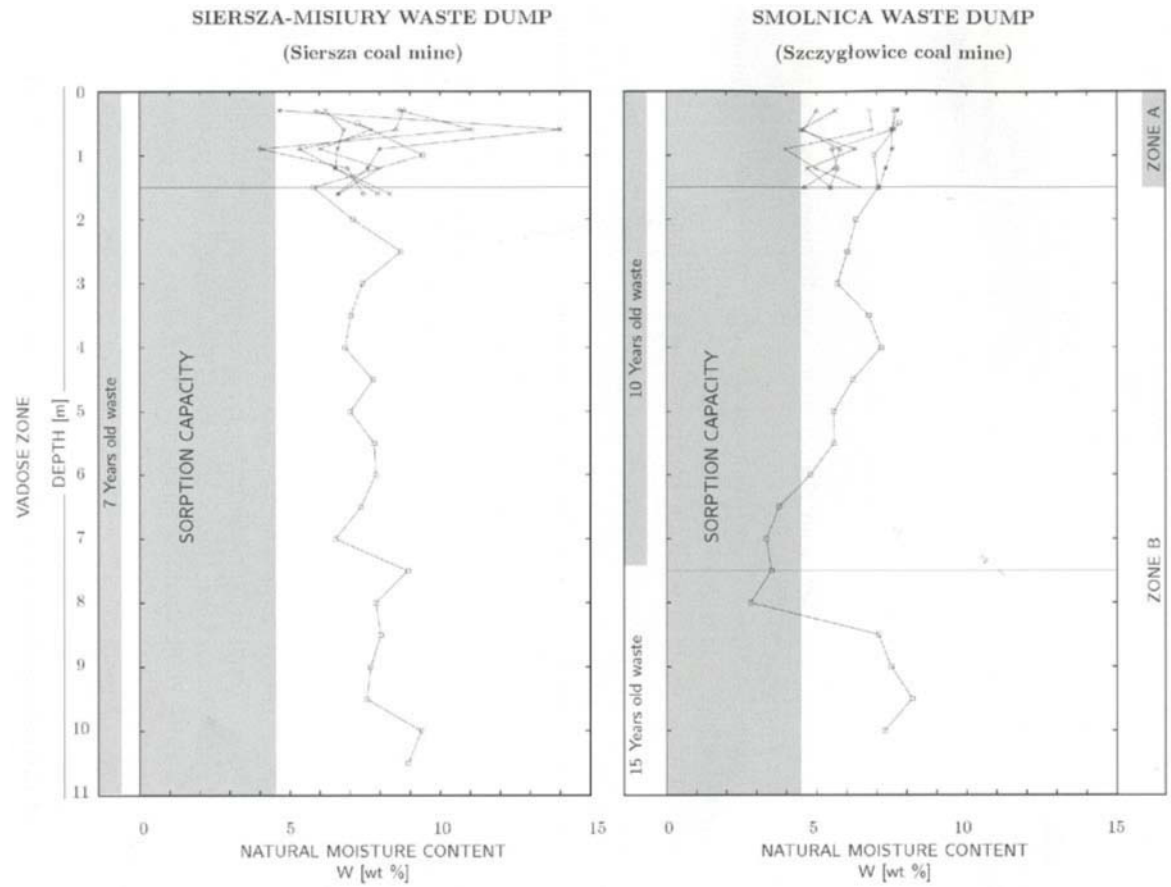


Figure IV.5.7. Conditions of contaminant migration in the anthropogenic vadose zone formed of coal mining waste dumps in the USCB, Poland. Scheme of soil-core sampling for assessment of natural moisture content in the vadose zone of the Siersza-Misiury and Smolnica dumps.

Table IV.5.4. Values of mean vertical migration velocity U_a in the natural and anthropogenic soils in the vadose zone estimated from Equation (IV.5.7) and from the program CXTFIT on the basis of breakthrough curve for conservative tracer (Cl^- ion).

Soil type		$U_a = \frac{I}{W_0}$ (m/year)	U_a (m/year) (estimated with use of CXTFIT program-Parker & Van Genuchten, 1984)	Data source
Natural	Loess	0.33	0.31	Bury (1994)
Anthropogenic	Coal mining waste USCB	3.33	4.45 (fresh waste) 4.42 (8 years old) 2.59 (12 years old) 2.04 (18 years old)	Szczepańska and Krawczyk (1994)

- up-gradient of groundwater flow with respect to the site location (assessment of a natural hydrogeochemical background);
- within the dumping site (assessment of maximum concentrations of contaminants percolating through the site bedrock);
- down-gradient of the waste disposal site (contaminated water zone).

In the down-gradient area, LMGW monitoring wells should be installed in three zones distant from the dump contour selected to be adequate to the different time of water flow in the aquifer: $T_{\mathrm{I}} < 200$ days, $T_{\mathrm{II}} = 2$ years, and $T_{\mathrm{III}} > 2$ years and defined from the equation $L_n = UT_n$ where n = I, II and III, respectively (Fig. IV.5.8A,B).

In the LMGW, existing dug wells, observation boreholes (piezometers) as well as seepage and outflow from the dump toe may be used as monitoring points. The basic scheme of groundwater sampling in the LMGW in the solid waste disposal sites, sample preservation and quality assurance procedure (QA/QC) during sampling and analysis is presented in Figure IV.5.9.

The principles of groundwater monitoring, well construction and installation are widely presented in several fundamental handbooks where also the procedure of sampling and monitoring, as well as QA/QC requirements, which ascertain correct characterization of chemical composition of water in the monitored endangered aquifers, is discussed in detail (Nielsen, 1991; Lesage and Jackson, 1992; Sara, 1993, 1994; Wilson, 1995; Asante-Duah, 1996; Looney and Falta, 2000; Boulding and Ginn, 2003), along with the guide to major references including U.S. EPA (1988) and ASTM (1994–2003).

IV.5.3. Use of variance analysis for quality assurance/quality control (QA/QC) in groundwater monitoring

QA/QC in LMGW for solid waste disposal sites is of particular stringency when the monitoring data have either direct legislative liability or economic consequences in assessing fees/penalties on facility owners, or used for research purposes. QA/QC in

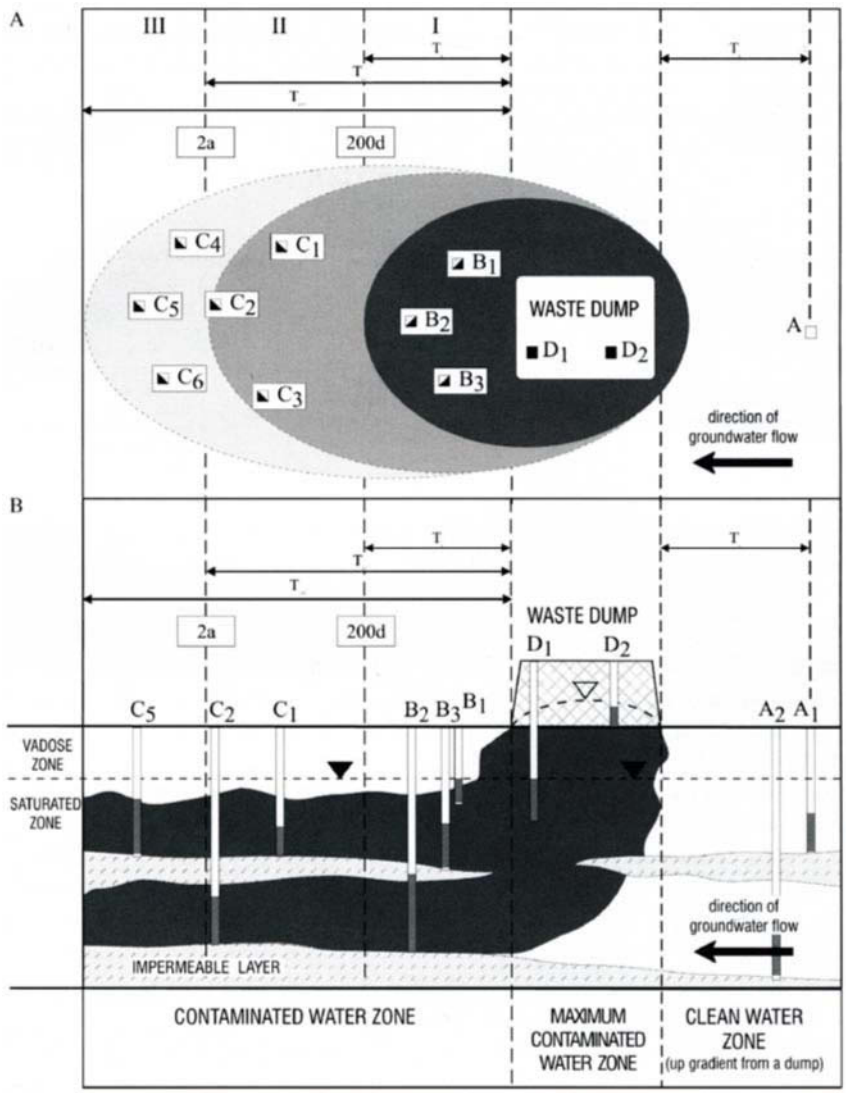


Figure IV.5.8. Local monitoring of ground water quality (LMGW) in a solid waste site. A – location of the monitoring network sites. B – Scheme of permanent monitoring well installations for observation of contaminant migration in the upper and lower level of the aquifer (after DVWK, 1992).

groundwater monitoring consists of two independent field and laboratory procedures, which are aimed at identifying and eliminating errors generated during sample collection, preservation, storage and transportation to the laboratory, as well as chemical analysis in the field and in the laboratory. The basic routine QA/QC procedures comprise collection and analysis of additional samples (10–20%), which consists of blanks, field, replicate, duplicate, split, and spiked samples, as well as use of SRMs, and are widely discussed in

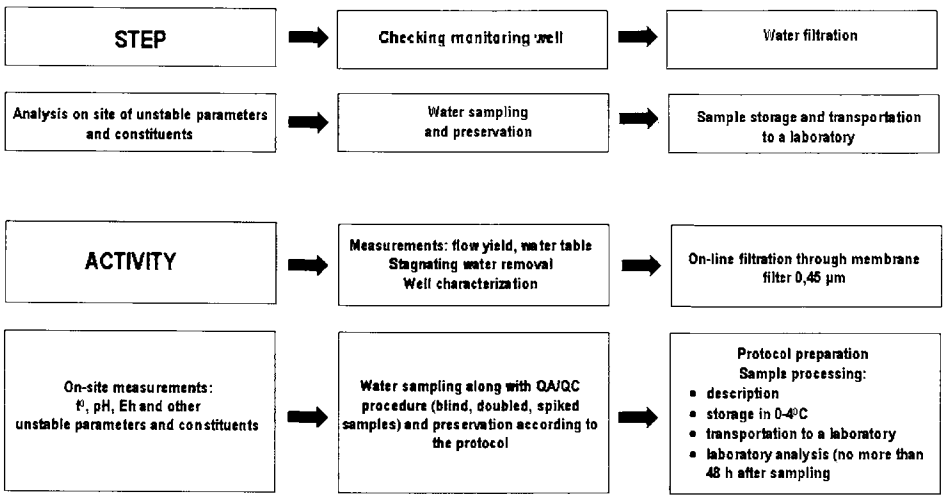


Figure IV.5.9. Basic flow diagram of water sampling, preparation and analysis procedure in monitoring of groundwater quality (after Witczak and Adamczyk, 1994.

the numerous U.S. EPA reports/guidances and other relevant sources quoted in the handbooks referred to previously. A particularly rich and systematic reference index on QA/QC in the vadose zone and groundwater monitoring is contained in the fundamental handbook prepared by Boulding (1995).

A valuable tool for analysis of precision in the groundwater quality monitoring is the analysis of variance ANOVA approach (ANOVA/MANOVA, 1984–2003) put forth by Garrett (1969) and developed in the present form by Ramsey et al. (1992). The current practice of QA/QC in groundwater monitoring shows that ANOVA is the most cost-effective method of reliably estimating random errors occurring in the sampling and analytical procedures (Szczepańska et al., 1999). Opposite to standard deviation, variance is additive and can be totaled if variance sources are independent. In the ANOVA method, natural spatial variability of physico-chemical parameters of groundwater can be assessed numerically by hydrogeochemical variance σ_g^2 for duplicate samples taken in the LMGW network.

The total observed spatial variation can be presented in the form of the total variance (σ_t^2):

$$\sigma_t^2 = \sigma_g^2 + \sigma_s^2 + \sigma_a^2 \tag{IV.5.9}$$

where σ_g^2 is the hydrogeochemical variance, σ_s^2, the sampling variance, and σ_a^2, the analytical variance.

The impact of sampling cannot be distinguished from laboratory errors without conducting the special extended quality control sample analysis (Fig. IV.5.10A), where the number of analyses is doubled with respect to the routine QC program (Fig. IV.5.10B). In the routine QC program, the technical variance σ_{tech}^2, which is a sum of the sampling and

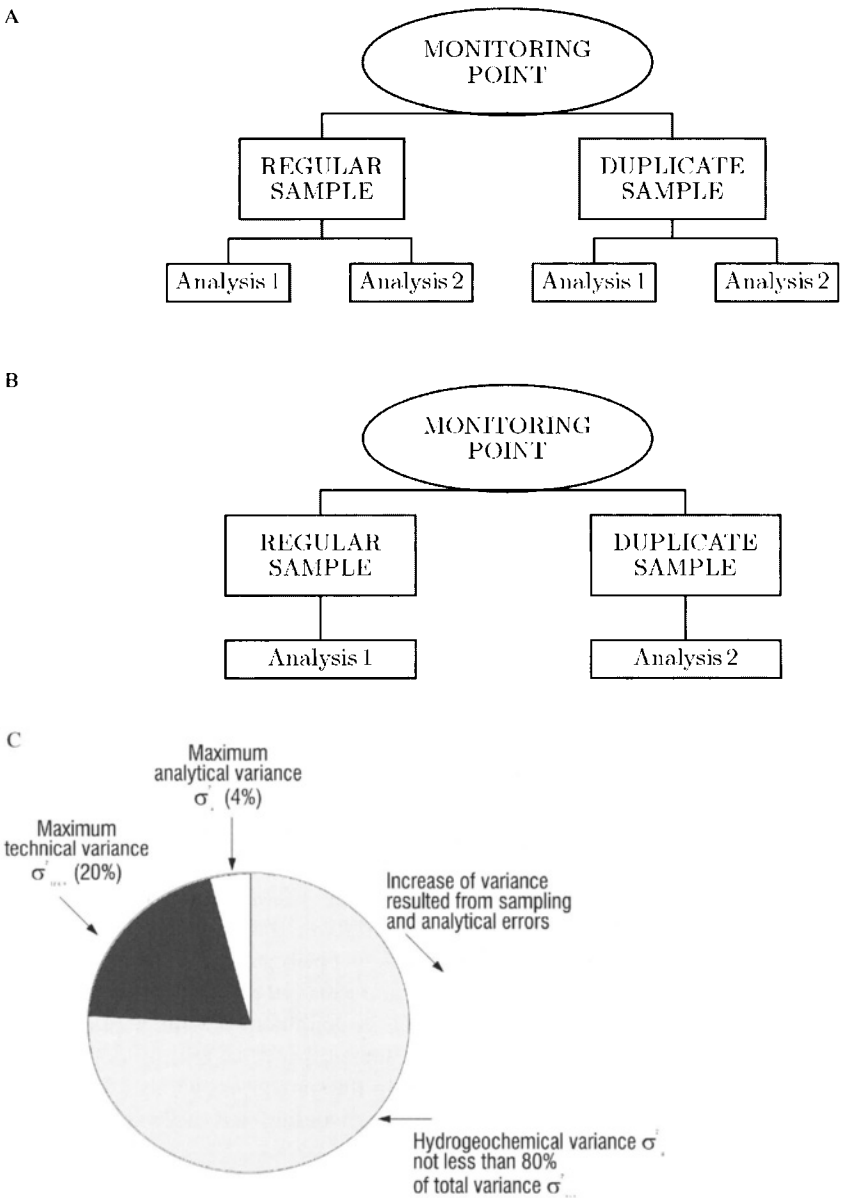


Figure IV.5.10. Sampling of groundwater quality monitoring site for ANOVA analysis of variance (after Ramsey et al., 1992). A – Diagram of procedure for evaluation of sampling variance (σ_s^2) and analytical variance (σ_a^2). B – Diagram of procedure for evaluation of technical variance ($\sigma_{tech}^2 = \sigma_s^2 + \sigma_a^2$). C – Maximum acceptable level of sampling (σ_s^2), analytical (σ_a^2) and technical variance ($\sigma_{tech}^2 = \sigma_s^2 + \sigma_a^2$).

analytical variance, is estimated:

$$\sigma_{tech}^2 = \sigma_s^2 + \sigma_a^2 \qquad \text{(IV.5.10)}$$

Precision is considered satisfactory, if the technical variance (σ^2_{tech}) does not exceed 20% of the total variance, σ^2_t, while analytical variance, σ^2_a, should not exceed 4% of the total variance, σ^2_t (Fig. IV.5.10C) (Ramsey et al., 1992).

IV.5.4. Use of neural networks for long-term prognosis

As has been shown, generation and leaching of contaminants from solid waste disposal units, e.g. mining waste piles may last for decades, thus posing threat to the aquatic environment. This requires conducting adequate long-term monitoring of groundwater at the disposal site. Due to complexity of weathering processes in such heterogeneous systems as ARD-generating mining waste, where contaminant release is governed with kinetically defined process of sulfide oxidation, geochemical computer modeling with use of many existing popular programs such as WATEQ4F (Ball and Nordstrom, 1991, 1994) Visual MINTEQ v. 2.01 (Allison et al., 1991) is encumbered with serious predictive uncertainties. Much greater capabilities displays PHREEQC – a computer program of USGS for speciation, batch reaction, dispersion, advective-transport and inverse geochemical calculations (Parkhurst, 1995; Scott et al., 1997; Parkhurst and Appelo, 1999; Zhu and Anderson, 2002) in particular the newest version PHREEQC Interactive 2.8.0.0 (2003), or a sophisticated software package for aqueous geochemical analysis AquaChem (SSG, 2003; Waterloo Hydrogeologic, 2003) that incorporates PHREEQC. This program allows multi-component reaction kinetics and transport modeling in complex geochemical systems and is thus the most applicable for simulation of ARD generation and transport (Appelo et al., 1998; Postma and Appelo, 1999), also with uncertain data (Parkhurst, 1997). For simulating flow and organic contaminant transport in the vadose zone of landfills, the WHI UnSatSuite graphical environment (SSG, 2003; Waterloo Hydrogeologic, 2003) provides a comprehensive tool. Nevertheless, all these programs require a developed set of input data that are often not available. In such cases, neural networks, which permit "incomplete" input data and are capable of parallel data processing, can be of use. Their beginning has been generally associated with the appearance of a historical work by McCulloch and Pitts (1943) who for the first time gave a mathematical description of the neural cell in conjunction with a problem of data analysis. The major merit of neural networks is their ability of "learning" complex pictures and trends of data change and human-like using the gained knowledge for solving new problems. Development of the neural network modeling has been supported by the progress in computer techniques and programs.

On the basis of results of long-term lysimetric studies on coal mining waste conducted by the authors in 19 years natural hydrologic cycle, it was found that for the prognosis of contaminant release from waste as a function of time and for assessment of a time span in which the concentration of leached contaminants will reach the permissible level (Directive of the Minister of Health, 2000), models of supervised neural networks of multi-layer perceptron (MLP), radial basis function (RBF) or Bayesian network (SPSS Inc., 1997, 1999) can be successfully applied.

Models of neural network were constructed with use of the Neural Connection v. 2.1 program (an example of a used simple supervised neural Bayesian network is presented in Figure IV.5.11). The details of models of supervised neural network construction and use

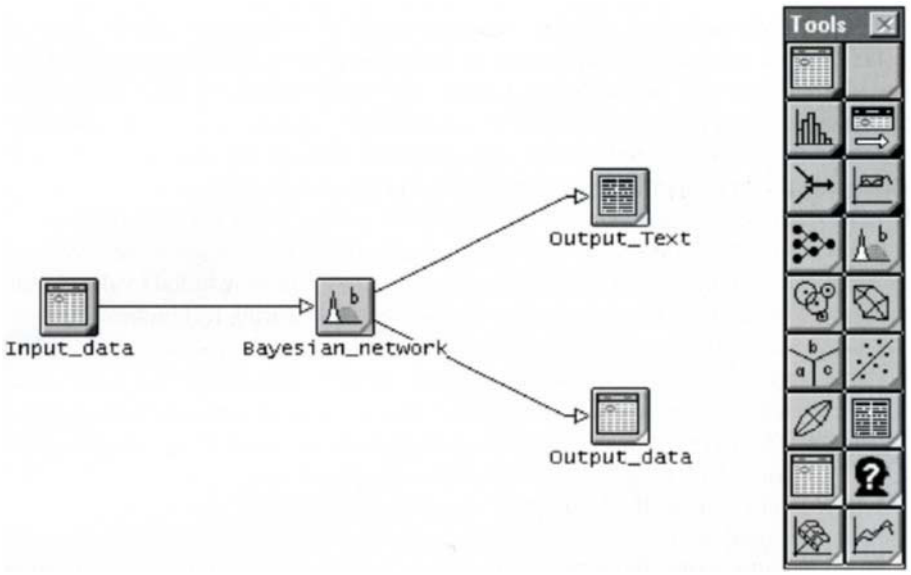


Figure IV.5.11. Scheme of a simple supervised neural Bayesian network. Screen projection from the Neural Connection program v. 2.1 (SPSS Inc., 1999).

for simulation of contaminant leaching from coal mining waste are discussed elsewhere (Kmiecik, 2000; Szczepańska and Kmiecik, 2001; Kmiecik et al., 2003).

The precision of prognosis appeared to be satisfactory for practical purposes, as the relative error does not exceed several percent. With use of neural networks, the time span in which the concentration of contaminants of interest will reach the permissible level or their release will terminate can be assessed, so that the groundwater deterioration as a function of duration of the waste disposal can be evaluated. The evaluation with use of this tool requires much lesser number of observations than in the traditional methods; thus it allows significant reduction of time and costs of a monitoring program.

IV.5.5. Concluding remarks

Monitoring of the vadose zone is gaining increased recognition in the regulatory and implementation arena as an instrument of early detection and subsequent prevention/interception/attenuation of aquifer contamination in the most cost-effective and efficient way. It should be considered complimentary to saturated zone monitoring as a warning system indicating an alarming extent of contaminant migration to the aquifer, while saturated zone monitoring provides data on the actual status of the groundwater quality in the SWMU sites.

In the USA, regulatory amendments of the U.S. EPA (1988–2003) require vadose zone monitoring at RCRA hazardous waste disposal sites on a case-by-case basis, there is though still lack of regulations in this respect in the EU and other countries. The authors' experience in the studies of non-hazardous waste disposal utilities shows that anthropogenic vadose zone (waste layer) screening/monitoring can be particularly useful in the detection of

the eventual unfavorable weathering transformations of such waste, which may cause massive delayed release of contaminants in a hazardous level from the old high-volume waste dumps that are often located over the unprotected aquifers amenable to contamination. Routine invasive soil-core and soil-pore liquid screening/monitoring of the anthropogenic and natural vadose zone provides data on the migration of the non-organic and organic contaminants in these zones and thus permit long-term validation of the risk assessment and undertaking of cost-effective corrective actions if required. The disadvantages of these methods, which are repeated disturbance of the monitored media, and complicated sampling/sample preservation procedure can be avoided by development of non-invasive and near-time innovative vadose zone monitoring techniques.

Although currently most of these methods are still expensive and have also technical limitations, further improvement of indirect non-invasive monitoring techniques should result in providing sophisticated representative vadose zone networks, which assure economically beneficial contaminant prevention and remediation in potentially endangered sites.

For simulation and prognosis of the duration of adverse impact on the aquatic environment of solid waste containing unstable phases (e.g. sulfide-bearing mining wastes), application of supervised neural networks appears to be a useful tool that allows reducing the required time of studies for obtaining input data, and as a result, a substantial reduction of costs for vadose zone monitoring.

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IV.6

Specimen banking as a source of retrospective baseline data and a tool for assessment and management of long-term environmental trends

Antonius A.F. Kettrup and Petra Marth

IV.6.1. Introduction

According to the "European Inventory of Existing Commercial Substances" EINECS (after GDCh/BUA, 1987), more than 100,000 different chemical substances are produced worldwide. 1000–2000 new chemicals are entering the market every year in addition to those already in circulation. For most of them we lack sufficient information about their effects on man, animals and plants and about their further reaction fate transport mechanism, and effect on the environment (SRU, 1987). New technologies *always* produce unintended and unpredicted wastes and impacts. According to the single integrated EC waste list (Commission Decisions 2000/532/EC, 2001/118/EC), the majority of waste from organic chemical processes (code 07) and significant part of waste from inorganic chemical processes (code 06) are considered as a hazardous waste. A large number of the European Community legislation in force and in preparation is focused on various chemical waste and waste chemicals. It can be found in the EUR-Lex register 15.10.30.30 "Waste management and clean technology", Web site: http://www.europa.eu.int/eur-lex/en/lif/reg/en_register_15103030.html.

Usually the introduction of chemicals into the environment represents an irreversible step. A considerable number of chemicals reaching the environment do not degrade at all or only very slowly. They accumulate in the environment and, having been distributed, become ubiquitous of certain pollutants, e.g. PCBs, herbicides and chlorinated insecticides. Persistent biologically active chemicals, even at concentrations below our ability to analyze or detect, can pose serious pervasive and possible irreversible threats to human health and the integrity of the biosphere (Lewis, 1988).

Numerous industrial countries have passed laws to assess the hazards of chemicals for man and the environment. EC legislation on chemicals is collected in the register EUR-Lex 15.10.20.50 "Chemicals, industrial risk and biotechnology" in the Web site http://www.europa.eu.int/eur-lex/en/lif/reg/en_register_15102050.html. Among others, it comprises the Council Directive 76/769/EEC (1976) relating to restrictions on the marketing and use of certain dangerous substances and preparations, with numerous current amendments, fast one of 2002 (*OJ L* 183 12.07.2002), as well as four lists of priority substances established by the Decision No 2455/2001/EC of the European

Parliament and of the Council in the field of water policy, and Commission Regulations (EC) No 1179/94 (1994), No 2268/95 (1995) and No 143/97 (1997) as foreseen under Council Regulation (EEC) No 793/93 (1993). The principles for assessment of risks to man and environment of different chemicals were laid down in Commission Directive 93/67/EEC (1993), Regulations (EC) No 1488/94 (1994), as well as in Commission recommendations, e.g. 1999/721/EC (1999) and C(2001)439.

Investigations on forecasting the impacts of chemicals are afflicted by special costs and problems (Fig. IV.6.1) (Wagner, 1994a,b).

Living organisms and their associations are enormously heterogeneous, complex and open systems are characterized by poorly defined boundaries. Under the best circumstances, we can evaluate most quantitative features of biological systems only for certain properties and only by using certain samples or subsets of the class. Results are always statistical in nature and extrapolation from the sample to the class is necessary. Many environmental factors that cannot be reproduced or represented in the laboratory or by models can modify the environmental behavior and effects of chemicals. The error in

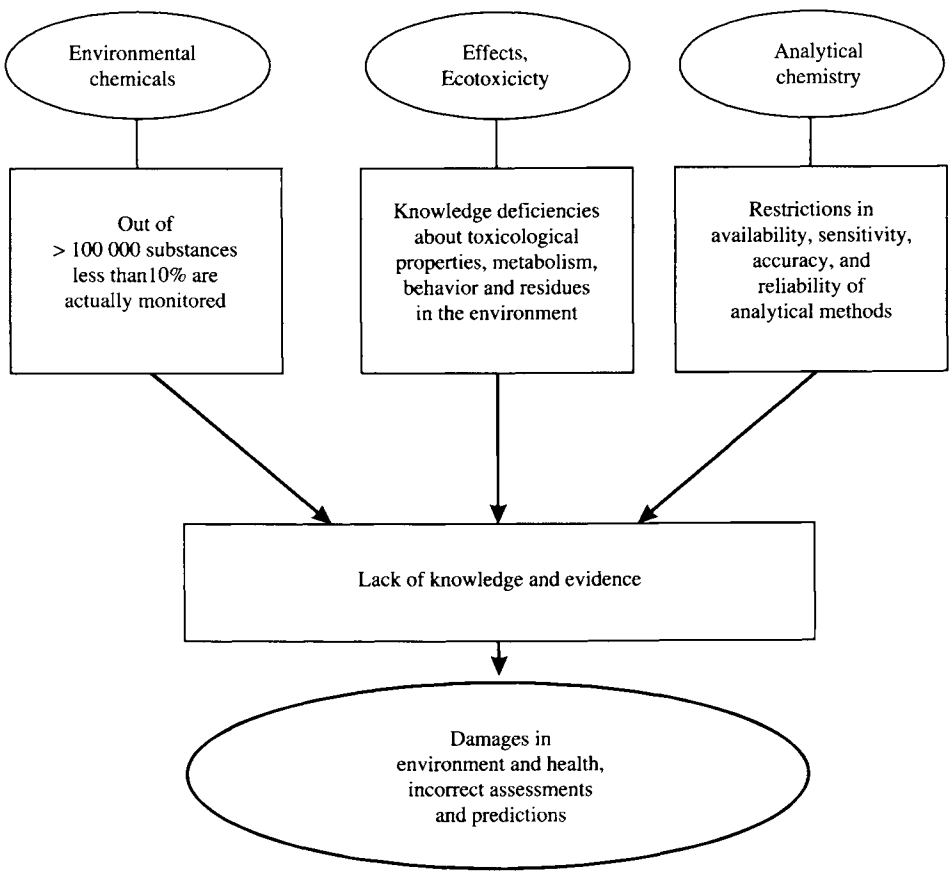


Figure IV.6.1. Deficits in assessment and control of environmental chemicals (after Wagner, 1994a,b).

forecasts based upon trend extrapolations, without knowing the relationships of environmental variables may become enormously enlarged with time. Recognizing the actual form of a trend among reasonable alternatives is difficult and often subjective. Thus, the level of uncertainty of most forecasts and assessment of chemical impacts upon man and the environment is often quite high. Even today, we repeatedly confront serious and unexpected consequences of our technologies, products and wastes. Politicians and administration can only develop effective damage protection and risk contaminant strategies, if they have reliable scientific information available.

IV.6.2. Bioindicators

The idea that organisms can provide an indication of the quality of their environment is widespread and at least as old as agriculture (Thalius, 1588). It is not possible to establish any clear definition for the term "bioindicator" considering the large amount of published literature. The following definitions are suggested congruent to many European authors (Wittig, 1993):

- *Bioindication* is the use of an organism (a part of an organism or a society of organisms) to obtain information on the quality (of a part) of its environment. Organisms that are able to give information on the quality (of a part) of its environment are bioindicators.
- *Biomonitoring* is the continuous observation of an area with the help of bioindicators, which in the case may also be called biomonitors. With the aid of organisms trends in time and space concerning the distribution and ecological effects of environmental chemicals can be observed by a semi-quantitative evaluation of the results.

Biological samples, from the environment, are mainly used and analyzed as representatives for larger entities or similar or related environmental compartments. This requires the selection of standardized (bio)indicator systems, which react with known specifics and sensitivity to environmental chemicals and have the capability of spatial and/or temporal integration. Such indicator systems can be efficiently and reproducibly analyzed and evaluated vicariously for the total entity of sensitive targets in the environment to be observed, which are often extremely variable with respect to the space, time and physiology. Bioindicator systems can be applied in such cases, where potential integral effects of complex or unknown immission types have to be detected and quantified. Such effects may occur on different levels from specific organs of single organisms up to whole ecosystems. Bioindicators are also preferred, where they offer advantages due to their high sensitivity towards a broad spectrum of substances or because of their ability to accumulate a substance over an extended period or to integrate its influence in an area of known and relevant size. This is the case, if the sensitiveness of available analytical methods for dangerous substances is too low to find them in other environmental media (air, water and soils).

In addition to the concentrations of toxic substances and their metabolites biological specimens can also be analyzed for essential components and a broad spectrum of possible biochemical, physiological, morphological and/or genetic effects. Organisms and biological communities normally do not react to single components or substances in

their environment. They show the effects of the totality of all the acting substances and environmental factors. Decisive for the use of biological specimens is their ecotoxicological relevance that means the relevance or indicative function of the found effects for other living organisms and communities including men.

IV.6.3. Idea of environmental specimen banking

With respect to effects of pollutants, the acquisition of reliable information regarding their quantities and distribution under natural conditions requires a systematic program of environmental monitoring in which concentrations of hazardous chemical substances are measured in suitable environmental specimens of various trophic stages and food chains. But actual monitoring of the environment can only be as good as our present knowledge, analytical capabilities, and quality assurance and quality control allow. From among the multitude of substances found in the environment only those can be monitored, which have already been recognized to be hazardous. The present assessment of the measured environmental concentrations of hazardous substances – and thus, the quality of regulatory decisions – suffers from the fact that no results are available on pollutant burdens of former times or that the data which are available are ambiguous (Kayser et al., 1982).

Before this background at the beginning of the 1970s the idea of using biological samples as reference material to furnish proof of environmental pollution was put forward by Frederick Coulsten of the Albany Medical College, Albany, New York and Friedhelm Korte of Institute of Ecological Chemistry, GSF-Forschungsungszentrum, Munich-Neuherberg.

In an environmental specimen bank (ESB) carefully selected, relevant environmental samples are stored systematically at temperatures below $-150°C$ immediately after collection. In these conditions either no, or as small as possible, chemical changes occur over a long period of time. Baseline levels of contaminants in the environment can be established by taking samples with use of known approved methods and preserving them at the present time for future demand in ecological–chemical research. Long-term storage of samples with indicator functions represents a necessary complement to the actual monitoring of the environment and a safety net in the assessment of chemical risk.

A systematically established archive of frequently collected representative environmental specimen samples fulfill the following important functions (Kayser et al., 1982; Wise and Zeisler, 1984, 1985; Lewis, 1988; Keune, 1993):

- They may be used for the determination of the environmental concentrations of those substances, which, at the time of storage, were not recognized to be hazardous or which at present cannot be analyzed with adequate accuracy (retrospective monitoring).
- They may serve as reference samples for the documentation of the improvement of analytical efficiency and for the verification of previously obtained monitoring results.
- Early detection of environmental increases in hazardous chemicals thought to be under control is possible. Also, the effectiveness of restrictions, regulations or management practices that have been applied to the community, the environment, or to the manufacture, distribution, disposal or use of toxic chemicals can be assessed.
- Depending upon the analysis and evaluation of stored materials ESB can save considerable time and money when unexpected impacts are observed.

- Sources of chemicals may be identified. Often, by the time a chemical is recognized as a health or environmental problem it is sufficiently widespread to defy identification of the principal sources or pathways.
- ESB can offset the lack of reliable data on pollutant burdens of earlier times because inconsistencies or ambiguities among available data usually limit assessments and regulatory decisions.

In Germany the Federal Minister for Research and Technology supported a comprehensive pre- and pilot phase of ESB between 1976 and 1984. During this period the technical feasibility regarding the sampling of different species, handling and shipping of samples, deep-freezing, homogenization, ultra trace analysis, packing materials, logistics, storage temperature and documentation was confirmed (Boehringer, 1988). The results were so encouraging that in 1985 the German government decided to set up a permanent ESB under the responsibility of the Federal Ministry for the Environment, Nature Conservation and Reactor Safety (BMU), coordinated by the Federal Environmental Agency (Umweltbundesamt). Two specimen banks are subsumed under the general heading of the German ESB:

- The Specimen Bank for Environmental Specimens at the Institute of Applied Physical Chemistry of the Research Center Jülich (KFA).
- The Specimen Bank for Human Organ Specimens at the Institute of Pharmacology and Toxicology of the University of Münster.

The work is distributed among five institutions depending on their special scientific capabilities. In Table IV.6.1 the participating institutions of the German ESB and their responsibilities are summarized.

Table IV.6.1. Participating institutions of the German ESB.

Institution	Task
KFA Research Center Jülich, Institute of Applied Physical Chemistry	Specimen Bank for Environmental Specimens, central banking facilities, logistics, element analysis, sampling of marine specimens
University of Münster, Institute of Pharmacology and Toxicology	Specimen Bank for Human Tissues, sampling, characterization, storage and analysis of human samples, data banking system
GSF Research Center Neuherberg Institute of Ecological Chemistry	Analysis of CHC
Biochemical Institute for Environmental Carcinogens, Grosshansdorf	Analysis of PAHs
University of the Saarland, Saarbrücken Institute of Biogeography	Selection and characterization of areas and specimen types, sampling of terrestrial and limnic specimens, ecological questions
Fraunhofer-Institute of Environmental Chemistry and Ecotoxicology	ERGO Ltd., Hamburg

In the meantime the national ESBs in the several countries and international cooperation of ESBs in the Federal Republic of Germany, USA, Canada, Japan, Finland, Sweden, Norway and Denmark have been established (Wise and Zeisler, 1985; Wise et al., 1988; Zeisler et al., 1992; Stoeppler and Zeisler, 1993; Kubin et al., 1997; Pugh, 2001).

IV.6.4. Realization

IV.6.4.1. Sampling

IV.6.4.1.1. Selection of sampling areas

Sampling areas have been chosen as to form a national Network of Ecological Assessment Parks coordinating environmental specimen banking with long-term ecological research and environmental monitoring (Lewis, 1985, 1987; Paulus et al., 1990; Lewis et al., 1993). An overall concept has been developed by a committee of experts under the auspices of the BMU, taking into consideration different types of ecosystems with corresponding representative sampling areas according to the following criteria:

- stability of utilization,
- assured long-term use,
- sufficient minimal size,
- availability of suitable samples,
- practicability, e.g. accessibility, public ownership (National Park), no conflict with the protection of biotopes and species, high level of information, nearby suitable institutions for research.

The list of, at present, 14 areas (Fig. IV.6.2) comprises the major ecosystems and habitat types that occur within the Federal Republic of Germany including

- limnic and marine ecosystems,
- urban industrial ecosystems,
- forest and agricultural ecosystems and
- semi-natural ecosystems.

Since 1985, continuous sampling has been carried out every 2 years but it should be converted into a 1 year sampling frequency to utilize the analytical, biometric and meteorological data much more effectively in the sense of real-time monitoring.

IV.6.4.1.2. Selection of specimen types

The selection and assignment of representative specimen species of the terrestrial, limnic and marine ecosystems for the ESB was undertaken by a committee of experts in consideration of the above-mentioned indicator functions so that a broad spectrum of different types of matrices (all trophic levels) and media (air, sediment and soil) with environmentally relevant concentrations of xenobiotics is available (see Figure IV.6.2)

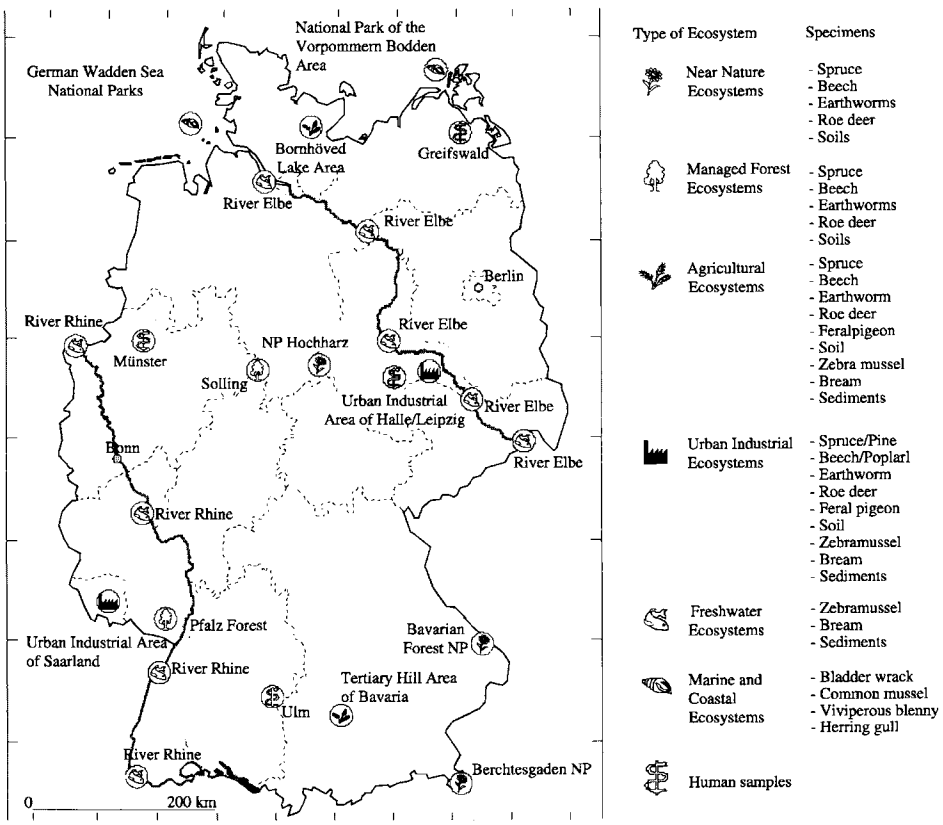


Figure IV.6.2. Sampling areas and specimens of the German ESB-program.

(Lewis, 1985; Lewis et al., 1993). The following requirements must be fulfilled for using a matrix as bioindicator:

- The chemicals must be accumulated comparable to levels occurring in the environment.
- Contamination trends in the environment must correspond to those in the matrix.
- The matrix should have a widespread distribution and must be available in time and place to a sufficient extent.
- The organism should be sedentary and easy to identify.
- The species should accumulate the pollutant without being killed or rendered incapable of reproduction.

IV.6.4.1.3. Standard operation procedures

Standardized sampling guidelines or standard operating procedures (SOP) are the basis for the comparability, reliability and repeatability of the banked samples. They contain detailed instructions for the

- selection of sampling sites and specimens,
- sampling,
- providing cover for repeatability of sampling,
- area and sample characterization,
- sample treatment and long-term storage,
- documentation of sampling and storage conditions,
- chemical analysis,
- data processing and evaluation and
- quality assurance (Wagner, 1994a,b).

Sampling of biological and other environmental specimens is always influenced by factors which may modify the exposure as well as the accumulation behavior of the specimen types in relation to xenobiotics, e.g. by climatic factors, weather conditions and changes in the population sampled or in the structure of the whole ecosystem (Wagner, 1994a, 1995; Klein and Paulus, 1995).

Ecological and biometrical sample characterization provides basic information about changes in the quality of the sampled material and its comparability with previous and following samples from the same area or the same specimen type sampled in other areas. Biological sample characterization can also give information about ecological and ecotoxicological effects to the population sampled. Figure IV.6.3 demonstrates changes

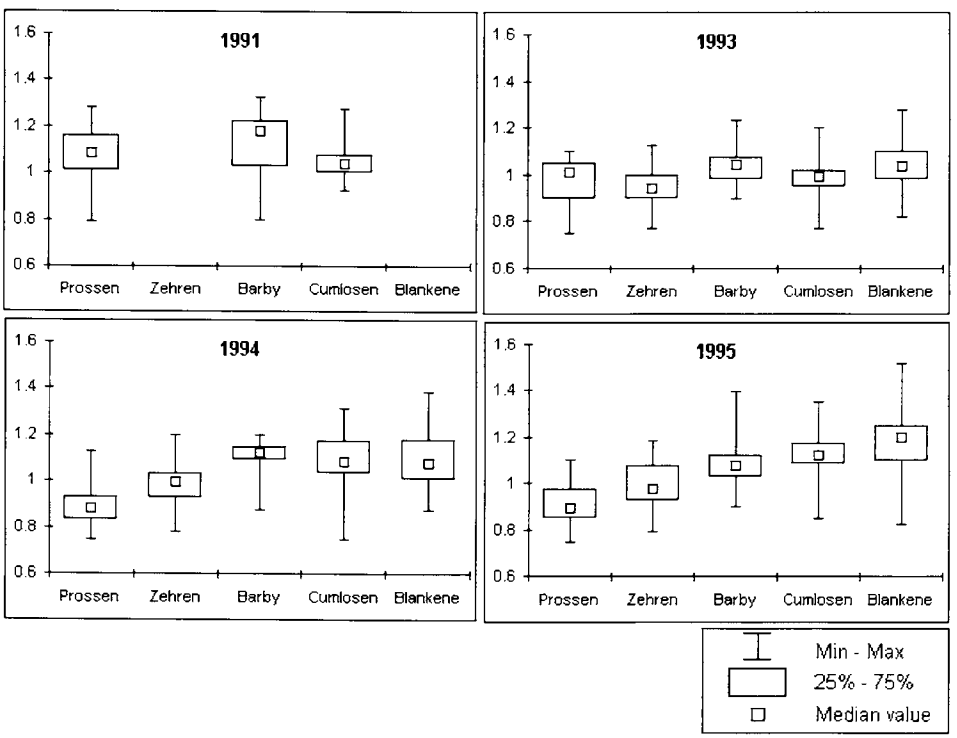


Figure IV.6.3. Condition index of breams caught along the Elbe River.

in the condition index, the relation between the body weight and the length of bream caught in different sites of the Elbe River from 1991 to 1995. While the values from 1991 show high variability, standardization of the sampling to a defined age class brought better reproducible values demonstrating clear increase of the condition index downstream the Elbe River and also increasing values in some of the sampling sites (Wagner et al., 1996).

Another key for the understanding and evaluation of analytical results is the land use structure of the sampling area and its annual changes. This means that not only the potential sources of chemical pollution have to be detected, characterized and monitored but also sources of anthropogenic nutritional and physical disturbance. Figure IV.6.4 shows a computer map of the urban industrial agglomeration of the Saar region in western Germany as an example for the land use mapping in extended sampling areas as a basis for the detection of temporal changes and the interpretation of analytical results. However, in agricultural areas the land use pattern has to be mapped much more in detail and actualized each year to recognize the potential or specific emissions and effects originating from each unit of used area (Müller et al., 1996).

In environmental specimen banking samples of different specimen types and ecosystems are frequently sampled, characterized, processed and stored with considerable effort to maintain the precautions necessary for deferred analysis on initially unknown substances or parameters. Quality assurance is therefore an absolute demand and an

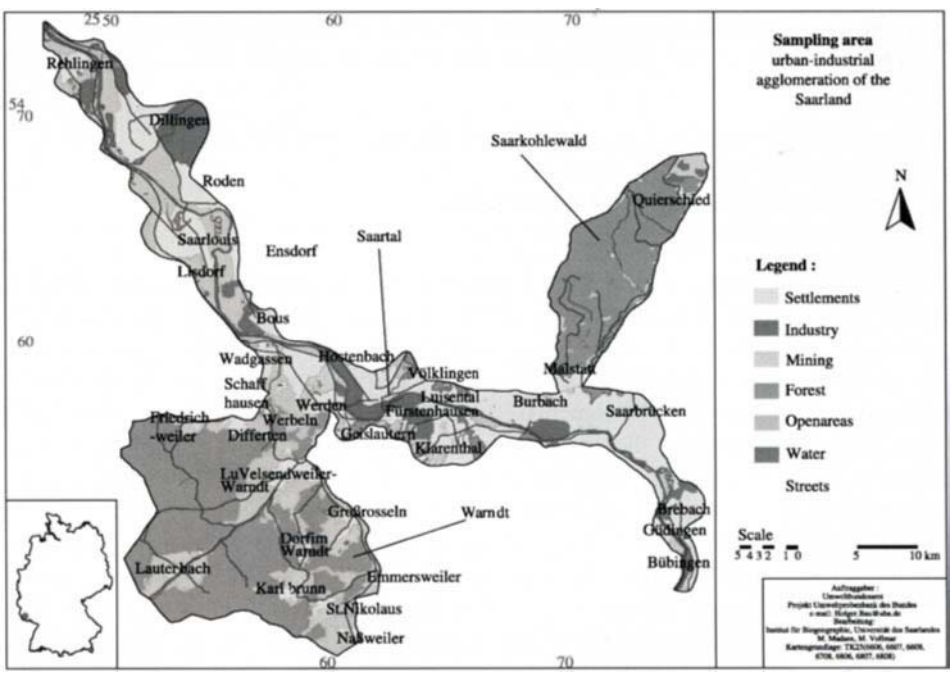


Figure IV.6.4. Computer map of the industrial agglomeration of the Saar region.

innovative challenge in ESB. Errors made during the sampling in the field, transportation and sample pre-treatment can seldom be recognized and never corrected afterwards during the following analytical measurements. Thus, the quality assurance system for ESB includes the whole process from planning, sampling, ecological and biometrical characterization, packing, transportation, storage, homogenization and subsampling up to the analytical procedures and the evaluation of the results (Klein et al., 1994; Paulus et al., 1995).

A flow chart of the entire preparation procedure for the final long-term storage of an environmental specimen is shown in Figure IV.6.5. On average 2.5 kg of material per specimen per sampling site was collected producing nearly 250 standardized subsamples of approximately 10 g each.

IV.6.4.2. Analytical sample characterization

The choice of pollutants or classes of pollutants for the analytical sample characterization took place according to ecotoxicological importance.

IV.6.4.2.1. Inorganic analysis

The analytical procedures for inorganic analysis of ESB samples were selected with emphasis on trace analysis capability and applicability for very complex biological matrices. During the pilot phase sample preparation was optimized in dependence on the matrix to be analyzed and the detection technique to be used (Emons, 1994, 1996; Umweltbundesamt, 1996). The following four groups of analytical methods are applied for trace analysis:

- Atomic spectrometry (GF-AAS, CV-AAS, Hydride AAS, ICP-AES)
- Mass spectrometry (IDMS, ICP-MS)
- Electrochemical methods (PSA, Voltammetry)
- Radiochemical methods (INAA, PGCNAA).

An important aspect of the ESB consists in the long-term monitoring of heavy metals in biological samples between different regions in Germany. For example, a clear decline in mercury pollution in the estuary region of the Elbe River past few years can be documented on the basis of samples of herring gull eggs (*Larus argentatus*) collected in the Trischen bird sanctuary (see Figure IV.6.6) (Schwuger, 1994; UPB, 1996). More than 90% of the mercury was present in the form of the highly toxic methyl mercury. Before the unification of the two German states (1988/89) the mercury concentrations in herring gull eggs from the island Trischen was twice as high as for the subsequent years (1991–1995). The decreasing temporal trend is probably associated with the closure of industrial plants in the upper regions of the Elbe River and its tributaries. As shown in Figure IV.6.6, birds living in the estuary of the Elbe River (Trischen) show higher uptakes of Hg than species living in the estuary of the Weser River (Mellum). This demonstrates the influence of mercury input from the Elbe River into the North Sea.

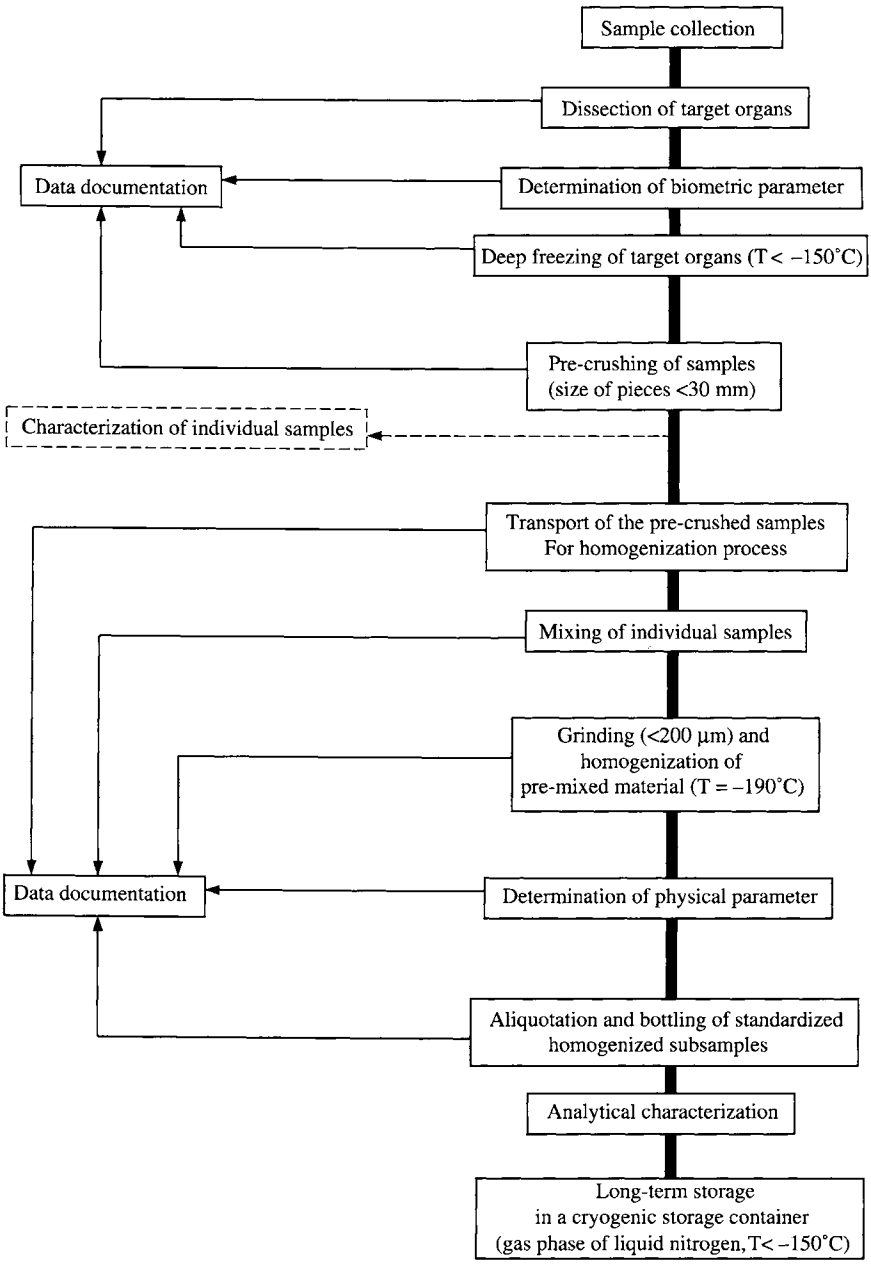


Figure IV.6.5. Flow chart of the sample preparation steps of the German ESB.

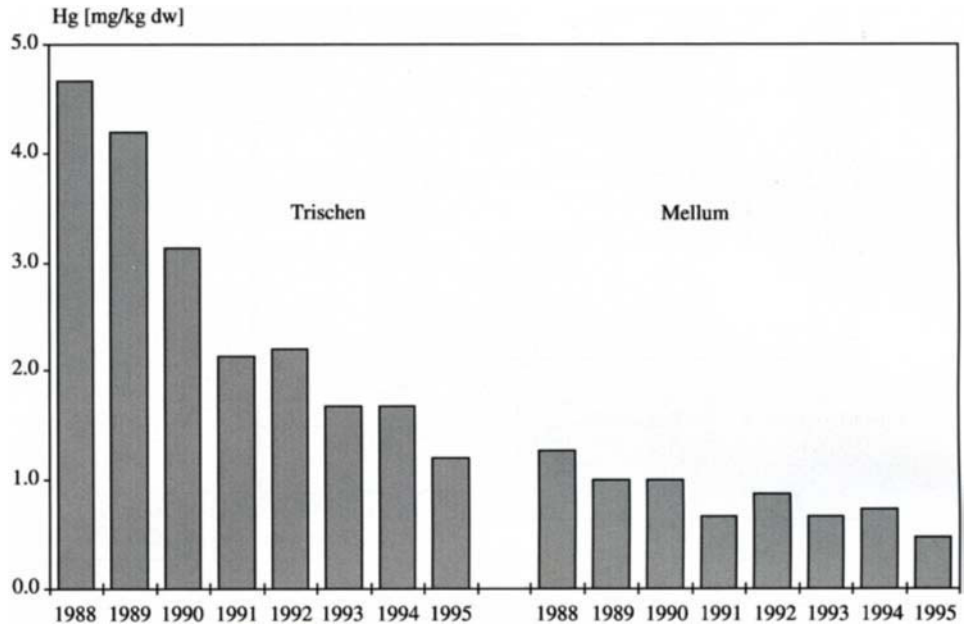


Figure IV.6.6. Temporal trend of mercury concentration in herring gull eggs from the islands Trischen and Mellum (after UPB, 1996).

IV.6.4.2.2. Polycyclic aromatic hydrocarbons (PAHs)

The determination of PAHs is of very high importance because they are considered to be the most relevant class of environmental carcinogens (Grimmer, 1993). PAH immission sources result from incomplete fossil fuel combustion, wood burning and waste gases from industrial and household combustion processes. The continuous measurement of PAH concentration in various selected environmental matrices representing the terrestrial, aquatic and atmospheric ecosystem provides the opportunity to recognize trends in the environmental pollution.

For PAH determination sample homogenates are extracted with toluene or cyclohexane by Soxhlet. Interferences are removed by liquid/liquid distribution and chromatography on silica and Sephadex LH20. The detection of PAHs is carried out by gas chromatography equipped with FID or MS (SIM) detectors (Grimmer et al., 1996).

Spruce and pine sprouts are passive sampler reflecting the atmospheric pollution by PAHs (Jacob et al., 1996). For example, the benzo[a]pyrene (B[a]P) concentration of spruce sprouts from the industrialized area of Saarland decreased by a factor of 3 within 10 years (see Figure IV.6.7).

The same trend in pine sprouts has been observed for a sampling area in East Germany (Dübener Heide) during the period 1991–1995 with B[a]P declining from 3.5 to 1.5 μg/kg. In principle, similar results were also obtained with poplar leaves from Halle, whereas samples from Leipzig showed no consistent temporal trend (Fig. IV.6.8). These findings show that the reduction of pollution by technical improvements such as modern

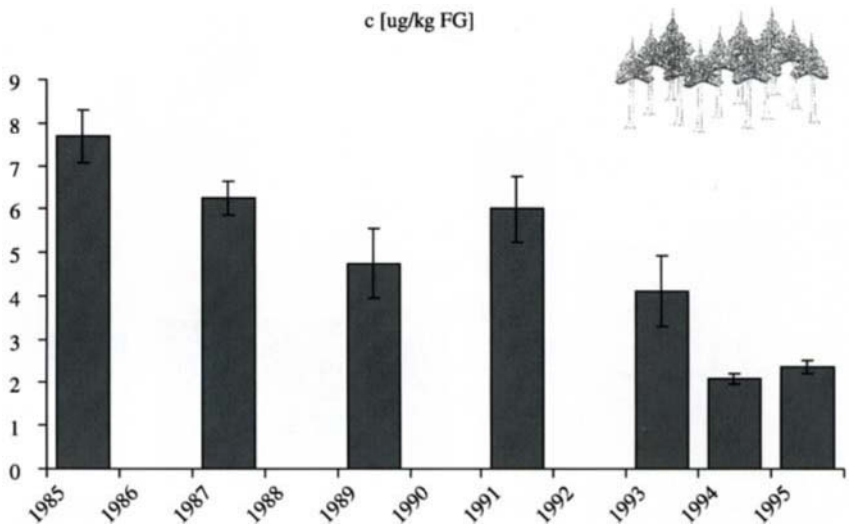


Figure IV.6.7. Time-dependent decline of the B[a]P concentration of spruce sprouts from Saarland-Warndt during 1985–1995.

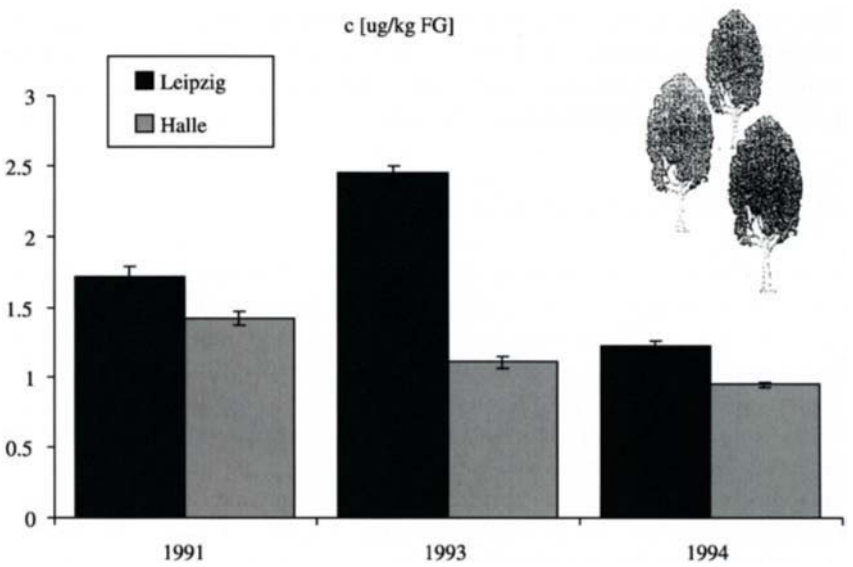


Figure IV.6.8. Temporal trend of the B[a]P concentration in poplar leave homogenate from two different sampling locations of Dübener Heide (East Germany) during 1991–1994.

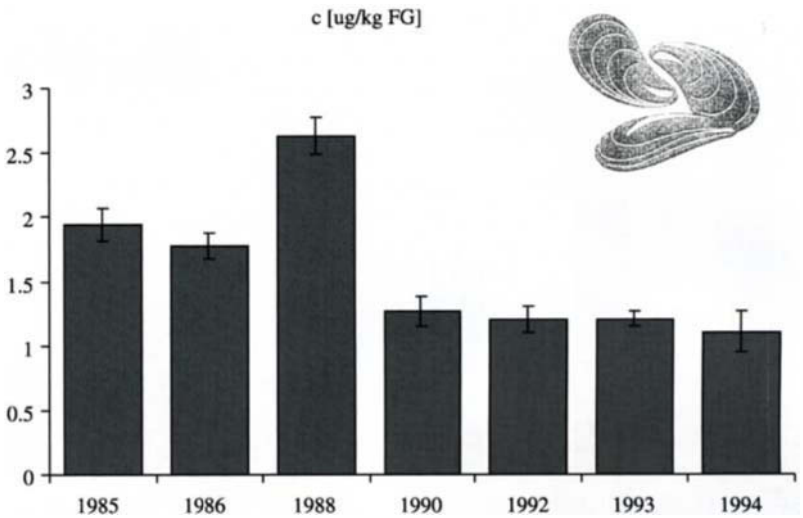


Figure IV.6.9. Temporal trend of the B[a]P concentration of mussel homogenate from Eckwarderhörne (North Sea) from 1985 to 1994.

vehicle conceptions as well as improved domestic and industrial combustion devices in the past were successful.

Mussels (*Mytilus edulis*) as a bioindicator of the marine environment for the North Sea (Eckwarderhörne) exhibited likewise a decline of the PAH concentration although to a lesser extent (Jacob et al., 1996). With the exception of 1988 when higher concentrations have been measured, the B[a]P decreased from 1.9 μg/kg in 1985 to 1.2 μg/kg in 1990 and remained practically constant since then as presented in Figure IV.6.9. Long-distance transfer by atmospheric pollutants from other countries and the dilution effect play an important role for the contamination of the North Sea.

IV.6.4.3. Chlorinated hydrocarbons (CHC)

Numerous chlorinated insecticides and industrial chlorinated hydrocarbons (e.g. polychlorinated biphenyls (PCBs) or polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F)) are extremely resistant to degradation in the environment. Residues of these xenobiotics have been identified throughout the world, although most of them have been banned since the 1970s. Because of their toxicological properties and accumulation effects, long-term studies on their residue levels are essential to understand the environmental contamination in the past and to predict future trends. The German environmental specimen bank has played a crucial role in monitoring and evaluation of long-term trends in occurrence and distribution of CHC in different ecosystems in Germany (Marth et al., 1999a,b, 2001).

For the CHC determination the samples are mixed with anhydrous sodium sulfate/sea sand to form a free flowing product, which is extracted in a column with

n-hexane/acetone (2:1 v/v). Clean up is performed with gel-permeation and high performance liquid chromatography. Quantification is carried out by high-resolution gas chromatography (HRGC) equipped with electron capture detection using two columns of different polarity. More details about the applied method are given by Oxynos et al. (1992).

Herring gull eggs are a suitable bioindicator for lipophilic xenobiotics since they express the local and temporal environmental conditions (Oxynos et al., 1993). The time series of herring gull eggs at the sampling locations on the island of Mellum and Trischen are shown in Figure IV.6.10. The location influenced by the Elbe River (Trischen) exhibited higher concentrations than the location Mellum, which is influenced by fluxes of pollutants in the river Weser. The significantly higher DDE concentrations in eggs from Trischen in 1989 can be explained by DDT applications in the former GDR in the late 1980s.

Figure IV.6.11 summarizes the PCDD/F levels of herring gull eggs from 1988 to 1993 at Trischen and Mellum (Schramm et al., 1996). A decreasing trend of the contaminants is obvious. This development shows the result of the legislative actions to minimize the dioxin emissions, e.g. the ban on sea burning of hazardous waste.

Investigations of sediments and fish (bream) along the Elbe River (Fig. IV.6.12) in 1991 have shown that the eastern sampling sites (Prossen, Dresden) have been heavily contaminated by hexachlorobenzene (HCB), octachlorostyrene (OCS), DDT-metabolites and PCBs (Fig. IV.6.13) (Oxynos et al., 1995). This observation is probably a result of the considerable pollution of the Elbe River by the industrialized areas (e.g. Pardubice, Neratovice, Usti) of the former CSFR (Nesmerak, 1993). Sediments at the station Dresden are highly contaminated because they were strongly subjected to effluents of a pulp mill and chemical industries until 1991 (IKSE, 1992). A 30% decrease of the CHC concentrations in bream muscle tissue was found between station Dresden and Vockerode, further downstream, the total CHC burden remained nearly constant. Elevated levels of hexachlorocyclohexane isomers (HCHs) in bream muscles and livers were observed downstream between Aken and Heinrichsberg due to the influxes of the Mulde and Saale Rivers as well as discharges from pesticide plants located in Magdeburg (Marth et al., 1996).

The comparison of the CHC-pattern (Fig. IV.6.14) in bream livers exhibits significant distinctions between the different ecosystems. DDT-metabolites and PCBs contributed to one-third, respectively, to the total CHC burden of bream livers from the limnic ecosystem of the Elbe River. PCBs were the major organochlorine contaminants (70%) in breams of a typical industrialized area (Saarland) in contrast to agricultural areas of East Germany, where DDT-metabolites were the dominant pollutants (80%). This is caused by the continued application of DDT in the former GDR after DDT was banned in Western Europe.

These investigations have proved usability of herring gull eggs and breams as bioindicators for monitoring temporal and spatial trends of CHC (Marth et al., 2000).

Significantly higher concentrations of DDT-metabolites were found in pigeon eggs from Leipzig (East Germany). Fortunately, a decreasing trend of these pollutants can be observed (Fig. IV.6.15).

Besides CHC, other chlorinated compounds were studied in samples of the German environmental specimen bank, e.g. chlorinated phenols (CP) (Martens et al., 1999).

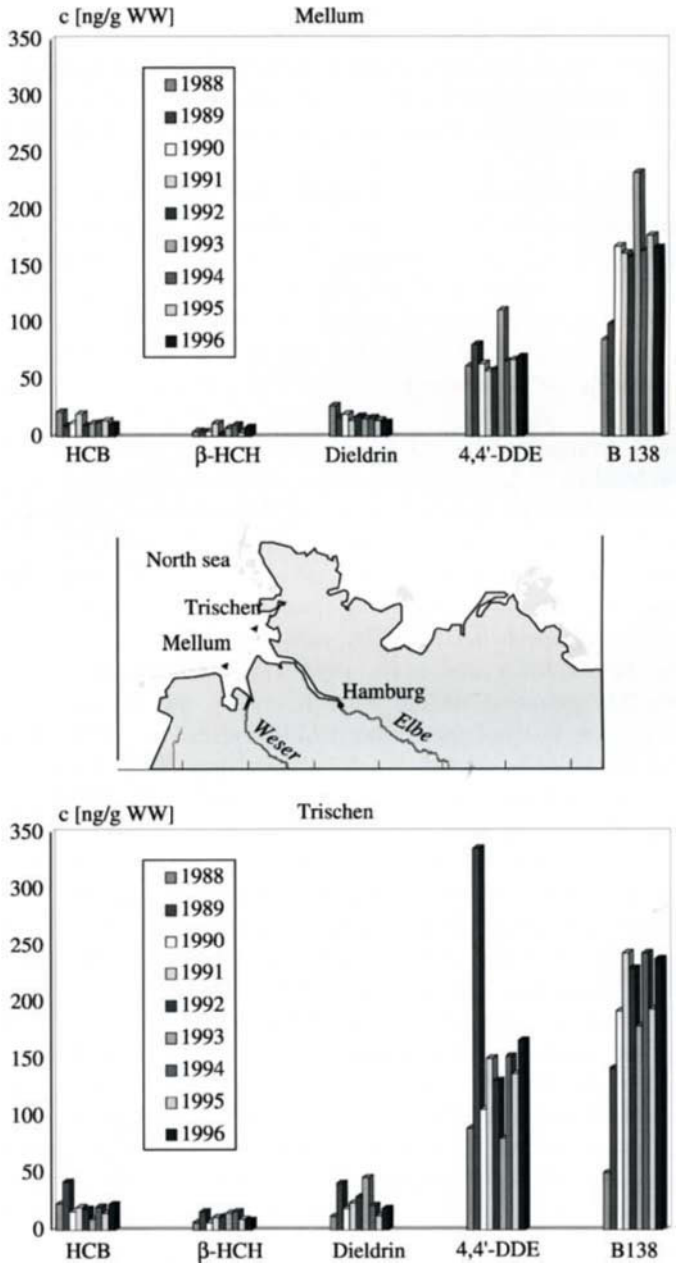


Figure IV.6.10. Temporal trend of selected CHC in herring gull eggs from the islands Trischen and Mellum.

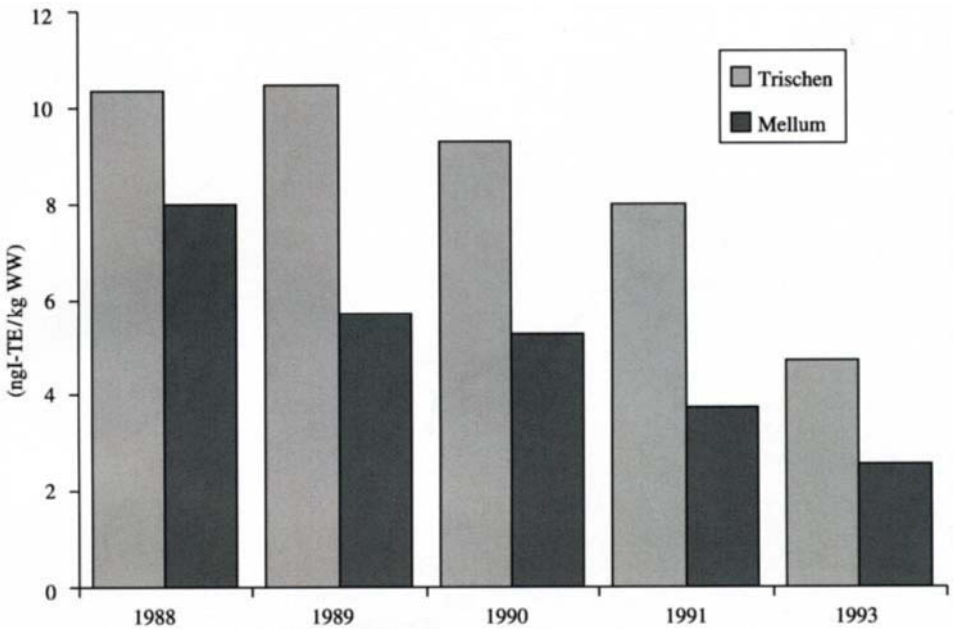


Figure IV.6.11. Temporal trend of PCDD/F-ITE in herring gull eggs from the islands Trischen and Mellum.

IV.6.5. Conclusion and future perspectives

Twenty years of practical experience in environmental specimen banking have demonstrated that the concept of long-term storage of biological specimens for the retrospective analysis has contributed to traditional environmental pollution monitoring as an important complement. The ESB can serve as a valuable resource for the assessment of long-term trends of pollutants affecting human and environmental health, in particular for those pollutants that have been unnoticed (Kettrup et al., 1999).

The results fulfill the proposed goals of the ESB as far as political and administrative decisions concerning the emission levels or other regulations on pollutants can be confirmed by their decrease in the environment (e.g. introduction of unleaded fuel, ban on sea burning of hazardous waste). Illegal applications of chemicals could have been identified, e.g. DDT applications in the former GDR.

The generated SOP (Umweltbundesamt, 1996) for analytical and sampling procedure are well documented and similar to the demands of Good Laboratory Practice or the European Standards for Analytical Work. Thus, in this field it became possible to identify and to avoid possible errors in the future. Due to high quality standard of sampling and analysis the collection is of particular value for future analytical work on environmental contaminants of which we presently know very little.

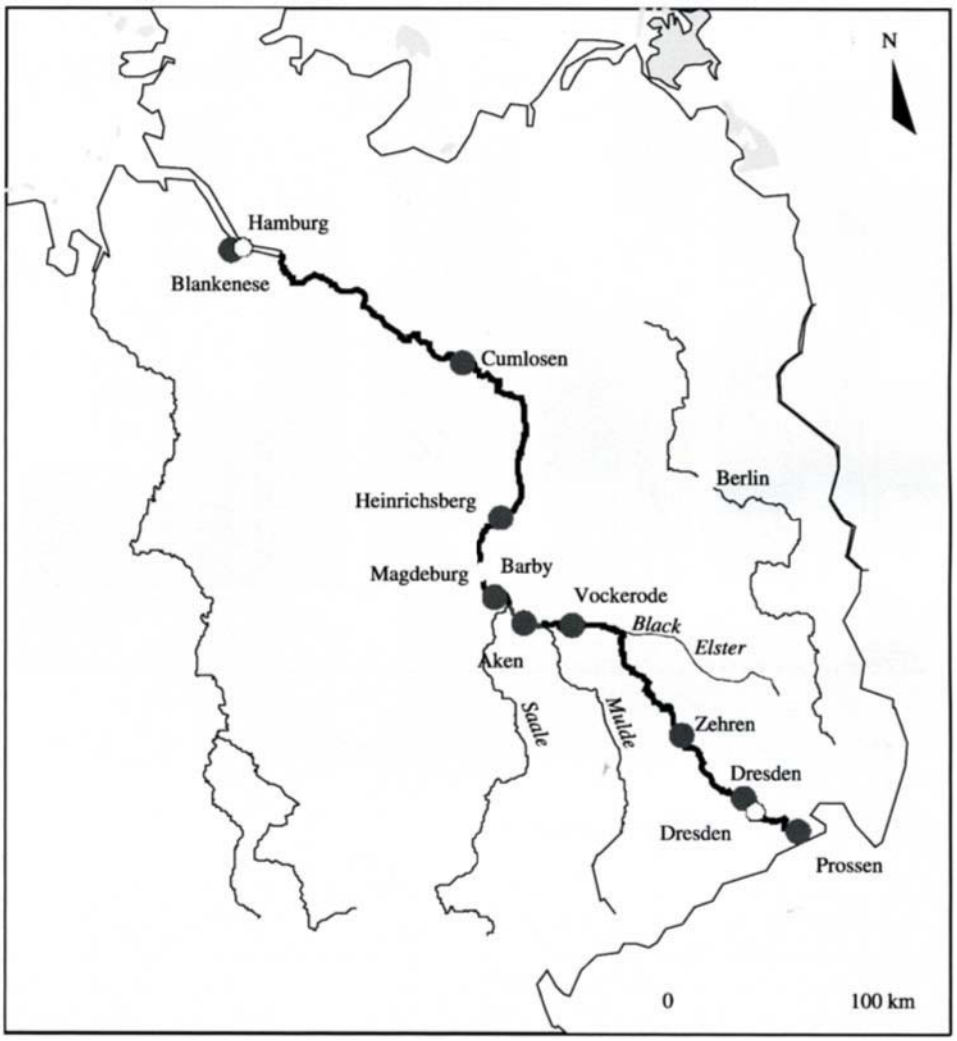


Figure IV.6.12. Sampling sites of bream along the Elbe River.

The increasing amount of generated data now allows the verification of many relationships discovered in the past in the environmental research with very high accuracy that are bioaccumulation, biomagnification, distribution, transport and at least degradation of chemicals. The history of the conceptual development of the ESB has resulted in a pool of knowledge that can be used for future decisions and recommendations for researchers and politicians (Marth and Kettrup, 1998; Kettrup et al., 1999).

As a new instrument for science, administration and management, ESB can support analytical and environmental research and monitoring generally in many ways and make it more effective and reliable, e.g. supply reference materials for environmental

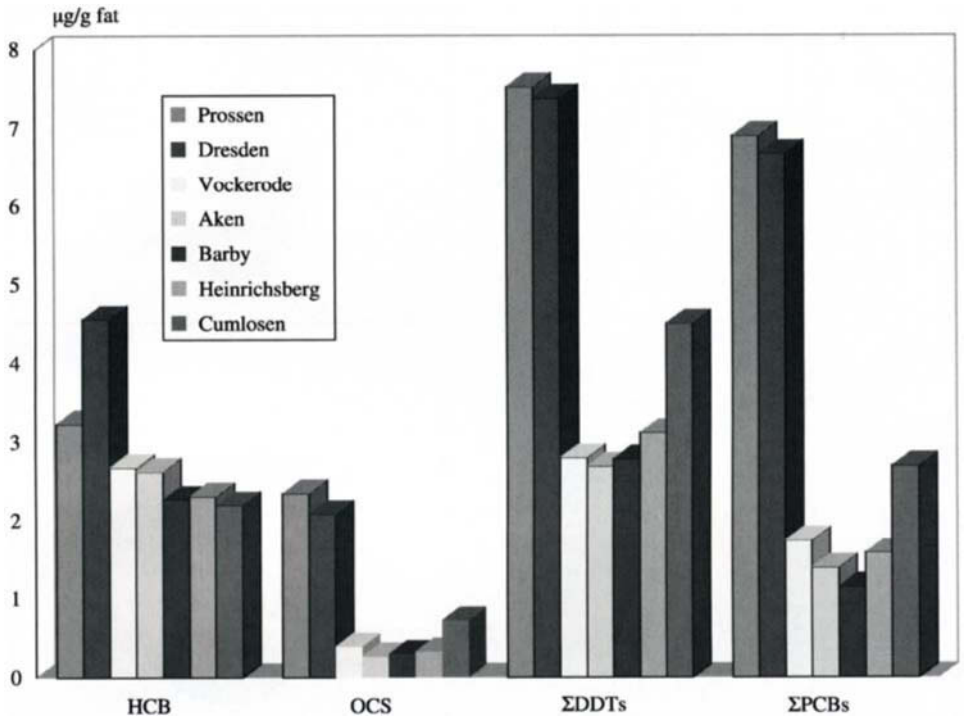


Figure IV.6.13. Levels of major contaminants related to fat content in bream muscle tissue from the Elbe River in 1991.

analysis, preservation of authentic records as an archive for long-term comparisons of environmental change, securing and perpetuation of evidence in biology, medicine, forensic medicine, biotechnology, deposition or conversion of problematic wastes, environmental planning, risk and exposure assessment (Zenick and Griffith, 1995; Subbramanian and Iyengar, 1997; Kettrup et al., 1999).

For future scientific activities the following aspects are recommended:

- Extension of the set of chemicals that are analyzed.
- Selection of the most important bioindicators to minimize costs and labor.
- Creation of a pattern library for sources and bioindicators by normalizing and archiving chromatographic raw data and applying multivariate statistics.

Other countries contribute with their research/monitoring programs to the extension of analyzed chemicals or environmental matrices of specific or common interest, e.g. Swedish EPA within environmental specimen banking program screened in environmental samples: in 1999 – chlorinated paraffins and extended list of metals; in 2000 – flame retardants HBCD and TBBPA; in 2001 – organic tin compounds, phosphorylated flame retardants, highly fluorinated compounds, antimony, octylphenol, triclosan, pesticides and CPs. In urban areas, studied matrices comprised such

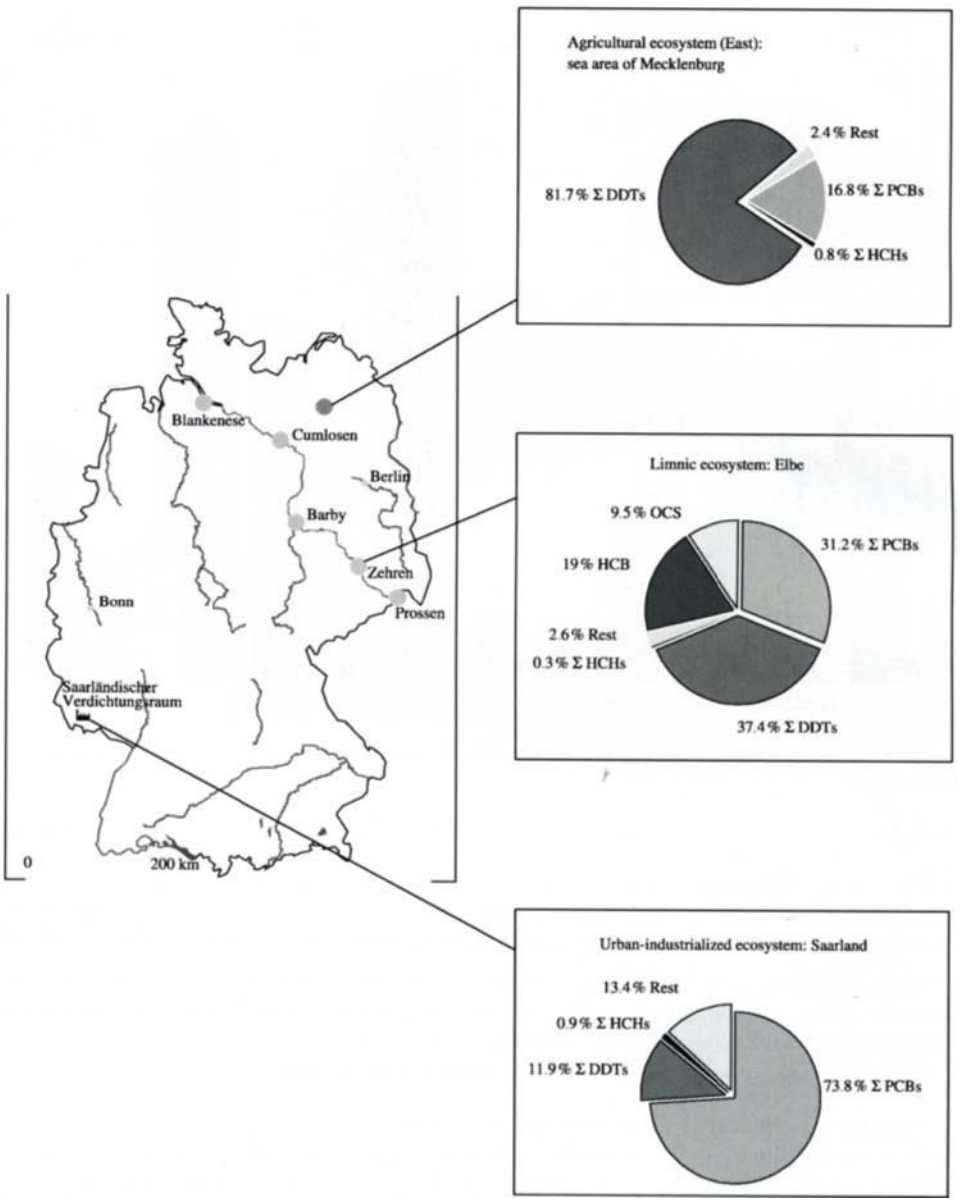


Figure IV.6.14. Comparison of different ecosystems with bream (*Abramis brama*) as bioindicator.

problematic waste as fly ash (current studies) and sewage sludge (started in 2002) (Hedlund, 2001).

One of the major tasks for the ESB in the future will be to make ties to ESBs of other nations and in cooperation with these establish an international forum for exchange of information and samples.

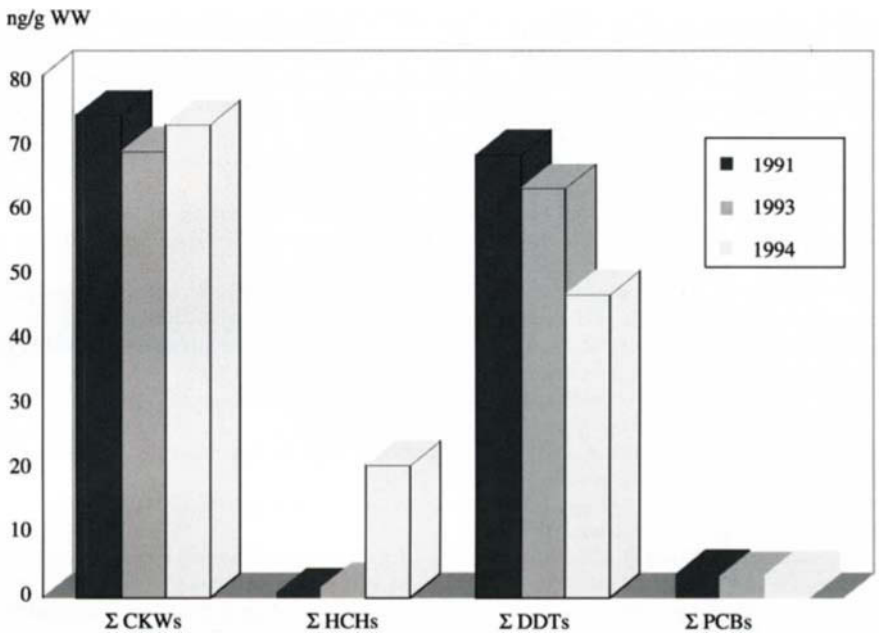


Figure IV.6.15. Temporal comparison of CHC in pigeon eggs from Leipzig.

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IV.7

QA/QC in solid waste characterization, waste disposal monitoring and waste management practice*

Quality Assurance organizational–catalytic–technical

Guy F. Simes

IV.7.1. Introduction

According to recent national studies, over two-thirds of all participants in quality assurance (QA) and quality control (QC) systems are disappointed in the results. Quality is clearly a good thing, but quality systems are not dynamic when two out of three lead to disappointment. What's wrong? Is it possible that dynamic quality systems (Fig. IV.7.1) incorporate special additives (catalysts) that normal quality systems (Fig. IV.7.2) do not?

In a normal quality system for the monitoring and the remediation of solid wastes, two distinct levels of QA requirements are addressed: the organizational (or institutional) level and the technical (or project) level. Dynamic quality systems, on the other hand, not only include the normal components but also integrate catalytic components. These catalytic components are critical to the foundation supporting the quality system pyramid (QSP), however, they are often overlooked in the design stage of many quality systems. While this chapter does consider the characteristics of a normal quality system, an intentional focus is levied at the seldom-explored dimension – catalysts.

IV.7.2. Organization (or institutional) QA

The essential elements of QA management systems have been discussed widely in the literature. For instance, the 9000-series documents of the International Organization for Standardization (ISO, 2000) list 20 components of QA management systems, with

* *Foreword*: This chapter has been written by an author with many years' professional experience as a Quality Assurance Manager at US EPA National Risk Management Research Laboratory. It presents basic principles and mechanisms of the successful dynamic QA systems, equally applicable both to solid waste management issues as a part of the environmental field and to other relevant project-oriented endeavors, e.g. health sciences. This broader character of the QA system's philosophy is of particular value. The quality assurance and quality control in specific solid waste management activities are addressed in the references and web sites to this chapter that provide the details of the relevant procedures and case studies.

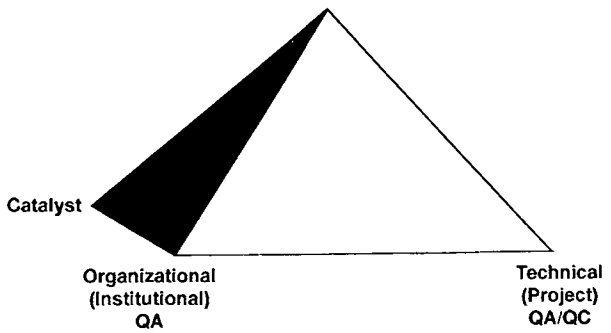


Figure IV.7.1. Dynamic quality system pyramid.

emphasis on production and engineering organizations. ISO/IEC 17025 (2000) (formerly ISO Guide 25) from the same organization adapts these guidelines to routine testing laboratories. Since early 1990s the US Environmental Protection Agency has been developing general QA management requirements intended for organizations generating environmental data (US EPA, 2001a). Other agencies have produced similar guidelines for their areas of concern (e.g. US DOE, 1991), and private authors have also presented their views on the essential elements of general QA management (Garfield, 1991).

These standards and guidelines, while differing in organization and emphasis, specify similar elements. In all cases, an organization's general QA practices must be documented in a QA management plan, which at a minimum describes the organization's policy and goals; the organizational structure of the QA effort and its relationship to the larger institute; the authorities and responsibilities of all parties, including both production and QA personnel; and the general activities and tools of the QA group. Depending on the nature of the organization, these documents also specify that the QA management plan addresses document control, flow-through provisions for subcontractors and vendors, product traceability, calibration requirements for instrumentation, training requirements, etc. Thus, the QA management plan provides the basic infrastructure that enables consistent quality procedures to be applied to similar projects.

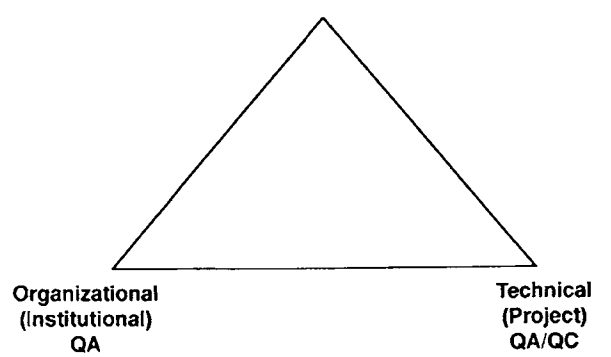


Figure IV.7.2. Normal quality system triangle.

Nevertheless, a quality system containing all the expected elements is no guarantee of success. Much like an Olympic athlete who possesses all the same body parts as the average person, so the quality systems of both mediocre and superior organizations possess the same QA elements. For both the athlete and the organization, it is how well these elements operate together that distinguishes the champion from the ordinary. It is not only the organizational elements, but also the sum of the attitudes and relationships – the culture of the organization – that lead to success or failure.

IV.7.3. Catalytic QA

The following text describes those catalytic aspects of QA management that are essential for an effective QA system. Much like a catalyst lowers the boundaries between reagents, the following "catalysts" make all of the organizational elements fit together to yield a product that is greater than the individual parts.

Communication is the glue that holds any organization together, and its importance to the QA system cannot be overemphasized. Like actual glue, communication must be applied consistently, must be accepted by all members, and must be allowed time to take hold.

What should the QA staff do to foster effective communication? First, the QA staff needs to take the initiative in identifying both internal and external customers of QA programs. (Here external customers are the end users of a company's product and internal customers are other groups within the institution who use QA services.) The QA staff must regularly contact these persons to establish effective communication. The *first* meeting should demonstrate the QA staff's sincere and serious commitment to a dynamic quality system. It is a confidence builder, plain and simple! *Second*, because the customer will likely spend several meetings venting past dissatisfaction or discussing both constraints and problems that affect their group, the QA staff needs to be good listeners. Listening is the least practiced form of communication. Effective listening will help the QA staff adjust their speaking and writing to get the QA message across. Active, attentive listening also communicates one's desire to understand and to engage in a mutual process. *Third*, the QA staff must be prepared to explain what QA can contribute and what QA requirements need to be satisfied. However, the QA staff should not plan to present everything at once. A more effective approach is to provide information when needed, when the user is likely to be most receptive. *Fourth*, the QA staff must be persistent. Developing effective working relationships requires time even when all parties are highly motivated. A major goal of the QA staff is to develop shared goals and effective mechanisms for achieving these goals.

Independence. The QA staff must report directly to top-level management to make independent judgments without concern for retribution and without the pressures of day-to-day production. This arrangement fosters independent thinking by the QA staff, for the benefit of all parties.

Management support. If the relationship with management is strained or not well established, a great deal of resistance to QA may result. For this reason, the QA manager should report regularly to management on QA activities, plans, and accomplishments.

The support of middle management is perhaps the most difficult to win, but the most important condition necessary for an effective QA program. Not only do middle managers

strongly influence what resources will be directed towards QA efforts, but they also set the attitudes of much of the technical staff. Management must be approached on a basis of mutual trust and respect at the starting point. Comments by the QA staff regarding management or organizational performance must be non-threatening, lest critical information be obscured by a defensiveness that leads to attacks on the QA program. In the long run, relationships with project managers will become fruitful only when they realize that QA contributes to the quality of their projects and helps minimize rework/costs. The relationship with middle management should be a creative tension that is productive even if disagreements occasionally occur.

Employee involvement. Ideas for improvements can arise from any level within an organization. All employees should understand how their work product is used by others, and should be encouraged to contribute their ideas for product improvement. Incentive programs can assist in this area.

Full-time commitment. To benefit any organization, a QA program must be an empowered, intrinsic part of that organization, not an appendage. In establishing a QA program, the first step is committing full-time resources to QA, with no strings attached and no other assigned duties. Total commitment is paramount in reaching ultimate performance.

Substantial contributions. QA activities must make a difference. Otherwise, QA will be viewed as an irrelevant nuisance to be ignored while getting on with the "real work".

Customer awareness. The QA staff must be aware of the motivations and pressures on management and technical staff (the internal customer) in presenting its case. Resistance can be expected if QA procedures restrict the availability of traditional resources, add constraints, or require an excessive amount of documentation or labor. Sometimes changes recommended by QA simply meet institutional inertia, or challenge the egos of those who have labored long to establish the current procedures. Technical staff may also be concerned about additional labor requirements and delays, or may be facing imminent deadlines. If the project manager is packing for a sampling trip on Tuesday, then a lengthy QA review should not be planned for Monday!

Legitimate issues must be addressed in a forthright manner; after all, QA does require additional documentation, and sometimes QA reviews do unavoidably occur immediately before a sampling episode. The QA staff must strive to eliminate unnecessary cost and should avoid inopportune meetings, whenever possible. Discussions may need to be restricted to the most pressing issues with remaining topics postponed when deadlines are imminent. It is also helpful if the QA staff is able to provide convincing testimony regarding the long-term benefits of QA.

Since the QA staff can have an impact on the professional staff's decision to make a change, it is critical that credit and ownership go to the professional staff and not to the QA staff. Peak performance within an organization is the natural outgrowth of a partnership between management, the technical staff, and the QA staff. From persuasive presentations to painful prodding, the QA staff must help management and the technical staff to achieve their successes.

Lessons learned. The QA staff should be the corporate memory regarding lessons learned that might be helpful to future projects. Did some concerns that seemed critical during the planning stage turn out to be trivial? Were other important concerns overlooked? Were innovative procedures developed that might be useful for future

projects? The QA staff should not only keep a log of such case studies as a benefit to future projects but also ensure dissemination of the information.

Celebrating success. How did QA benefit each project? Were some projects saved from failure by early intervention? Were some projects lost because QA advice was ignored? Were cost savings realized by a better focusing of effort? Success stories that embody the value of QA need to be shared with everyone, especially management.

Measuring quality. Quality should be measured over time to objectively assess quality improvement. For instance, a laboratory might track the percentage of reports delivered within schedule, or a research group might record the number of times their work is cited in the literature. These examples suggest that such measurements must be consumer oriented and must present data that allow the organization to take effective action.

Back-up support. A QA staff cannot possibly have all the technical expertise to cover every problem that may arise. It may be necessary to enhance the quality system by judiciously employing external QA support. This arrangement permits access to a wide range of practical experience and resources that are often unavailable within the organization.

Individual recognition. Undoubtedly the most important factor in achieving a quality product is the ability and dedication of the technical staff and management. Managers are acutely aware of this and spend great effort in recruiting and retaining talented scientists and engineers. To retain productive staff, the best performers should be awarded with improved salaries and increased professional challenges and opportunities. The QA staff can assist upper management in identifying the best performers by informing them of any outstanding achievements.

Education and training. The essence of an effective quality system is learning, not coercing or controlling. Learning takes time; it requires real problems to be solved; and it involves trial and error, experimentation, and tolerance for mistakes.

Training is an important component for any quality system. Training must be general and specific; appropriate and relevant; and timely. Quality training must target both specific audiences and specific skills.

Initial employee training should expose employees to QA concepts and philosophy. It should focus on general QA principles to make everyone cognizant of the "who, what, where, when, and why" of the QA process.

Awareness training, however, is of little benefit if specific skill training is not provided in a timely manner. Skill building must answer the "how to" question by introducing the customer to the tools and mechanisms for pursuing quality.

Finally, training benefits are best recognized when there are opportunities to apply the new knowledge. Consequently, "just-in-time" training – giving people the skills they need immediately before a project – is critically important. Unfortunately, "just-in-time" training requires a one-on-one training approach and is often neglected because of the short-term drain on resources. However, those organizations investing in this approach very quickly realize substantial returns.

Continuous improvement through "rapid inching". All quality systems must constantly evolve to remain relevant to the challenges of tomorrow. Take fast but small steps (rapid inching). Tweak your program and continually seek out small increments of optimization. Solicit constructive criticism and be prepared to change.

Vision. Envision the QA future in rich detail and then turn vision into action by practicing the nine E's:

1. *E*nvision the challenge.
2. *E*ntice others to become interested in the challenge.
3. *E*nable participants through education and understanding.
4. *E*ngage participants to create alliances.
5. *E*mbrace the cause of the team.
6. *E*mpower the team to action.
7. *E*mploy the team in action.
8. *E*njoy the rewards.
9. *E*nvision new challenges.

By envisioning the future, one embraces the belief that the future can be influenced. That belief helps create the fact.

IV.7.4. Technical (project) QA

The previous section discusses the attitudes and relationships, the QA catalysts, essential to an effective QA system. How are these general concepts applied to a specific project? Given the task of designing and verifying a cleanup action, or the task of assessing the effectiveness of a new test kit, or that of establishing the efficacy of a new vaccine; how does the QA staff apply the aforementioned concepts?

To illustrate some concepts applicable to projects in general, consider first a specific example, namely, an evaluation of a nearly mature, pilot-scale environmental control technology at a specific site. Figure IV.7.3 represents the general flow of activities for such a project from initial planning to release of the final report. Here, activities led by the QA group are shadowed to distinguish them from other project activities.

Project activities can be summarized as follows:

a. *Complete necessary preliminary studies.* For a project of this maturity, information from treatability studies and site characterization activities may be available to aid in experimental design. Further, any questionable measurement methods will be "debugged" before proceeding with the test. The extent of prior knowledge may vary significantly for other projects.
b. *Agree to project objectives.* Project objectives should be stated in the most quantitative form possible to aid in the subsequent design. An effective statement of project objectives must reflect the goals of all principal participants to the project, must be practical, and must define the scope of the investigation. Arriving at a clear statement of project objectives is perhaps more difficult but more important as the complexity of the project or the number of principal participants increases. Less explicit objectives may be needed for more exploratory projects.
c. *Prepare a written project plan.* Preparation of a written document relating project objectives to the individual measurements is central to any complex test. This document is important for the data producers in that it serves as the project "Standard Operating Procedure" for those groups involved in the sample collection,

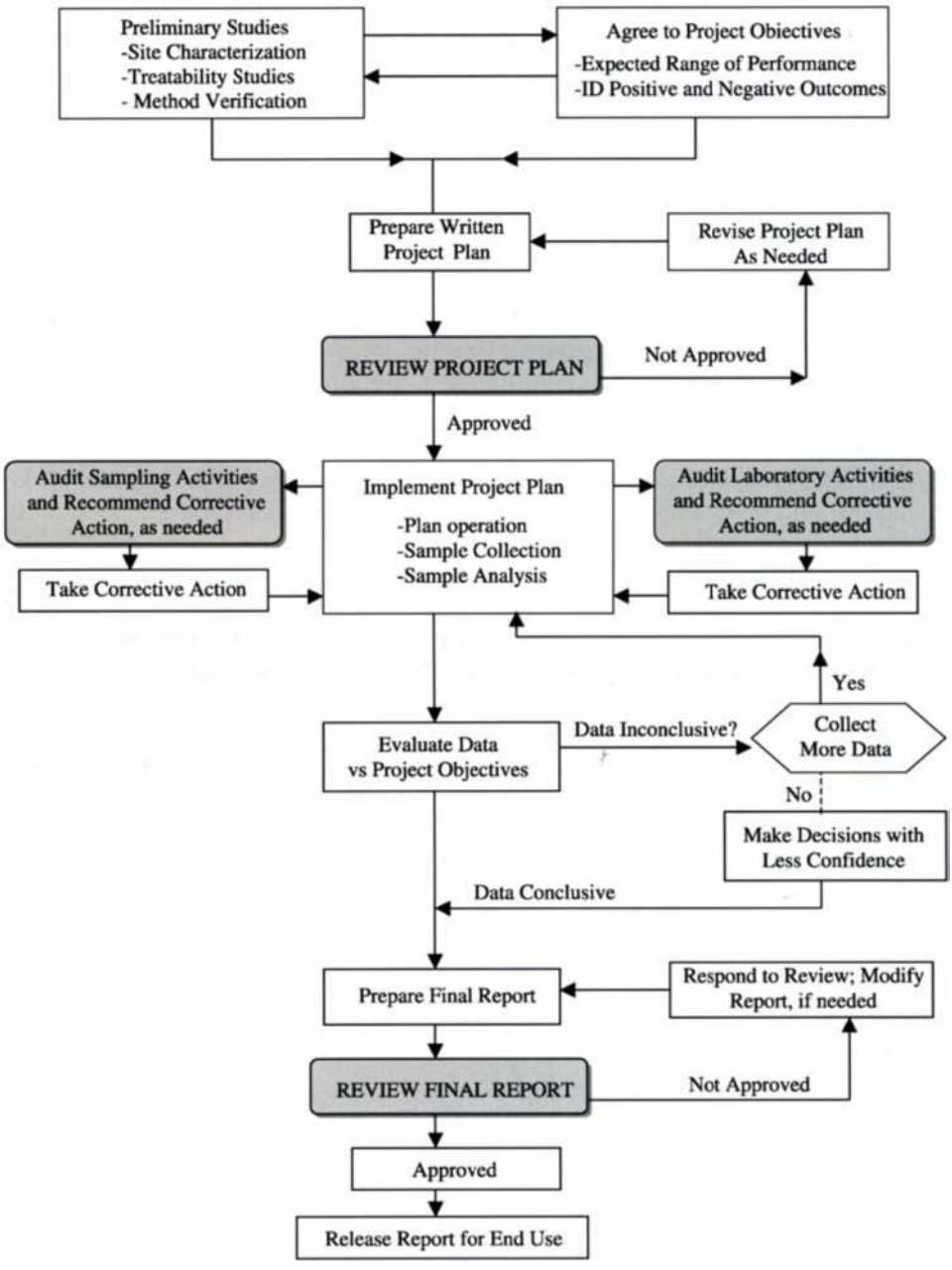


Figure IV.7.3. Typical flow of project activities.

preservation, transport, custody, storage, preparation, analysis, QC procedures (including corrective action), and data reduction. This step is common to essentially all projects although the complexity of the document varies with the nature of the project and may be handled on a project-by-project basis.

d. *Review the written project plan.* The project team should be supplemented by technical experts not involved in the plan preparation who should review this document and recommend changes, if necessary.
e. *Implement the project plan.* At this stage the test is actually performed and data are generated. As might be expected, this is the period of most intense activity. Ideally all measurements follow the plan, but in practice, unanticipated occurrences often lead to adjustments in approach, especially for the more exploratory projects.
f. *Audit the sampling and laboratory activities.* The QA involvement at this stage is to perform on-site audits of the sampling and laboratory activities. Concerns are identified by the QA staff and corrected by project personnel, as needed.
g. *Evaluate the data.* Before preparing the final report, data are evaluated against project objectives. More data may be collected, if needed. Although collecting more data may be the norm for exploratory projects, for major studies this is often impractical or impossible. Sometimes decisions must be made even when data are incomplete or inconclusive.
h. *Prepare and review the final report.* No project is complete until the final report is prepared and reviewed. As shown in Figure IV.7.3, project personnel prepare the final report, which is then reviewed by the QA department prior to release.

This sequence of activities is similar whether one is evaluating a pollution control technology, assessing the health effects of radon exposure, or establishing the efficacy of a new vaccine.

As suggested by Figure IV.7.3, the most intense interactions with the QA function occur at limited but important junctures, in this case as reviews of project plans and final reports, and as audits during data generation. However, an equally important juncture involves the early interaction among project management, the customer and the QA staff in developing the blueprint for the project plan. This early group interactions as well as project plan reviews, audits and final report reviews are explained in the following text.

IV.7.4.1. Developing the blueprint

It is either prudent (low risk project) or imperative (high risk project) that earnest project planning activities precede implementation activities. The blueprint activities, when done correctly, can help ensure that proper focus is given, adequate resources are provided, and difficult issues are resolved. The process for planning a project comprises seven steps (US EPA, 1994):

1. State the problem.
2. Identify the decision.
3. Identify the inputs to the decision.
4. Define the study boundaries.
5. Develop a decision rule.

6. Specify tolerable limits on decision errors.
7. Optimize the design.

Implementation of these seven steps results in qualitative and quantitative statements that pinpoint specific study objectives, define the types of data needed, define the statistical population the data are considered to represent, and specify the tolerable risks for false positive and false negative decision errors.

IV.7.4.2. Initial inputs (steps 1–3)

The initial inputs include a concise statement of the problem that is being addressed, the decision(s) that will be made based on the results of the study, and all of the critical parameters that are needed to make the decision(s). Parameter inputs may include decisions such as: list of analytes, sampling strategies, type of sample containers needed, sample preservation requirements, analytical methods that can be used, types of QC samples needed, approaches to statistical interpretations, etc.

IV.7.4.3. Define the study boundaries (step 4)

This step involves the defining of the physical boundaries of the site being investigated as well as the boundaries of the inference space (i.e. defining the conceptual population represented by the sample data). Defining the boundaries of the study, however, goes beyond defining the physical boundaries of the site. It also includes defining temporal boundaries (i.e. considering and addressing the potential impacts of seasonality or other time-related considerations and how these will be addressed in the data collection process).

One of the fundamental ideas that must be kept in mind when defining the boundaries of a study is that the decisions made, ultimately, rest on inference. Although one talks about measuring the concentration at a site and basing decisions on the data, what one actually does is make decisions on the basis of inferences that are, in turn, based on estimates. The analytical result on one sample is only one out of a theoretically infinite number of possible results for a theoretically infinite number of possible analyses of that sample.

IV.7.4.4. Develop a decision rule (step 5)

The decision rule is a summary statement that defines how a decision maker expects to use data to make the decision(s) identified in step 2. The same way that multiple decisions, for example, might pertain to multiple areas within a site, there may be (and often are) multiple decision rules for different areas of the site or for different pollutants. Development of a decision rule involves the following check steps:

- Specify the statistical parameter (e.g. mean, 90th percentile, upper tolerance limit, etc.) that characterizes the population of interest.
- Specify the action level of the study.
- Develop an "if...then" statement that describes the decision rule in terms of alternative actions.

IV.7.4.5. Specify tolerable limits on decision errors (step 6)

As noted in the discussion on defining study boundaries, decisions about a site ultimately rest on estimates of parameters of statistical populations. The true average concentration at a site is not known and is not knowable because it is a mean of an infinite population. Therefore, decisions based on average site concentration must be made using estimates of the true site average, developed on the basis of limited sampling data for an infinite population. This introduces sampling error into the estimate that is used as the basis for decision making. These estimates, which are based on measurement data, also have an inherent uncertainty associated with them because of random and systematic errors in the measurement process. These elements of uncertainty reflect measurement error. Because decisions are based on estimates that contain inherent uncertainties, there is always some risk of error in the final decision.

Decision errors are commonly divided into false positive errors and false negative errors. To reduce the risk of decision errors, the study design must include sufficient data collected in a statistically sound manner to adequately estimate the population parameter used as the basis for decision making. Uncertainty due to sampling error can be reduced by collecting large number of samples. Uncertainty due to measurement error can be reduced by using more precise and accurate analytical methods and by performing multiple analyses of each sample and averaging the results. However, reducing uncertainty and associated risk of decision errors increases the cost of collecting data. Therefore, one of the most important steps in the initial planning process is the sixth step, in which the acceptable risks of the two types of decision error are established.

IV.7.4.6. Optimize the design (step 7)

The seventh and last step of the initial planning process is to develop and optimize the project design. This involves integrating the outputs of the previous steps into the most resource-effective data collection design that satisfies the data user (i.e. customer) needs. The outcome of this last step will provide the necessary information to decide on one of two plans of action: (1) given the available resources, the project objectives can be achieved and, therefore, the project can move forward or (2) given the available resources, the project objectives cannot be achieved and, therefore, the initial planning process (steps 1–7) must be repeated with an adjustment to resources, project objectives or both.

IV.7.4.7. Reviewing the project plan

Even if no formal QA review were planned, preparing a written project plan is an essential step in any formal investigation. Preparing such a plan has the virtues of

- clarifying the thinking of all involved parties;
- integrating the goals and efforts of disparate project participants into a single document that can be reviewed by all;
- permitting a review by independent experts;
- providing clear instructions to data generators; and finally,
- fostering agreement on how data will be interpreted.

To achieve these goals, the project plan must not merely list the methods to be used, but must demonstrate how the intended measurements will achieve the project goals. This plan must provide concrete steps for assuring that the data will be of known and adequate quality, and should provide means for documenting data quality. The project plan should also assign responsibilities and establish means for regular communication among project participants.

The QA staff reviews this document in detail using experts in the field of interest. The primary question asked by the reviewers is "Will the planned test achieve the project objectives?" Questions relating to this central issue include the following: "Are objectives clearly stated? Are sampling and analytical methods appropriate, and are the applicable QC methods clear and adequate? Will data reduction and statistical procedures permit unbiased statements of overall uncertainty?" In short, the QA reviewer "thinks through" the entire project to recognize any problems beforehand, and then writes up observations in a detailed report that delineates each concern and its potential implication. This report is then sent to project management.

It is noteworthy that the project plan is "repaired" not by the QA staff but by project staff. It is thus essential that the reviewer describes all concerns clearly, emphasizing the effect that the planned approach will have on the outcome of the project. Once the cause-and-effect relationships are clear, project staff normally is anxious to solve the concern before it can develop into an intractable and perhaps embarrassing problem. It is also important that the QA reviewer avoids "nit-picking" and concentrates on the most important issues. Consequently, QA reviewers must be aware of the general programmatic setting and must be experienced and knowledgeable in the technical field of interest. Often it is necessary to employ multiple reviewers with complementary expertise to address all aspects of a project. To maintain the necessary objectivity and to provide a fresh outlook, it is also best that the QA reviewer not be previously involved in the project.

Keeping with the philosophy that project management – not the QA office – is responsible for overall quality, project management may choose to address all or some of the QA review comments. However, in the vast majority of cases, all review comments are satisfied before the project proceeds.

IV.7.4.8. Auditing the project

The audit can be divided roughly into three parts – planning, the site visit, and reporting. The planning stage must begin by defining the goals and scope of the audit, i.e. by defining the standard against which the audit will be performed. The auditor must become familiar with the planned measurements and should attempt to anticipate likely areas of concern. The auditor must also contact the principal participants to identify their requirements and to set up schedules. The site visit is the central activity and consists largely of personal interviews with technicians and other data generators. During this stage the auditor must inspect relevant operations, samples, and documentation. Any apparent concern must be brought up promptly and discussed as needed. A closeout meeting must be conducted at the end of the review to inform management of any concerns and to discuss possible corrective action, if needed. While a formal written report must be prepared after completion of the review, project management should not be "surprised" by any major findings in the follow-up report.

To be useful, the audit must be conducted early in the project cycle to permit corrective action before irreversible harm has occurred. Identifying concerns late in a project cycle is usually not constructive and does little more than build resentment.

Perhaps more than other QA tasks, the audit requires verbal and interpersonal skills. The auditor must take the lead and set the tone but at the same time must foster the free exchange of ideas. During an audit, most information is obtained from personal interviews with the individual technicians who handle the samples, and in this situation the auditor must be patient, perceptive, and persistent. While the auditor likely arrives with certain routine questions in mind, it is often the unexpected finding that leads to the most significant concern. After all, the technicians have likely been audited before and have consequently corrected the most common problems. Thus, flexibility and inquisitiveness are very important during the audit process.

Sometimes the auditor meets resistance and must persist to fully uncover an adverse situation. In these cases, it is particularly important to explain the potentially deleterious effect on the project, and to consider the opinions of all parties. The auditor must convince project management that the concern truly matters if corrective action is to occur.

IV.7.4.9. Reviewing the final report

The review of the final report is the last "inspection" before the "product" is released. As in the case of the project plan, the final report is reviewed by technical experts who were not involved in the project. The principal goal here is to assure that the data support the conclusions, that the major areas of uncertainty are identified, and that data are developed in a logical and consistent manner. A written review is prepared identifying all concerns and providing recommendations, as needed.

IV.7.5. Rules of engagement

The previous section briefly describes the tools available to the QA staff operating in a project environment. The following discussion presents guidelines to the QA staff regarding how they can apply these tools effectively.

Do your chores. QA staff in a project environment typically find themselves dealing with a variety of subject matter and personnel. Indeed, it is this feature that primarily distinguishes a project management environment from routine production setting. Nevertheless, the QA staff is expected to carry out certain routine tasks for nearly every project. For environmental projects, these tasks include reviews of test plans and final reports, on-site inspections during testing, and occasionally assistance to project management. Regardless of the setting, though, these operations constitute the most tangible and immediate contribution to project execution, and it is in this context that interaction with project management most often occurs. Consequently, such operations must be given first priority as the mechanism for making significant contributions and for building rapport with project management.

Require a written project plan. A written plan describing how project objectives will be achieved and how the needed quality will be assured is considered central to any investigation. For this reason, groups as diverse as the US Environmental Protection

Agency (US EPA, 1998, 2001b), the Japanese Ministry of Trade and Industry (1984), and the Organization for Economic Cooperation and Development (OECD, 1992) have for many years required that projects begin with a written plan. Subsequent experience has shown that preparation and review of a written plan clarifies issues and helps avoid errors. The various benefits of preparing a written plan were discussed previously.

Document your needs. The agencies cited previously provide only general guidelines for QA compliance. Unless the QA staff translates these into specific requirements for the projects typical of their work place, project managers will not know what is expected. In this situation QA requirements may simply be ignored, or efforts may be extensive but misguided. It is thus essential that the QA staff develop written guidelines translating the general organizational goals into specific, local requirements.

Be flexible. Diversity and variety are one hallmark of a project management setting. It is not unusual for the QA staff to deal with projects as disparate as basic research, demonstrations of mature technology, legal investigations, or even epidemiological studies. Professionals involved may include engineers, scientists, legal staff, economists, or medical personnel. In a university research setting, speed of response and flexibility are of utmost importance, and experiments can simply be repeated if results are inconclusive. In contrast, a demonstration of pilot-scale technology or a major epidemiological study may waste millions of dollars if results are inconclusive. In such situations the QA staff must adapt to the nature of the work and the potential risks, allowing the basic researcher maximum freedom while minimizing the risk of costly errors. This means providing different QA guidelines for different types of projects.

Set priorities. To make the most significant contribution, QA efforts must be weighed against the potential benefit. This means that QA involvement should be focused where the cost of wrong decisions is greatest, or in those areas most prone to problems. From this perspective, natural areas of focus are large programs requiring the participation of multiple parties.

Don't dilute responsibility. As is suggested by Figure IV.7.3, QA is only a small (but very important) part of the overall project effort. Here the QA manager may be likened to a visiting uncle who provides child-rearing advice to the parents. No matter how insightful the advice may be, the uncle's understanding of the situation is always less than complete, and consequentially the final authority and responsibility must rest with the parents. Further, unless such advice is offered with tact, it will be ignored and perhaps even resented. Similarly, the project management martials the resources, selects the personnel, makes the day-to-day decisions, and is fully involved over the entire duration of the project. The project manager must have the final authority and responsibility for the quality of the project. This means that the project manager may reject the advice of the QA staff, although in practice this is not likely to occur very often.

It has been said that "quality is everyone's responsibility." This is true in the sense that everyone needs to look beyond his/her limited assignment and take initiative to improve the final product. This statement means that the QA staff must perform their tasks competently and always be alert for additional methods of improving the final product. Nevertheless, the project manager has special responsibility for directing the effort and for acting as the "gatekeeper" of the product, not allowing the release of any product of inadequate quality.

Be on time, be prepared, and be an expert. There is a saying among project managers, "On time, on budget, on spec. – choose two!" In contrast, the QA staff must deliver in all three regards to gain the cooperation of project managers. The most insightful review, delivered when the subject activity is complete, is worthless. This means that on-site reviews must be completed early in the project to permit effective corrective action, if needed. Similarly, efforts must be completed within budgetary constraints and with minimum disruption to the project. Finally, it is not enough to be merely an expert in QA; the QA reviewers must also be technical experts in the subject area. If the QA team does not have the appropriate technical background, then it becomes necessary to find someone who does.

Be clear, but not confrontational. The QA staff should neither equivocate nor be unnecessarily confrontational. State the potential concern in terms of its possible impact on the project. Listen respectfully to possible explanations and suggested corrective action. Remember, what originally appears to be a serious shortcoming frequently becomes reasonable once further explanation is provided. If need be, contact upper management to resolve the problem. However, almost without exception, concerns can be resolved by the mutual effort of project participants.

Find the principles. In a large organization it may be difficult to identify what projects are underway and who is working on them. This means that some projects may evade QA oversight entirely, or that QA documentation may be prepared without the needed guidance. The QA staff may discover such projects only when a poorly prepared project plan is delivered for review. To provide uniform QA oversight in the most cost-effective manner, the QA staff must implement a mechanism for identifying active projects and the accountable project managers.

Take the initiative. The QA staff, because of their exposure to a wide range of projects, is uniquely situated to identify frequently occurring problems. For instance, the QA staff may become aware that several investigators need help in selecting appropriate statistical procedures in certain recurring situations, or that an important QA procedure is frequently overlooked. The QA staff should take the initiative and recommend solutions. The QA personnel should also be alert to possible cost savings that might be realized without degrading quality. Some project planners provide for an excessive number of expensive measurements, and such situations should be brought to the attention of project management for cost reasons, even when there is no adverse effect on quality.

IV.7.6. Summary

As depicted in the QSP (Fig. IV.7.1), a dynamic quality system consists of three interdependent parts:

- *Organizational (institutional) QA*: The management structure that provides the needed organization, tools, and resources.
- *Catalytic QA*: The attitudes and relationships among staff needed to make all of the organizational elements fit together to yield a product that is greater than the individual parts.
- *Technical (project) QA*: The application of concepts to a specific project.

None of the parts can be successful without the other parts. While the principles previously described are taken from the perspective of one working in the environmental field, it seems likely that they would apply equally well (with some adjustments) to other project-oriented endeavors such as the health or forensic sciences.

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For further information

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PART V

Evaluation and prognosis of the vadose zone and groundwater pollution and protection at solid waste disposal sites

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Solid Waste: Assessment, Monitoring and Remediation
Twardowska, Allen, Kettrup and Lacy (Editors)
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V.1
Modeling reactive metal transport in soils

Michael C. Amacher and H. Magdi Selim

V.1.1. Introduction

Models that can accurately predict the retention and movement of heavy metals in soils can be useful in helping to select the most cost-effective technology for mitigating contaminated soil sites. Furthermore, such models are useful in assessing the degree of cleanup required. For example, if a model predicts that a particular metal is relatively mobile in a particular soil environment, then extraction of the metal from the soil may be the best treatment choice. If on the other hand, a model predicts that a particular metal is relatively immobile in a particular soil environment, then a method that further immobilizes or fixes the metal in place might be the most suitable choice.

In this chapter, models that govern retention reactions and transport of heavy metals in the soil are presented. Models of the equilibrium type are first discussed then followed by models of the kinetic type. Retention models of the multiple reaction type including the two-site equilibrium–kinetic models, the concurrent- and consecutive multireaction models (MRMs), and the second-order approach will be derived. In addition, competitive type models where ion exchange is assumed to be the dominant retention mechanism are presented. Selected experimental retention and breakthrough results for Cu, Pb, Cr, Cd, and Zn are illustrated for the purpose of model evaluation and validation.

V.1.2. Equilibrium models

Over the last three decades, numerous models for describing reactive solute retention in soils have been developed (Selim, 1992, 1999; Selim and Amacher, 1997, 2001; Kretzschmar and Voegelin, 2001). Table V.1.1 provides a summary of several equilibrium and kinetic type retention approaches. Below we describe major retention approaches of the equilibrium type followed by selected kinetic type approaches. The Langmuir isotherm is perhaps the most commonly used equilibrium type isotherm, which may be expressed as

$$\frac{S}{S_{\max}} = \frac{\omega C}{1 + \omega C} \tag{V.1.1}$$

where S is the amount of solute retained by the soil (μg/g soil), C is the solute concentration in solution (μg/ml), and ω and $S_{\max}$ are adjustable parameters. Here ω (cm^3/μg) is

Table V.1.1. Selected equilibrium and kinetic type models for heavy metal retention in soils.

Model	Formulation[a]
Equilibrium type	
Linear	$S = K_d C$
Freundlich	$S = K_f C^b$
General Freundlich	$S/S_{max} = [\omega C/(1 + \omega C)]^{\beta}$
Rothmund–Kornfeld ion exchange	$S_i/S_T = K_{RK}(C_i/C_T)^n$
Langmuir	$S/S_{max} = \omega C/[1 + \omega C]$
General Langmuir Freundlich	$S/S_{max} = (\omega C)^{\beta}/[1 + (\omega C)^{\beta}]$
Langmuir with sigmoidicity	$S/S_{max} = \omega C/[1 + \omega C + \sigma/C]$
Kinetic type	
First order	$\partial S/\partial t = k_f(\Theta/\rho)C - k_b S$
*n*th order	$\partial S/\partial t = k_f(\Theta/\rho)C^n - k_b S$
Irreversible (sink/source)	$\partial S/\partial t = k_s(\Theta/\rho)(C - C_p)$
Second-order irreversible	$\partial S/\partial t = k_s(\Theta/\rho)C(S_{max} - S)$
Langmuir kinetic	$\partial S/\partial t = k_f(\Theta/\rho)C(S_{max} - S) - k_b S$
Elovich	$\partial S/\partial t = A \exp(-BS)$
Power	$\partial S/\partial t = K(\Theta/\rho)C^n S^m$
Mass transfer	$\partial S/\partial t = K(\Theta/\rho)(C - C^*)$

[a] A, B, b, C^*, C_p, K, K_d, K_{RK}, k_b, k_f, k_s, n, m, S_{max}, ω, β, and σ are adjustable model parameters, ρ is the bulk density, Θ is the volumetric soil water content, C_T is the total solute concentration, and S_T is the total amount sorbed of all competing species.

a measure of the bond strength of molecules on the matrix surface and S_{max} (μg/g soil) is the maximum sorption capacity or total amount of available sites per unit soil mass. The Langmuir sorption isotherm has been used extensively by scientists for several decades. Moreover, Langmuir isotherms were used successfully to describe Cd, Cu, Pb, and Zn retention in soils. Figure V.1.1 shows experimental and fitted isotherm examples of use of the Langmuir equation to describe Cu retention in McLaren and Cecil soils (Selim and Amacher, 1997).

Several modifications of the Langmuir approach have been developed by a number of scientists. The presence of two types of surface sites responsible for sorption was postulated and an adaptation of the original equation was proposed. This adaptation was successfully used to describe Cr(VI) and Zn for a wide range of soils. Figure V.1.2 shows experimental and fitted isotherms illustrating the use of the two-site Langmuir approach for Cr(VI) retention for three soils (Selim and Amacher, 1988). A more recent adaptation of the two-surface Langmuir approach is the incorporation of a sigmoidicity which proved desirable in describing sorption isotherms at extremely low concentrations for Pb, Cd, and Cu in a surface Luvisol (Schmidt and Sticher, 1986).

Another commonly used equilibrium approach is the Freundlich isotherm,

$$S = K_f C^b \tag{V.1.2}$$

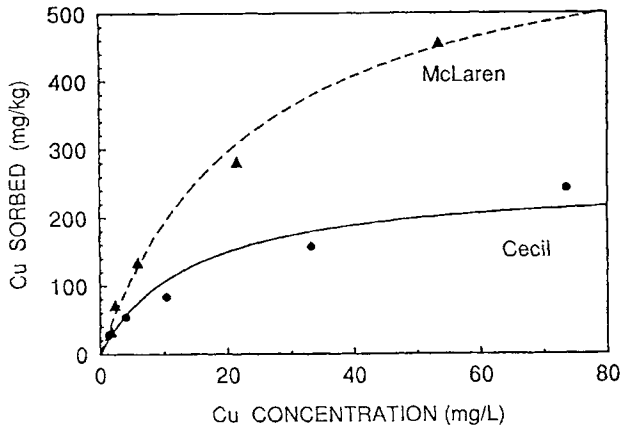


Figure V.1.1. Retention isotherms for Cu after 8 days of reactions for Cecil and McLaren soils. Solid curves are calculated isotherms using equilibrium Langmuir model.

where K_f is the distribution coefficient (cm^3/g) and the parameter b is dimensionless and typically has a value of $b < 1$. The distribution coefficient describes the partitioning of a solute species between solid and liquid phases over the concentration range of interest and is analogous to the equilibrium constant for a chemical reaction. For b equals unity, the Freundlich equation is often referred to as the linear retention equation (see Table V.1.1).

There are numerous examples for solute retention, which were described successfully by use of the Freundlich equation (Sposito, 1984; Buchter et al., 1989; Sparks, 1989).

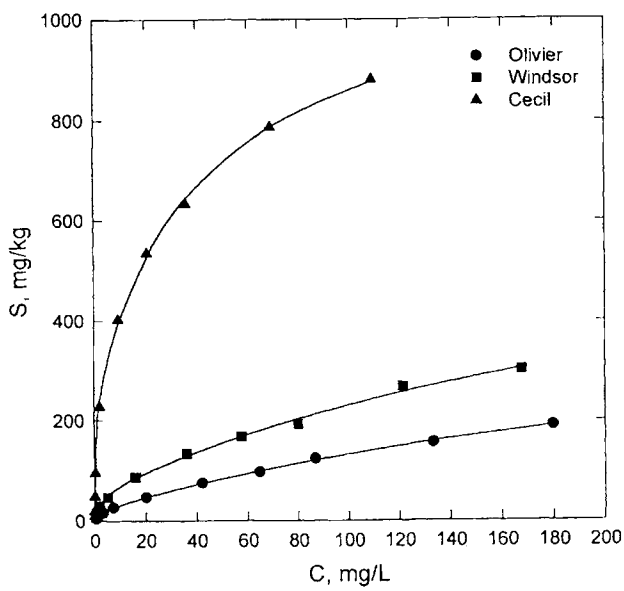


Figure V.1.2. Two-site Langmuir sorption curves for Cr(VI) retention by Olivier, Windsor, and Cecil soils after 336 h of reaction.

Logarithmic representation of the Freundlich equation is frequently used to represent the data as illustrated in Figure V.1.3. Here the slope of the best-fit curve provides the nonlinear parameter b and the intercept as K_f according to ($\log(S) = K_f + b \log(C)$) as long as a linear representation of the data in the log form is achieved. In Figure V.1.3, we illustrate the use of the Freundlich equation for Pb isotherms for several soils (Buchter et al., 1989).

Another type of equilibrium retention approaches is that based on competitive ion exchange processes. Such mechanisms describe interactions of multiple species present in the soil solution and that on exchange surfaces of the soil matrix (Sposito, 1981). For the simplest case of binary homovalent exchange, and assuming similar ion activities in the solution phase, results in the following ion exchange isotherm equation,

$$K_{ij} = [{}^{\nu}K_{ij}]^{1/\nu} = \frac{(s_i/c_i)}{(s_j/c_j)} \tag{V.1.3}$$

where ν is the ion valency, K_{ij} is a generic selectivity coefficient of ions i over j (Rubin and James, 1973) or a separation factor for the affinity of ions on exchange sites. In addition, c_i and c_j are the relative ion concentrations (dimensionless) such that $c_i = C_i/C_T$ and $c_j = C_j/C_T$, where C_i, C_j, and C_T (mmol(+)/ml) are the concentrations in the soil solution of ions i and j, and the total concentration, respectively. Also s_i and s_j are amounts retained on the solid matrix surfaces (dimensionless) and are expressed as equivalent fractions where $s_i = S_i/\Omega$ and $s_j = S_j/\Omega$. Here, S_i and S_j are the amounts adsorbed (mmol(+)/g soil) and Ω is the cation exchange (or adsorption) capacity of the soil (mmol(+)/g soil).

Based on Equation (V.1.3), for $K_{12} = 1$, a linear isotherm relation is produced, represented by the solid line in Figure V.1.4. This clearly illustrates a 1:1 relationship between relative concentration in solution and that on the adsorbed phase. This also implies that the two ions 1 and 2 each have equal affinity for the exchange sites. In contrast, for $K_{12} < 1$, we have nonlinear sorption isotherms. Specifically, for $K_{12} > 1$, sorption of ion 1 is preferred and the isotherms are convex. For $K_{12} < 1$, sorption affinity is apposite and the isotherms are concave. Examples of homovalent ion exchange isotherms are illustrated in Figure V.1.4 (Cd–Ca in two soils) (Selim et al., 1992).

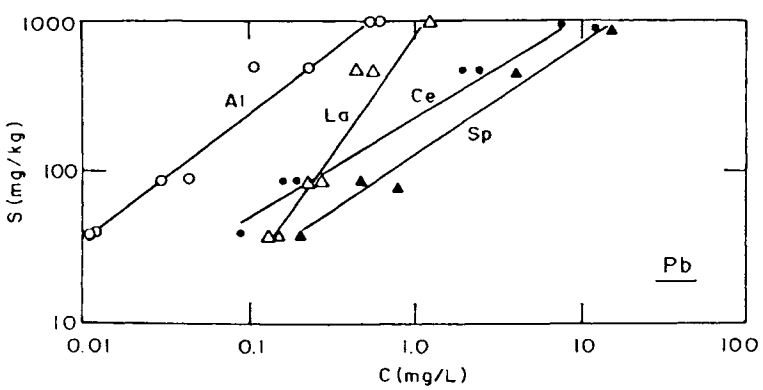


Figure V.1.3. Retention isotherms for Pb on selected soils. Solid curves are calculated isotherms using equilibrium Freundlich. The soils are represented by: Alligator (Al), Cecil (Ce), Lafitte (La), and Spodosol (Sp).

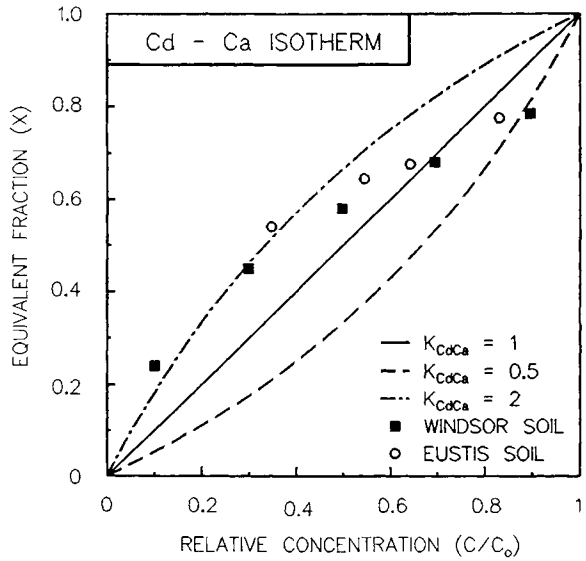


Figure V.1.4. Cadmium–calcium exchange isotherm for Windsor and Eustis soils. Solid and dashed curves are simulations using different selectivities (K_{CdCa}).

The capability of the ion exchange approach in describing multiple pulse applications is illustrated in Figures V.1.5 and V.1.6 (for Windsor soil). Here Cd input pulses were 10 and 100 mg/l, respectively (Selim et al., 1992). The ion exchange model well predicted the position of the BTC peaks and the assumption of equilibrium ion exchange adequately predicted the observed snow plow effect where effluent concentration exceeds that of the input pulse ($C/C_0 > 1$) for the two Windsor data sets.

The Rothmund–Kornfeld binary exchange is another equilibrium approach, which incorporates variable selectivity based on the amount of adsorbed (s_i) or exchanger composition. The approach is empirical and provides a simple equation that incorporated the characteristic shape of binary exchange isotherms as a function of equivalent fraction

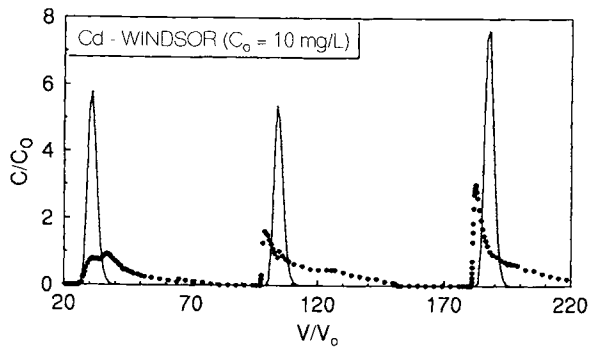


Figure V.1.5. Measured (closed circles) and predicted breakthrough curves in Windsor soil column for three Cd pulses of $C_0 = 10$ mg/l. Curves are predictions using equilibrium ion exchange model.

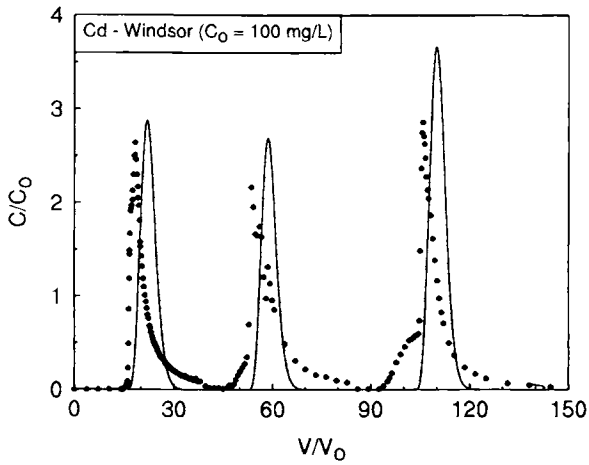


Figure V.1.6. Measured (closed circles) and predicted breakthrough curves in Windsor soil column for three Cd pulses of $C_0 = 100$ mg/l. Curves are predictions using equilibrium and ion exchange model.

of the amount sorbed (s_i) as well as the total solution concentration in solution (C_T). The Rothmund–Kornfeld formulation can be expressed as,

$$\frac{(s_i)^{vj}}{(s_j)^{vi}} = {}^{R}K_{ij}\left[\frac{(c_i)^{vj}}{(c_j)^{vi}}\right]^{n} \tag{V.1.4}$$

where n is a dimensionless empirical parameter associated with the ion pair i–j and ${}^{R}K_{ij}$ is the Rothmund–Kornfeld selectivity coefficient. The above equation is best known as a simple form of the Freundlich equation that applies to ion exchange processes. As pointed out by Harmsen (1977), the Freundlich equation may be considered as an approximation of the Rothmund–Kornfeld equation valid for $s_i \ll s_j$ and $c_i \ll c_j$, where

$$s_i = {}^{R}K_{ij}(c_i)^{n} \tag{V.1.5}$$

The ion exchange isotherms in Figure V.1.7 show the relative amount of Zn and Cd adsorbed as a function of relative solution concentration along with best-fit isotherms based on the Rothmund–Kornfeld equation for two acidic soils (Hinz and Selim, 1994). The diagonal line represents a non-preference isotherm (${}^{R}K_{ij} = 1$, $n = 1$) where competing ions (Ca–Zn or Ca–Cd) have equal affinity for exchange sites. The sigmoidal shapes of the isotherms reveal that Zn and Cd sorption exhibits high affinity at low concentrations, whereas Ca exhibits high affinity at high heavy metal concentrations. This behavior is well described by the Rothmund–Kornfeld isotherm with n less than one. An example of transport behavior of Zn in a Windsor soil column is presented in Figure V.1.8 (Hinz and Selim, 1994). Since the total concentration of the Zn and Cd input pulse solutions was much lower than that of the displacing Ca solution, chromatographic peaks were observed. Early appearance of Zn was well described by the predicted BTC (dashed curves) where equal Ca–Zn exchange affinity was assumed. In fact, the chromatographic effect for Ca and Zn was adequately described by the equal affinity BTCs. However, the tailing was not well predicted.

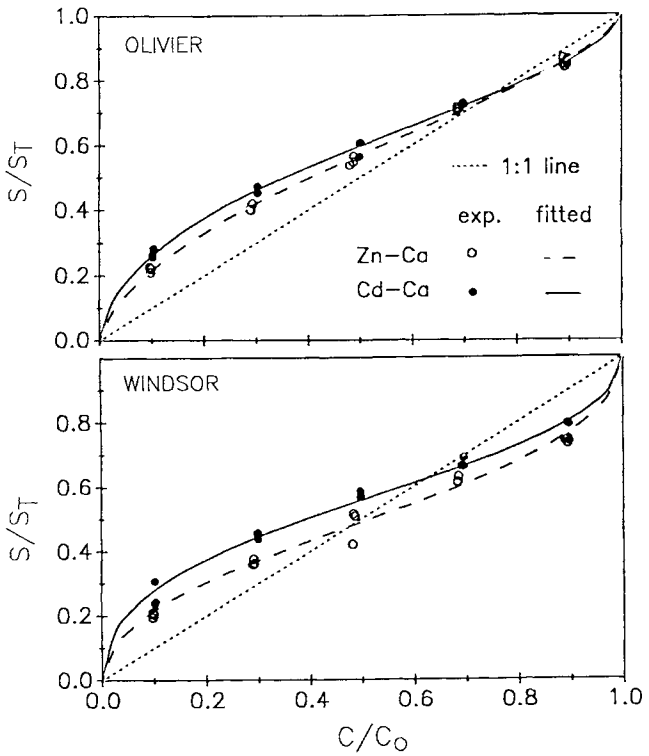


Figure V.1.7. Ion exchange isotherms of Cd–Ca and Zn–Ca for Olivier and Windsor soils (relative concentration (C/C_0) versus the sorbed fraction (S/S_T). Solid and dashed curves are fitted using the Rothmund–Kornfeld equation.

V.1.3. Kinetic models

The failure of equilibrium type models to adequately describe the retention of several heavy metals during transport in soils led Amacher et al. (1988) to propose a general purpose (equilibrium–kinetic) multireaction approach. Amacher et al. (1988, 1990) used an MRM to describe the time-dependent retention of Cr(VI), Cd, and Hg in a group of soils. Subsequent development of a two-site second-order kinetic model (SOTS) and incorporation of the nonlinear and second-order models into the convective–dispersive transport equation demonstrated that these models could also be used to describe Cr(VI) retention during transport through soil columns under steady water flow (Selim and Amacher, 1988; Selim et al., 1989). A schematic representation of the MRM is shown in Figure V.1.9.

In this model we consider the solute to be present in the soil solution phase (C) and in four phases representing solute retained by the soil matrix as S_e, S_1, S_2, S_3, and S_{irr}. We further assume that S_e, S_1, and S_2 are in direct contact with the solution phase and are governed by concurrent type reactions. Here we assume S_e as the amount of solute that is sorbed reversibly and is in equilibrium with C at all times. The governing equilibrium retention/release mechanism was that of the nonlinear Freundlich type. The reactions

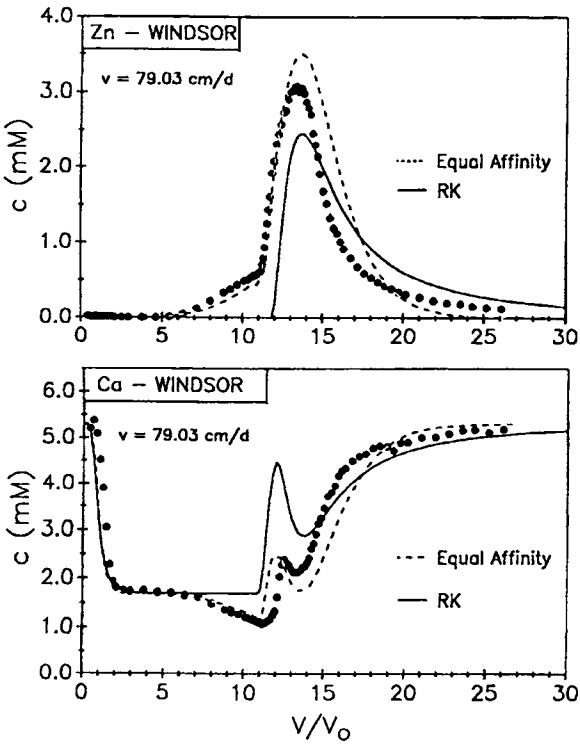


Figure V.1.8. Zn and Ca breakthrough curves in Windsor soil column at variable ionic strength. Predictions were based on equal affinity ($K_{12} = 1$) and the Rothmund–Kornfeld (RK) equation.

associated with S_1 and S_2 were considered to be reversible processes of the nonlinear kinetic type:

$$S_e = K_f C^b \tag{V.1.6}$$

$$\frac{\partial S_1}{\partial t} = k_1 \frac{\Theta}{\rho} C^n - k_2 S_1 \tag{V.1.7}$$

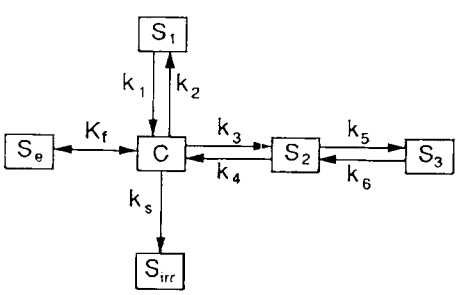


Figure V.1.9. A schematic representation of the MRM.

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\Theta}{\rho} C^m - k_4 S_2 \tag{V.1.8}$$

where k_1 to k_4 are the associated rate coefficients (h^{-1}) and r and Q are the soil bulk density (g/cm^3) and soil moisture content (cm^3/cm^3), respectively. These two phases (S_1 and S_2) may be regarded as the amounts sorbed on surfaces of soil particles and chemically bound to Al and Fe oxide surfaces or other types of surfaces, although it is not necessary to have *a priori* knowledge of the exact retention mechanisms for these reactions to be applicable. Moreover, these phases may be characterized by their kinetic sorption and release behavior to the soil solution and thus are susceptible to leaching in the soil. In addition, the primary difference between these two phases not only lies in the difference in their kinetic behavior but also on the degree of nonlinearity as indicated by the parameters n and m. The MRM also considers irreversible solute removal via a retention sink term Q in order to account for irreversible reactions such as precipitation/dissolution, mineralization, and immobilization, among others. We expressed the sink term as a first-order kinetic process:

$$Q = \rho \frac{\partial S_{\text{irr}}}{\partial t} = k_{\text{irr}} \Theta C \tag{V.1.9}$$

where k_{irr} is the associated rate coefficient (h^{-1}).

The MRM also includes an additional retention phase (S_3), which is governed by a consecutive reaction with S_2. This phase represents the amount of solute strongly retained by the soil that reacts slowly and reversibly with S_2 and may be a result of further rearrangements of the solute retained on matrix surfaces. Thus, inclusion of S_3 in the model allows the description of the frequently observed very slow release of solute from the soil. The reaction between S_2 and S_3 was considered to be of the kinetic first-order type, i.e.

$$\frac{\partial S_3}{\partial t} = k_5 S_2 - k_6 S_3 \tag{V.1.10}$$

where k_5 and k_6 (h^{-1}) are the reaction rate coefficients. If a consecutive reaction is included in the model, then Equation (V.1.8) must be modified to incorporate the reversible reaction between S_2 and S_3. As a result, the following equation

$$\rho \frac{\partial S_2}{\partial t} = k_3 \Theta C^n - \rho(k_4 + k_5) S_2 + \rho k_6 S_3 \tag{V.1.11}$$

must be used in place of Equation (V.1.8). The above reactions are nonlinear in nature and represent initial-value problems that were solved numerically using finite difference approximations (explicit–implicit).

Selected examples of experimental and MRM model predicted kinetic retention for Cd are given in Figure V.1.10. Here, the kinetic dependence of Cd retention, carried out in batch experiments, is shown for various soils (Selim, 1989). The amount of cadmium retained varied among soils with Cecil soil exhibiting the lowest retention, whereas Sharkey soil showed maximum Cd sorption from soil solution. The fast decrease in Cd concentration (with time) indicates a fast-type sorption reaction, which was followed by slower type reactions. It is also apparent that after 300 h of reaction time, quasi-equilibrium conditions were not attained. The capability of the MRM model to describe

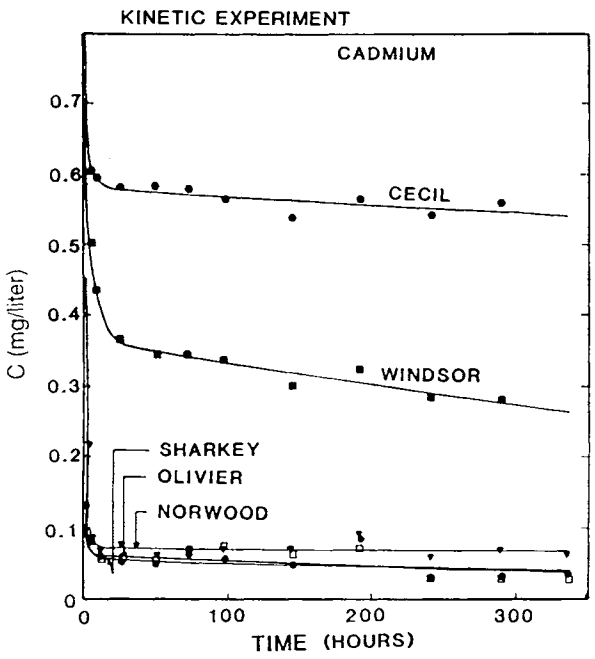


Figure V.1.10. Time-dependent retention of Cd by five soils at an initial Cd concentration (C_0).

the time-dependent characteristics for several soils is well demonstrated by the solid curves in Figure V.1.10.

For the second-order two-site approach (SOTS), one assumes that there exist two types of retention sites on soil matrix surfaces. In addition, the reactions associated with the two sites 1 and 2 were considered as kinetically controlled, heterogeneous chemical retention reactions. Therefore, one can assume that these processes are predominantly controlled by surface reactions of adsorption and exchange. We denote F as the fraction of type 1 sites to the total amount of sites S_T. We also denote ϕ as the amount of unfilled or vacant sites in the soil,

$$\phi_1 = S_{T1} - S_1 = FS_T - S_1 \tag{V.1.12}$$

$$\phi_2 = S_{T2} - S_2 = FS_T - S_2 \tag{V.1.13}$$

where ϕ_1 and ϕ_2 are amounts of vacant sites and S_1 and S_2 are amounts of solute retained on type 1 and type 2 sites, and S_{T1} and S_{T2} are the total amount of type 1 and type 2 sites, respectively. As the sites become occupied by the retained solute, the amount of vacant sites approaches zero ($(\phi_1 + \phi_2) \rightarrow 0$) and the amount of solute retained by the soil approaches that of the total capacity of sites ($S_1 + S_2) \rightarrow S_T$. As a result, the rate of retention may be expressed as,

$$\rho \frac{\partial S_1}{\partial t} = k_1 \Theta \phi_1 C - k_2 \rho S_1 \qquad \text{for type 1 sites} \tag{V.1.14}$$

$$\rho \frac{\partial S_2}{\partial t} = k_3 \Theta \phi_2 C - k_4 \rho S_2 \qquad \text{for type 2 sites} \tag{V.1.15}$$

where k_1 to k_4 are the associated rate coefficients. It is convenient to regard type 1 sites as those where equilibrium is rapidly reached. In contrast, type 2 sites are highly kinetic and may require several days or months for apparent local equilibrium to be achieved. This SOTS model was also extended to the diffusion-controlled mobile–immobile (SOMIM) or two-region model where a fraction of the dynamic to the stagnant sites and a mass transfer between the mobile and immobile water regions were incorporated (see Selim and Amacher, 1997).

The time-dependent retention of Cr(VI) by several soils was well described using the second-order two-site (SOTS) model (Selim and Amacher, 1988). An example of experimental and SOTS predicted time-dependent adsorption for a Windsor soil is shown in Figure V.1.11. Moreover, to illustrate the versatility of SOTS, two model versions were examined, a three-parameter or a one-site version (k_1, k_2, and k_{irr}) in which S_T was not differentiated into type 1 and type 2 sites ($F = 1$) and a five-parameter or a two-site version (k_1, k_2, k_3, k_4, and k_{irr}) in which two types of reaction sites were considered. For most input concentrations (C_0's), either the three- or five-parameter versions described the data adequately with high r^2 values and low parameter standard errors (data not shown). For Windsor soil, the five-parameter model version provided the best description of the data at low C_0's, whereas the three-parameter model version was best for higher C_0's.

To further examine the capability of the SOTS model, Selim and Amacher (1988) utilized Cr(VI) transport data for three soils from miscible displacement experiments.

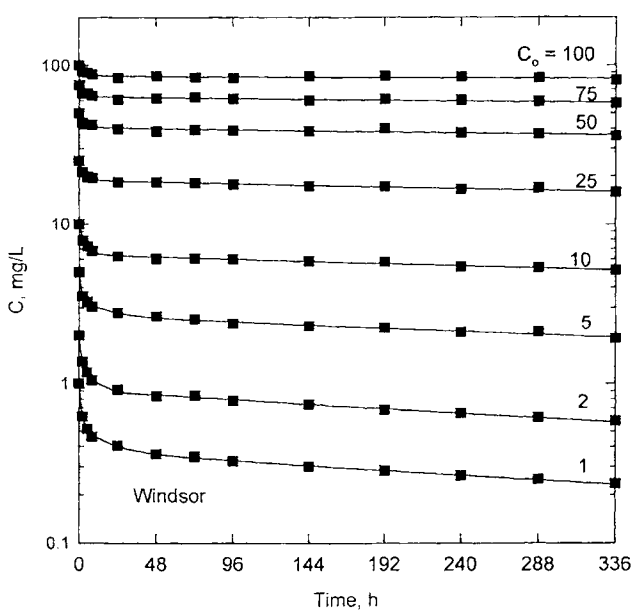


Figure V.1.11. Time-dependent retention of Cr(VI) by Windsor soil. Closed squares are the data points and solid lines are second-order two-site model predictions for different initial concentration curves (C_0 = 1, 2, 5, 10, 25, 50, 75, and 100 mg/l).

For Windsor soil, the predicted BTCs shown in Figure V.1.12 were obtained using different sets of model rate coefficients. This is because a unique set for the rate coefficients was not obtained from the batch data, rather a strong dependence of rate coefficients on input concentration was observed (Selim and Amacher, 1988). The use of batch rate coefficients at $C_0 = 100$ μg/ml, which is the concentration of Cr pulse inputs, grossly underestimated Cr retention by the predicted BTCs for the Windsor soils. Reasons for this failure are not fully understood with a most likely explanation is that the model is an apparent rather than mechanistic rate law which may not completely account for all reactions and reaction components. Closest predictions were realized using batch rate coefficients from C_0 of 10 or 25 μg/ml.

The capability of the second-order mobile–immobile (SOMIM) model to describe Cr miscible displacement results was also examined and predictions for Windsor soil are shown in Figure V.1.13. Predicted BTCs were obtained using different sets of model rate coefficients due to their strong dependence on input concentrations (C_0's). Closest predictions to experimental Cr measurements were obtained from batch rate coefficients at low C_0 values ($C_0 \leq 10$ μg/ml). Moreover, the use of rate coefficients at higher C_0's resulted in decreased tailing and reduced retardation of the BTCs. These observations are consistent with previous predictions using the SOTS model (Fig. V.1.12). Reasons for the observed less than adequate predictions of BTCs for the three soils using SOMIM are likely due to the poor estimates for the fraction immobile water content, the mass transfer and perhaps lack of nonequilibrium conditions between the mobile and immobile fractions. It is also conceivable that a set of applicable rate coefficients over

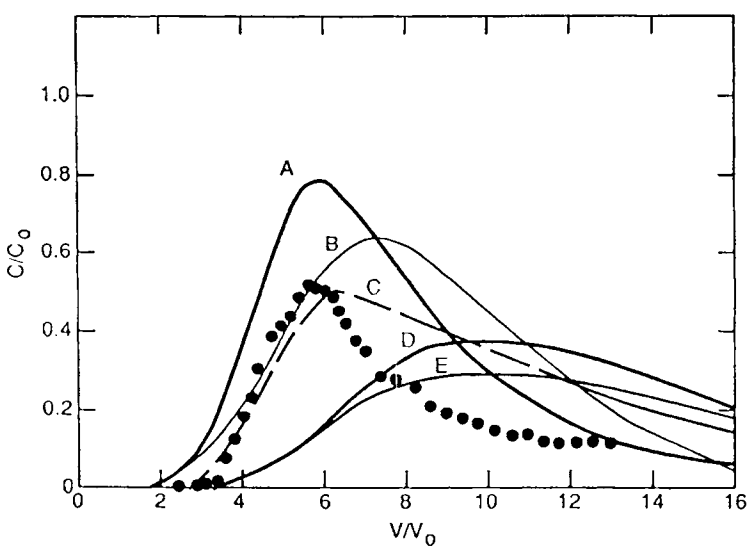


Figure V.1.12. Effluent concentration distributions for Cr(VI) in Windsor soil. Curves A, B, C, D, and E are predictions using the second-order two-site model with batch rate coefficients for C_0 of 25, 10, 5, 2, and 1 mg/l, respectively.

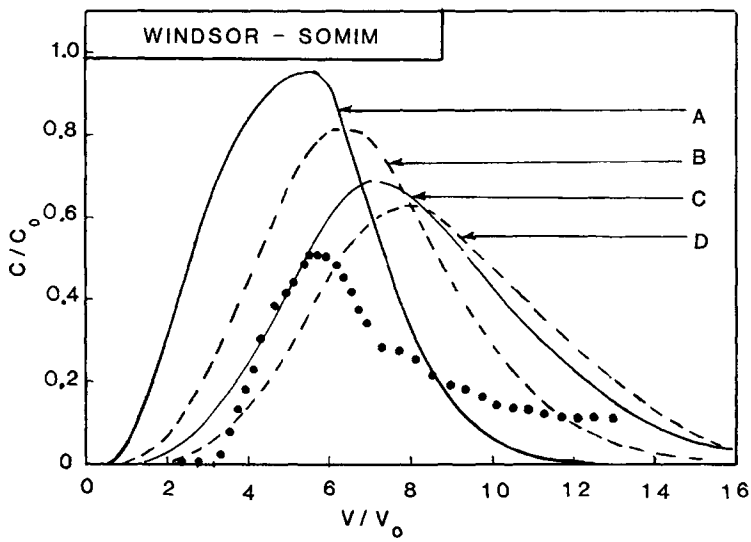


Figure V.1.13. Effluent concentration distributions for Cr in Windsor soil. Curves A, B, C, and D are predictions using the second-order mobile–immobile model with batch rate coefficients for $C/C_0 = 25$, 5, 2, and 1 mg/l, respectively.

the concentration range for Cr transport experiments cannot be obtained simply by use of the batch data sets.

The preceding examples illustrate various possibilities of using mass-action type equilibrium and kinetic approaches for describing reactive metal transport in heterogeneous porous media such as soils. In cases where specific reaction mechanisms are better understood, such as the interaction of a reactive oxyanion with a well-characterized mineral surface (see Scheidegger and Sparks, 1996 for some pertinent examples), more precise equilibrium and kinetic equations that describe the interaction of the reactive solute with the charged surface can be developed (e.g. Grossl et al., 1997). However, until sorption processes in heterogeneous media containing mixed assemblages of reactive mineral and organic surfaces (e.g. soil) are better understood and characterized, we will need to continue using more general and empirical mass-action type models such as those presented here to describe reactive metal transport in soils.

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V.2
Modeling bioavailability of PAH in soil

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V.2.1. Introduction

Soils contaminated with organic pollutants such as polycyclic aromatic hydrocarbons (PAH) may cause serious risks for ecosystems and humans. To reduce these risks, a lot of research into remediation processes has been carried out over the last 20 years. Initially, the remediation was focused on the cleanup of excavated soil by means of thermal treatment or wet classification/extraction. The aim was to reduce the concentration of pollutants in the soil below a so-called target value. Below this target value the soil can be considered non-polluted. In a later stage, biological treatment techniques and *in situ* treatment were developed and applied (Wilson and Jones, 1993; Mueller et al., 1996). During the last 5–10 years, the approach to solve the problem of contaminated soil has changed strongly. The assessment of risks of polluted soil for ecosystems and humans, and ways to reduce these risks, have become central issues. In this approach, the decision whether a site has to be remediated or not, and if it has to be remediated, in which way, is dependent on the risks of this site for humans and ecosystems.

Regarding the actual cleanup of soil contaminated with organic pollutants such as PAH, the attention is shifting more and more to extensive bioremediation systems such as natural attenuation, *in situ* bioremediation or a combination of these methods. In bioremediation, pollutants are biodegraded by micro-organisms such as bacteria and fungi. For this biodegradation process, favorable environmental conditions with respect to pH, redox potential, presence of nutrients, temperature and moisture content are required, as well as the presence of appropriate micro-organisms and the absence of components which may inhibit the biodegradation process (Sims and Overcash, 1983; Wilson and Jones, 1993). Besides, the organic pollutants have to be available for conversion by the micro-organisms (Bosma et al., 1997; Alexander, 2000). In general, the rate and extent at which micro-organisms biodegrade organic pollutants depends on three factors:

- the presence of the appropriate micro-organisms and the environmental conditions;
- the rate of uptake and metabolism of the pollutants by the micro-organisms;
- the rate of transfer of the pollutants to the micro-organisms.

In bioremediation research, a lot of effort has been put into the stimulation of the activity of micro-organisms by optimization of the environmental conditions for bioconversion and by augmentation (Mueller et al., 1996). However, very often this did not lead to improved bioremediation rates, especially when the bioremediation of soil polluted with PAH was considered. It has become evident that the reason for this phenomenon has to be found in the limitation of mass transfer of the pollutant to the soil micro-organisms (Chung et al., 1993; Bosma et al., 1997). This limitation of mass transfer primarily involves the limited transport rate in soil micro-regions. The slow release of PAH from the soil constituents in the soil micro-regions to the aqueous phase (moisture phase) around the soil particles, where the micro-organisms are present, is proven to be limiting for the overall biodegradation rate in many cases (Mulder, 1999; Bonten, 2001). Low mass-transfer rates caused by the low solubility of PAH in water, strong sorptive interactions of PAH with soil organic matter and diffusion limitations are responsible for the low bioavailability of PAH in soil. In general, mass transfer of pollutants to the micro-organisms is controlled by various physical/ chemical transport processes, such as dissolution, diffusion, desorption, adsorption, redesorption. Also, chemical incorporation and conversion in the natural organic soil matrix may occur for PAH (Richnow et al., 1999).

In view of the previous discussion, bioavailability can be defined as the extent to which pollutants may become available for uptake by micro-organisms, soil animals and plants, leading to biodegradation, bioaccumulation and/or toxicity (Cuypers, 2001). For pollutants such as PAH, which have a low solubility in water and a strong binding to the soil matrix, bioavailability is directly related to the mass transfer rate in the soil micro-regions. A limited bioavailability is in that case defined as a limitation by mass transfer in the soil micro-region.

Insight in and understanding of the phenomenon of the limited bioavailability of pollutants is currently very poor. Better understanding of the bioavailability of pollutants not only by modeling but also by empirically quantifying bioavailability is of crucial importance for:

- assessment of the toxicological risks of a polluted site;
- evaluation of the expected decrease in risks as a result of remediation of a polluted site;
- evaluation of the potential applicability of bioremediation as cleanup method for a contaminated site;
- optimization and steering of a bioremediation process.

For a proper risk assessment, focused on the long-term prediction of anthropogenic and geogenic contaminant pathways of pollutants, quantitative insight is necessary into transport processes of the pollutants and the way these pollutants may affect soil organisms. This is also necessary for a proper assessment of potential remediation methods, and if a specific method is chosen, for an optimal control and steering of this method. Basically this quantitative insight can be obtained by the development of mechanistic transport models in which a description is given of the basic processes responsible for the transport of pollutants and the intrinsic parameters that govern this transport process. However, especially regarding transport processes of pollutants in the

soil matrices, there is a lack of quantitative insight (Luthy et al., 1997; Mulder et al., 2000, 2001). The main reason is of course the extremely complex structure of the polluted soil on the micro-scale level. Approaches mentioned in literature mainly use simplified or complex equilibrium models, which relate the concentration of organic pollutants (such as PAH) in the soil matrix and the equilibrium concentration in a surrounding water phase, although some authors also consider diffusion aspects of pollutants in soil matrices more qualitatively. These approaches may lead to incorrect calculations of transport and bioremediation processes. Another way to quantify the bioavailability of pollutants is the use of analytical tools to measure the overall bioavailability. For PAH, various methods can be mentioned:

- extraction with a water phase containing solid adsorbents, such as Tenax (Cornelissen et al., 1998);
- extraction with an aqueous solution of cyclodextrins (Reid et al., 2000; Cuypers et al., 2001);
- supercritical extraction with carbon dioxide (Hawthorne and Grabanski, 2000);
- superheated water extraction (Johnson and Weber, 2001);
- extraction with organic solvents or aqueous solutions of organic solvents (Alexander, 2000);
- oxidation with persulfate (Cuypers et al., 2000).

These methods give only limited insight into the mechanisms of the limitations of the bioavailability. They give no detailed insight into the transport processes, which take place on micro-scale in the various soil micro-domains. However, they are very often useful for an estimation of the bioremediation potential of a polluted site or a first estimation of the ecotoxicological risks of a polluted site.

This chapter primarily focuses on mechanistic models and not on empirical methods for quantifying bioavailability. The main aim of the chapter is to discuss an improved, more realistic, mechanistic transport model of PAH as an example of a group of organic pollutants, which have a low solubility in water, are omnipresent constituents of many solid waste originated from human activities, are often strongly bound to the soil matrix and can be present in various physical states in soil matrices, and to show the effect of some major intrinsic mass-transfer parameters on the environmental (bio)availability of these pollutants.

The mechanistic models will be limited to the transport of pollutants in the various types of micro-domains in the soil matrix. Additional hydraulic transport and/or micro-biological conversion processes are not discussed here. These processes are in general not limiting for the bioremediation rate and can, if necessary, e.g. in case of risk assessments, easily be integrated in these models.

In the following, first a short overview of some relevant physical/chemical properties of PAH is presented. Thereupon the physical state, the PAH pollutants may be present in soil will be discussed. Based on the various physical states, mechanistic models of the transport of PAH to a surrounding liquid phase or wet phase, where the micro-organisms are supposed to be present, are derived and results obtained with these models are considered. Finally the impact and practical applicability, as well as the limitations of these models with respect to the assessments of risks and remediation techniques are discussed. In this discussion also,

the state of the art and the present role of the empirical methods to measure the bioavailability of PAH pollutants are briefly included.

V.2.2. Properties of the pure PAH pollutants

In the evaluation of the cleanup possibilities of a soil contaminated with PAH, usually the PAH of the so-called EPA priority pollutant list are considered. Some relevant physical properties of the PAH mentioned in this list are given in Table V.2.1.

It is observed from this table that the solubility of PAH in water is extremely low, with the exception of naphthalene. The table further shows a tendency that the solubility decreases with increasing number of aromatic rings. In general, this means that the hydrophobicity of the PAH also increases with increasing molecular weight. This is also in agreement with the octanol/water partition coefficient. This coefficient in general increases with increasing molecular weight and corresponds with the phenomenon that high molecular PAH are strongly ad(b)sorbed onto organic soil substances. Strongly ad(b)sorbed PAH have of course a much lower equilibrium solubility in water and equilibrium vapour pressure than pure PAH.

A lot of research has been carried out into the biodegradability of the PAH (Mueller et al., 1996; Volkering, 1996). These studies were dealing with single PAH and mixtures of PAH. Biodegradation was studied in water, soil slurries and soil. The biodegradation process was studied with pure cultures or mixed cultures. The character of these studies

Table V.2.1. Physical and chemical properties of the most frequently occurring PAH (after Sims and Overcash, 1983).

PAH	Molecular weight	Aqueous solubility at 30°C (mg/l)	Vapour pressure (N/m^2 at 20°C)	Log octanol/ water partition coefficient
Naphthalene	128	31.7	6.56	3.37
Acenaphthylene	152	3.93	3.87	4.07
Acenaphthene	154	3.47	2.67	4.33
Fluorene	166	1.98	1.73	4.18
Phenanthrene	178	1.29	9.07×10^{-2}	4.46
Anthracene	178	7.3×10^{-2}	2.61×10^{-2}	4.45
Pyrene	202	1.35×10^{-1}	8.00×10^{-4}	5.32
Fluoranthene	202	2.60×10^{-1}	9.11×10^{-5}	5.33
Benz[*a*]anthracene	228	4.0×10^{-2}	6.67×10^{-7}	5.61
Chrysene	228	2.0×10^{-3}	8.40×10^{-5}	5.61
Benz[*a*]pyrene	252	4.0×10^{-3}	6.67×10^{-5}	6.04
Benzo[*k*]fluoranthene	252	1.2×10^{-3}	6.67×10^{-5}	6.57
Benzo[*b*]fluoranthene	252	5.5×10^{-4}	6.67×10^{-5}	6.84
Indeno[*123-cd*]pyrene	276	6.2×10^{-2}	1.33×10^{-8}	7.66
Benzo[*ghi*]perylene	276	2.6×10^{-4}	1.33×10^{-8}	7.23
Dibenz[*ah*]anthracene	278	5.0×10^{-4}	1.33×10^{-8}	5.97

varied from strongly fundamentally oriented to practically applicable. The observed biodegradation rates and also the final PAH concentrations that could be achieved varied strongly especially in experiments with soil. From the results it can be concluded that all PAH with three or less benzene rings, mentioned in Table V.2.1, are biodegradable (Kastner, 2000). As far as PAH with more than three rings are concerned, biodegradation is in general more difficult.

As already mentioned the rate of biodegradation of PAH in soil varies strongly. High molecular weight PAH is more recalcitrant to biodegradation than the low molecular PAH. Biodegradation is a real option for practical application, provided the conditions for biodegradation are optimal and mass transfer limitations, which often are the cause of the low bioavailability, are eliminated.

V.2.3. General concept of PAH polluted soil

Polluted soil has a very heterogeneous structure. The soil itself contains various types of soil substances in the form of particles of different size and composition, mostly aggregated to larger particles or domains. According to recent conceptual models presented in the literature, three major types of sorption domains in the soil can be distinguished, each with its specific affinity for PAH pollutants (Pignatello and Xing, 1996; Luthy et al., 1997; Cornelissen et al., 1998; Cuypers et al., 2000). These three major types are:

1. *Amorphous (natural) organic matter.* This type of organic material may also be referred to as expanded, rubbery or soft organic matter. It is likely to consist of polar structures of complex organic macromolecules integrated with a variety of low molecular weight organic compounds. The polar organic matter has relatively high oxygen content, low carbon content and low acidity. In sorption processes, the amorphous organic matter behaves like a homogeneous, gel-like partition phase, also called dissolution phase. The partitioning/dissolution phase is composed of thermally dynamic sites, which are constantly disappearing and reforming as a result of thermal motion of the humic backbone. Flexibility of the humic backbone is a result of weak cohesive forces and causes the sorption energies to average out as in a liquid phase. Sorption of hydrophobic organic contaminants to amorphous organic matter is characterized by isotherms that are linear over a wide solute concentration range. Moreover, sorption is reversible (non-hysteretic) and non-competitive. The sorption process is fast, with low activation energy and low heat of sorption. Transport is by diffusion, characterized with a high diffusivity.

2. *Condensed (natural) organic matter.* This type of organic material may also be referred to as glassy or hard organic matter. It is likely to consist of apolar structures of complex organic macromolecules that have a relatively high carbon/oxygen atomic ratio. These structures are formed by aliphatic and aromatic moieties in the organic macromolecule.

Sorption to condensed organic matter is a combination of partitioning/dissolution and specific sorption, which occurs at sorption sites provided by flexible (deformable) micropores. As a result of specific sorption, isotherms are non-linear, non-linearity being most expressed at relatively low aqueous solute concentrations. Non-linearity increases with increasing contact time. In general, sorption to the condensed organic matter domain

is more or less irreversible (hysteretic) and competitive, and characterized by slow sorption kinetics, high activation energy and a moderate to high heat of sorption. Transport is by diffusion, characterized by a low diffusivity.

A special kind of condensed organic matter is represented by highly aromatic coal or soot particles, which have an extremely high affinity for hydrophobic organic contaminants. Sorption sites in these particles are provided by rigid (non-flexible) pores.

3. *Micropores of mineral material.* This sorption domain is of particular importance in relatively dry material with little organic matter. In general, sorption in micropores is slow, hysteretic and competitive. In accordance, sorption isotherms are non-linear. In the pores, steric effects may occur due to strongly constricted regions. The sorption process is characterized by high activation energy and a moderate to high heat of sorption.

Besides absorption or adsorption of PAH in the above-mentioned soil domains, dependent on the anthropogenic activities which caused the pollution of the soil, PAH may also be present as (Rulkens and Bruning, 1995):

4. *particulate pollutants of pure PAH.*
5. *pure PAH pollutant in soil pores.*
6. *PAH dissolved in the water phase of water-filled pores in the soil.*
7. *PAH adsorbed to the pore walls of water-filled pores in the soil.*
8. *PAH present in a pure organic liquid phase, e.g. a mineral oil phase.*

It should also be noted that this overall picture of a polluted soil, schematically shown in Figure V.2.1, is beyond reality, which is much more complex. However, also from simplified models quantitative information regarding the environmental availability of pollutants, characteristic to the actual situation, can be derived. Because transport and release of pollutants, such as PAH, always take place via a surrounding water phase or wet phase, we will limit our further discussion to the situation that the soil particles are surrounded by a water phase. It is further assumed that the PAH concentration in this water phase is almost zero. In that case, the desorption and dissolving rates are maximal.

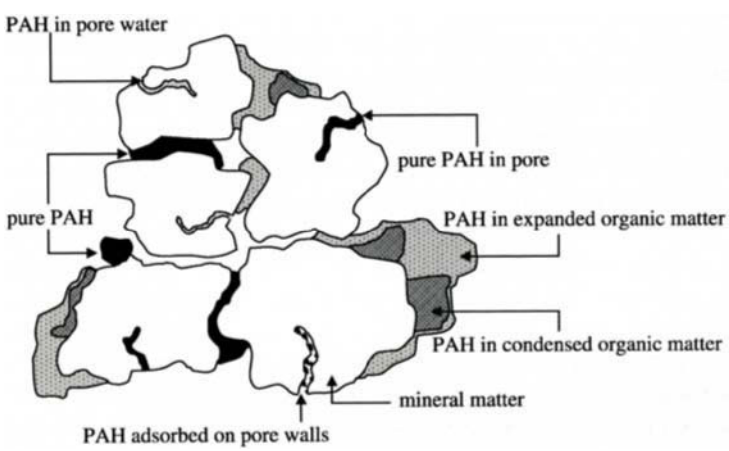


Figure V.2.1. Schematic representation of a PAH polluted soil.

The subsequent transport of the pollutants released from the soil micro-region via the water phase is not discussed here because there are already numerous models for this type of transport. We will consider now in detail the following four strongly simplified cases.

(a) Dissolving spherical particles consisting of pure PAH into a water phase in dependence of the solubility of PAH in pure water, C_s and the radius R_0 of the particle. It is assumed in the model that the mass transfer coefficient in the water phase outside the particle, k, can be calculated from $Sh = 2kR_0/D_l = 2$, where Sh is the Sherwood number and D_l the diffusivity of PAH in the water phase.

(b) Dissolving pure PAH out of pores (length L) of a soil matrix. Initially these pores are completely filled with PAH. Dissolving the PAH causes a retreat of the PAH–water interface in the pores. It is assumed that no resistance for mass transfer exists outside the particle.

(c) Diffusion of PAH out of a homogeneous spherical organic soil matrix consisting of either an amorphous expanded organic phase or a condensed organic phase. Transport is governed by the diffusivity D_s. It is assumed that no resistance for mass transfer exists outside the particle.

(d) Diffusion of PAH, adsorbed to the inner pore walls of a porous spherical soil particle in which the pores are homogeneously distributed. The transport process of pollutants in such a particle is mathematically analogous to the transport in a homogeneous particle. The diffusion process has to be now described by means of an effective pore diffusivity D_{por}, which is defined as $D_{por} = D_l/(1 + ma_s/\varepsilon)f_t$, where m is the ratio between the surface concentration of PAH at the pore walls and the equilibrium concentration of PAH in the water phase in the pore, a_s the specific surface area of the pore walls, ε the porosity of the particle and f_t the tortuosity of the pores.

The other cases which have been identified as being possible will not be discussed here because they can be described in a more or less similar way as will be given for the selected cases.

V.2.4. Mathematical models

V.2.4.1. The dissolving of a pure particulate pollutant

Figure V.2.2 shows the diagram of a single, solid spherical particle with initial radius R_0 and consisting of a pure pollutant that is more or less soluble in the surrounding liquid water phase. The mass flux N of this pollutant at the solid/liquid interface is expressed by the following equation

$$N = k(C_s - C_{bulk}) \tag{V.2.1}$$

where k is the mass transfer coefficient and C_s the concentration of the pollutant in the liquid phase at the interface (which is equal to the solubility of the pollutant). The mass transfer coefficient k depends on the flow conditions around the particle, which are characterised by the Reynolds number (Re)

$$Re = 2\rho v_p R/\eta \tag{V.2.2}$$

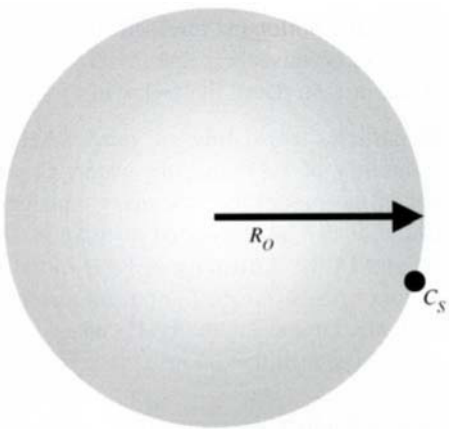


Figure V.2.2. Particle pollutant.

where ρ is the density of the liquid, v_p the relative velocity between the particle and liquid phase, R the radius of the particle and η the dynamic viscosity of the liquid. The value of k can be calculated from the following semi-empirical relationship:

$$Sh = 2 + 0.6Re^{1/2}Sc^{1/2} \tag{V.2.3}$$

In this equation, Sh represents the Sherwood number, which is defined by

$$Sh = 2kR/D_l \tag{V.2.4}$$

where D_l is the molecular diffusivity of the pollutant in the liquid phase. Sc represents the Schmidt number, which is given by

$$Sc = \eta/\rho D_l \tag{V.2.5}$$

If $Re << 1$, which is the case for small particles and for large particles if the relative velocity is small, then Equation (V.2.3) can be simplified by

$$Sh = 2kR/D_l = 2 \tag{V.2.6}$$

If it is assumed that $C_{bulk} = 0$, then it follows from Equations (V.2.1) and (V.2.6) that

$$N = D_l C_s/R \tag{V.2.7}$$

Radius R is not constant but will decrease over time t during the dissolving process. This process may be considered quasi-stationary and expressed as follows:

$$-\rho_s \frac{dR}{dt} = N \tag{V.2.8}$$

where ρ_s is the density of the solid particle. Substitution of Equation (V.2.7) in Equation (V.2.8) and integration of the resultant differential equation under the initial condition:

$$R = R_0 \qquad t = 0 \tag{V.2.9}$$

results in the following relationship between t and R:

$$R^2 = R_0^2 - 2D_l C_s t/\rho_s \tag{V.2.10}$$

The total time τ_{sol} required for complete dissolving of the particle can be calculated from Equation (V.2.10) and is given by

$$\tau_{sol} = \frac{\rho_s R_0^2}{2D_l C_s} \tag{V.2.11}$$

In practice, there are no great variations in the diffusivity D_l of a pollutant in an aqueous liquid phase. However, this does not apply to its particle radius R_0 and solubility C_s. The effect of R_0 and C_s on τ_{sol} is given in Figure V.2.3, assuming that $D_l = 10^{-5}$ cm^2/s and $\rho_s = 1$ g/cm^3. The figure shows that for particles with a radius of 1000 μm, τ_{sol} will decrease approximately from 10^6 to 10 days if the solubility increases from 0.005 to 500 mg/l. If the same range of solubility values is assumed for particles with $R_0 = 100$ μm, then the value of τ_{sol} will vary approximately between 10^{-1} and 10^4 days. For particles with $R_0 = 10$ μm, the value of τ_{sol} is always lower than 100 days.

It should be noted that Figure V.2.3 gives a simplified picture of the reality. In practice, C_s may be influenced by additives (e.g. surfactants) or natural complexing agents. This will result in lower dissolving times.

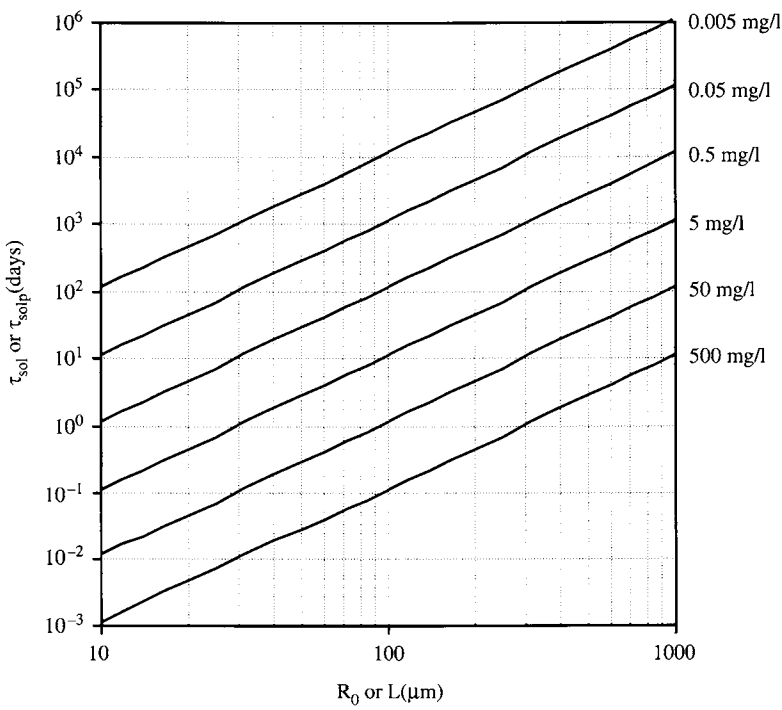


Figure V.2.3. Dissolving time of a particle pollutant with radius R_0 (τ_{sol}). Desorption time of a pollutant from a pore with length L (τ_{solp}). Parameter is the solubility (C_s).

V.2.4.2. The diffusion of pollutants from a soil particle

V.2.4.2.1. The diffusion of a solid pollutant out of a soil pore

Figure V.2.4 is a diagram of a pore in a spherical soil particle. Initially, the pore is filled with pure pollutant in the solid state. When it comes into contact with water, the pollutant will dissolve in the liquid phase. As a result, the pollutant–water interface will move inwards and the water will penetrate into the pore. At the interface, the concentration of the pollutant in the water is equal to its solubility. Because the pore diameter is relatively small, the transport of the pollutant through the liquid phase in the pore occurs by molecular diffusion. The velocity at which the liquid/pollutant interface moves inwards is relatively low, and this means that the diffusive transport through the liquid phase present in the pores may be considered quasi-stationary. Under this assumption, the concentration profile of the pollutant in the liquid phase in the pore may be considered linear. The mass flux N of the pollutant in the pore can then be expressed as follows:

$$N = D_l(C_s - C_{R_0})/l \tag{V.2.12}$$

where C_{R_0} is the concentration of the pollutant in the liquid phase at the particle surface. The mass flux of the pollutants at the particle surface is represented by

$$N = k(C_{R_0} - C_{bulk}) \tag{V.2.13}$$

If it is assumed that $C_{bulk} = 0$, then it follows from Equations (V.2.12) and (V.2.13) that

$$N = \frac{D_l k}{D_l + kl} C_s \tag{V.2.14}$$

The change in length l of the section of the pore that is filled with water is given by

$$\rho_s \frac{dl}{dt} = N \tag{V.2.15}$$

Substitution of Equation (V.2.14) in Equation (V.2.15) and integration of the differential equation, under the condition that initially $l = 0$ at $t = 0$, results in the

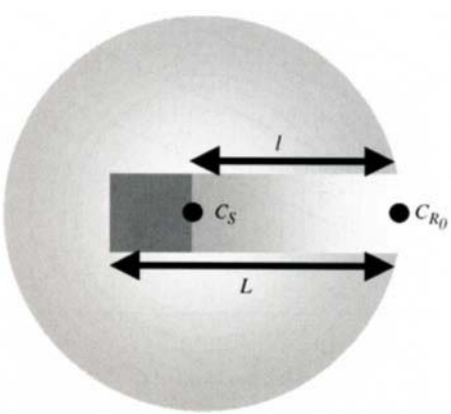


Figure V.2.4. Diffusion of a solid pollutant from a pore.

following relationship between l and t:

$$\frac{l^2}{2D_l} + \frac{l}{k} = \frac{C_s}{\rho_s} t \tag{V.2.16}$$

From Equation (V.2.16), it is possible to calculate the total time τ_{solp} required for the complete desorption of the pollutant from the pore

$$\tau_{solp} = \frac{\rho_s L^2}{2D_l C_s}\left(1 + \frac{D_l}{Lk}\right) \tag{V.2.17}$$

where L is the total length of the pore. The mass transfer coefficient k is given by Equation (V.2.3). From Equations (V.2.3) and (V.2.4), it is clear that for relatively large particles and pore lengths in the order of R_0 the value of k satisfies the relationship $k >> D_l/L$. Equation (V.2.17) can then be simplified to

$$\tau_{solp} = \frac{\rho_s L^2}{2D_l C_s} \tag{V.2.18}$$

For small particles ($Re << 1$) and/or pores with a length L considerably smaller than R_0, the value of τ_{solp} is higher than according to Equation (V.2.18). In Figure V.2.3, the value of τ_{solp} is given as a function of L with the solubility C_s as parameter. The equations for τ_{sol} and τ_{solp} are, in fact, similar. This means that the conclusions drawn for a spherical particle are also relevant to the transport of a solid pollutant from a pore.

V.2.4.2.2. The diffusion of pollutants from a homogeneous soil particle

Figure V.2.5 shows a homogeneously polluted, spherical soil particle. When it comes into contact with water phase, the pollutant will be transported by diffusion. The general diffusion equation for the transport of this pollutant in the spherical particle is given by

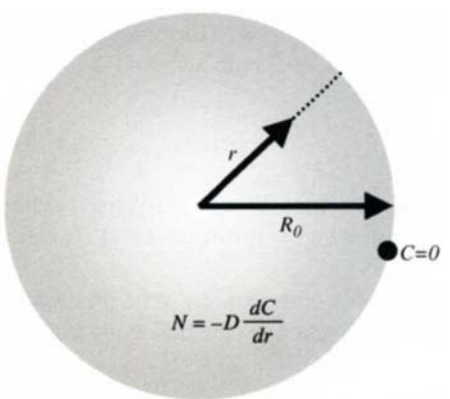


Figure V.2.5. Diffusion of pollutant from a homogeneous soil particle.

the following equation:

$$\frac{\partial C}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial C}{\partial r} \tag{V.2.19}$$

where D_s is the molecular diffusivity of the pollutant in the soil particle and r the coordinate in the direction of transport. Because generally D_s will be much smaller than D_l, it may be assumed that there is hardly any resistance to mass transfer on the outside of the particle. Assuming that the bulk concentration of the pollutant in the water phase is zero, the initial and boundary conditions of Equation (V.2.19) are

$$C = C_0 \qquad t = 0 \qquad 0 \leq r \leq R_0 \tag{V.2.20}$$

$$C = 0 \qquad t > 0 \qquad r = R_0 \tag{V.2.21}$$

$$-D_s\frac{\partial C}{\partial r} = 0 \qquad t > 0 \qquad r = 0 \tag{V.2.22}$$

From the solution of Equations (V.2.19)–(V.2.22), it follows that the ratio between the mean pollutant concentration in the sphere ($\bar{C}$) and the initial concentration (C_0) is a function of only the Fourier number (Fo), which is defined as

$$Fo = \frac{D_s t}{R_0^2} \tag{V.2.23}$$

If $Fo > 0.02$, then the relation between $\bar{C}$ and C_0 can be given by the following equation (Crank, 1964):

$$\frac{\bar{C}}{C_0} = \frac{6}{\pi^2}e^{-\pi^2 Fo} \tag{V.2.24}$$

In practice, the relative quantity of a pollutant that must be removed in order to satisfy clean-soil standards varies from less than 90% to more than 99%. From Equation (V.2.24), it can be derived that τ_{95}, the time necessary to remove 95% of the amount of pollutant originally present in the particle, corresponds with

$$Fo = \frac{D_s \tau_{95}}{R_0^2} = 0.25 \tag{V.2.25}$$

Figure V.2.7 shows how the value of τ_{95} is related to the particle radius R_0. The parameter is molecular diffusivity D_s. It is assumed that D_s can vary between 2.5×10^{-6} and 2.5×10^{-12} cm^2/s.

If it is assumed that 99% of the pollutant has to be removed in order to obtain a clean soil, then the time required τ_{99} is given by the following equation:

$$Fo = \frac{D_s \tau_{99}}{R_0^2} = 0.42 \tag{V.2.26}$$



Figure V.2.6. Diffusion of soluble and adsorbed pollutant Left: porous particle. Right: pore in porous particle.

V.2.4.3. The diffusion of soluble and adsorbed pollutants from the pores of a porous particle

Figure V.2.6 shows a porous, spherical soil particle where the pollutant is present in the water phase in the soil pores. The pollutant is partly adsorbed onto the pore walls and partly dissolved in the liquid phase in the pores. It is assumed that there is a proportional relationship between the equilibrium concentration of the pollutant in the pores (C) and the adsorbed concentration of the pollutant at the pore wall (C_{ad}):

$$C = C_{ad}/m \tag{V.2.27}$$

where m is a constant. It is also assumed that the concentration gradient of the pollutant in the radial direction in the pores is always negligible compared to the concentration gradient in the longitudinal direction. If a homogeneous distribution of pores in the porous particle is assumed, the diffusion equation for the transport of the pollutant in the porous sphere is given by

$$\varepsilon \frac{\partial C}{\partial t} + a_s \frac{\partial C_{ad}}{\partial t} = \varepsilon \frac{D_l}{r^2 f_t} \frac{\partial}{\partial r} r^2 \frac{\partial C}{\partial r} \tag{V.2.28}$$

where ε is the porosity of the soil particle, a_s the specific surface area of the pore walls and f_t the tortuosity of the pores. Substitution of Equation (V.2.27) in Equation (V.2.28) results in

$$\frac{\partial C}{\partial t} = \frac{D_{por}}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial C}{\partial r} \tag{V.2.29}$$

where

$$D_{por} = \frac{D_l}{(1 + m a_s/\varepsilon) f_t} \tag{V.2.30}$$

Assuming that the concentration of the pollutant in the surrounding liquid phase is zero and that there is no mass transfer limitation outside the particle, the initial and boundary

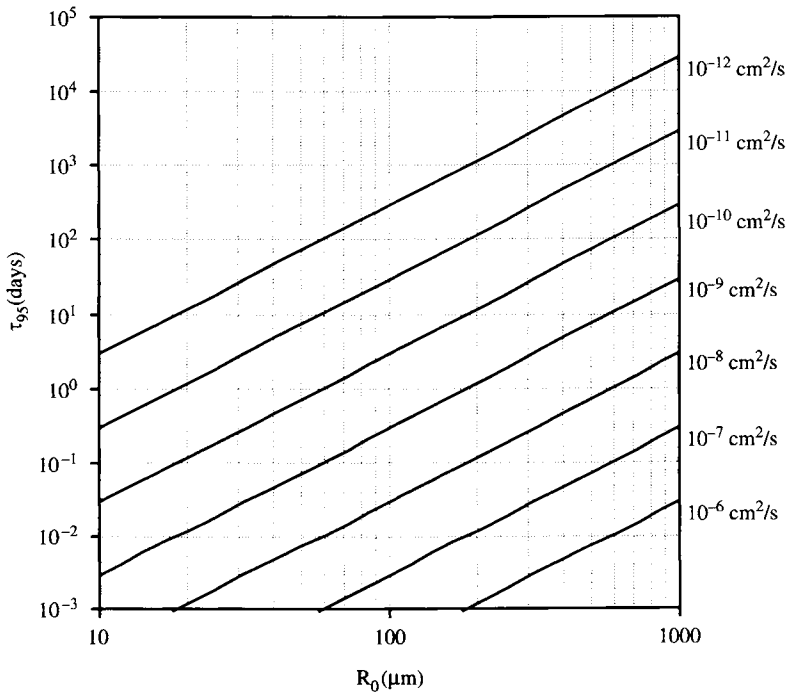


Figure V.2.7. Diffusion time necessary to remove 95% of the amount of pollutant (τ_{95}) as a function of particle radius R_0. Parameter is the diffusivity D_s or D_{por}.

conditions of Equation (V.1.2.29) can be given by

$$C = C_0 \qquad t = 0 \qquad 0 \leq r \leq R_0 \tag{V.2.31}$$

$$C = 0 \qquad t > 0 \qquad r = R_0 \tag{V.2.32}$$

$$-D_{por}\frac{\partial C}{\partial r} = 0 \qquad t > 0 \qquad r = 0 \tag{V.2.33}$$

The solution of Equation (V.2.29) is identical to that of Equation (V.2.19). The time τ_{95} necessary to remove 95% of the amount of pollutant originally present in the particle is given in Figure V.2.7 as a function of R_0 and with parameter D_{por}. It will be clear from Equation (V.2.30) that in the case of strong adsorption (corresponding with a high value of m) and a high specific adsorption area a_s, the value of D_{por} will be considerably lower than that of D_l. Consequently, in practice, long residence times are necessary in order to attain the almost complete desorption of a pollutant from the soil particle.

V.2.5. Discussion

In the foregoing paragraph, mechanistic models for the mass transport rate of PAH pollutants from specific separate micro-regions have been derived. The mass transfer rate

strongly depends on the physical state of the PAH pollutants, the characteristic dimensions of the micro-domains, the diffusivity in these micro-domains, the adsorption coefficient and the water solubility of these pollutants. The mechanistic models have been derived for well defined micro-domains. The reality is of course more complicated than these model micro-domains suggest. In reality, a large number of different PAH hydrocarbons will be present simultaneously with strong varying relative concentrations. The release of these PAH to the water phase or wet phase is much more complex than the mechanistic models suggest. It can be expected that initially especially the low molecular PAH will release from the matrix and that later on this occurs for the high molecular PAH. Due to differences not only in solubility, but also in diffusivity of the different PAH, the relative concentration of the different PAH in the water phase can strongly deviate from the relative concentrations of PAH in the soil matrix. Not only the relative concentrations, but also the absolute concentrations, will change with time due to microbial and chemical conversion or further transport of PAH in the water phase. The phenomenon ageing is also strongly influencing this process.

The micro-domains have seldom the well-defined simple structure as assumed in the mechanistic models. A micro-domain can be encapsulated by other micro-domains, so that the transport pathways for the pollutants are longer than the characteristic size of one micro-domain. Micropores inside several micro-domains can be connected with each other. Besides it has to be noticed that the microporous structure (and this also holds for the macroporous structure) of the polluted soil is not a fixed property but changes continuously with time. This not only holds for the size of the various micro-domains but also for the physical properties of these micro-domains, the size and length of the micro- and mesopores in these domains and the degree of aggregation and encapsulation of these micro-domains.

It is evident that not only the concentration of PAH but also the distribution of PAH over the various micro-domains will change with time. This change concerns three ways. It can be expected that the amount of PAH present as pure particulate PAH and also the size of these particles will decrease in time. Besides PAH will diffuse more deeply into condensed or expanded soil organic matter. Part of the PAH will also be incorporated into the natural organic matter of the soil. All these processes cause a decrease in the bioavailability of the PAH pollutants in soils in course of time. The phenomenon of decreased availability in course of time is also clearly observed in practise and is indicated as ageing or weathering. The final conclusion from this picture is that the (bio)availability should be handled as a dynamic process.

The practical value of the mechanistic models, as derived in the previous paragraphs, is that these models give at least a semi-quantitative indication of the bioavailability of the pollutant at a certain moment. A prerequisite to be able to use these models for practical purposes is that some relevant data regarding the micro-domains and the PAH in these micro-domains are available. These data are the size of the micro-domains, the diffusivity of the PAH in these domains, the distribution of PAH over these domains and the solubility of PAH in the water phase surrounding these domains. To obtain sufficiently accurate data it will be clear that advanced analytical techniques and tools are necessary. Experience in this respect is however still very limited. A long way still has to be gone. The assessment of ecotoxicological risks and also of bioremediation methods require information about possible changes of the porous structure in course of time.

In case of risk assessment, periods of several years up to more than 100 years have to be considered. However, as is pointed out in the foregoing paragraph, it can be expected that the bioavailability of PAH pollutants, assessed for the micro-domains, will decrease in course of time. This means that the risk assessments can safely be based on the actual bioavailability. In case of bioremediation, the time scale varies from one year or less to 10 years or more. Strong intrinsic changes of the structure of the micro-domains cannot be expected for that period. However, a change in the structure of the micro-domains may be possible due to the application of external processes which are applied to the soil during the bioremediation process such as heating, soil flushing, ultrasonic treatment and so on.

Due to the lack on advanced analytical techniques and tools or practical experience with existing tools, the mechanistic models have at present a limited significance. However, as already mentioned in the introduction, there are some tools to quantify the overall (bio)availability. The first technique is to carry out biodegradation experiments on lab scale. A drawback of this method is that a long experimental period is required to obtain reliable data. Other methods mentioned are solid phase extraction with water or an aqueous solution of cyclodextrin, extraction with an organic solvent or a mixture of water and an organic solvent and extraction with supercritical CO_2. The first method is also quite laborious and requires long-term experiments while the other methods are still in the laboratory stage. A very promising method is the use of a rapid oxidation method, using persulfate. With this oxidation method the PAH bound to expanded organic matter and probably also the PAH present as pure PAH can be easily determined. All methods have the drawback that they can insufficiently distinguish between the various physical states, PAH are present in the micro-domains of the soil. The practical applicability of these methods for risk assessment studies is less than those for assessment of the bioremediation potential and the steering of the bioremediation process.

V.2.6. Concluding remark

The main conclusion from the foregoing is that modeling and quantifying the bioavailability of PAH (and other organic pollutants) is very complex, mainly due to the heterogeneous structure of the soil and the lack of experience with advanced analytical techniques and tools. Nevertheless the mechanistic models derived here provide a basis for a first estimation of bioavailability of PAH pollutants in soil. Further developments are necessary to get a sufficiently accurate picture of bioavailability. Also, knowledge regarding changes in bioavailability in course of time is necessary. Analytical tools to measure the (macroscopic) overall bioavailability of PAH may support further developments of these mechanistic models to practical application.

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V.3
Computer modeling of organic pollutant transport to groundwater – exemplified by SNAPS

Herwart Behrendt, Rainer Brüggemann and Gunnar Nützmann

V.3.1. Introduction

Considerable efforts have been d one to evaluate pesticides with respect to their adverse effects on the environment. The spectrum of efforts spans a wide range of approaches. The simplest one begins with a comparison by substance data only, for example the GUS-index (Halfon et al., 1996). Even a simple consideration of different substance data can be extended to rather sophisticated methods (e.g. Lerche et al., 2002). The next step might be characterized by the PEC/PNEC-concept, e.g. presented by Beinat and van den Berg (1996), which is of high interest currently due to the "White Paper" of the EU (see e.g. discussion by Friege, 2002). Sophisticated approaches aim to combine exposure and effect models (Behrendt and Brüggemann, 1993); whereas effect models are still hardly ready to work routinely, exposure models are more or less ready to forecast the distribution behavior of organic pollutants in the environment. Here we focus on distribution processes within the unsaturated soil zone, i.e. on processes determining the concentrations of pollutants affecting the groundwater.

V.3.2. Exposure soil models

V.3.2.1. Preliminaries

Deterministic exposure models quantify the chemical mass flows and concentrations in environmental media such as soil, water or plants by more or less physically based mathematical equations (Hern and Melancon, 1986; Matthies and Klein, 1994; Van Leeuwen and Hermens, 1995; Trapp and Matthies, 1998). These models may be further classified into evaluative models and simulation models, although there is no sharp borderline between these two groups of models. In the following we will focus on soil exposure models as an example.

The starting point to develop models is the differential mass balance of a chemical, which can simply be formulated as:

Changes of the total concentration in a small soil volume element =

+ transport into the soil volume by a carrier (for example flow of water)
− dispersive/diffusive loss
− degradation processes
− volatilization, run-off, and uptake into plants (only at or near the soil surface)
− run-off (only at the soil surface)
+ sorption
− desorption

This (over)simplified scheme poses several questions that will be answered step by step. (Note that some chemicals may form their own phases, for example as micro-droplets, see Fauser and Thomsen (2002). Such kind of advanced studies is not considered here). Before going into details some classification principles should be discussed.

V.3.2.2. Classification principles

Mathematical models can be classified by the time and space scale they are appropriate, and also after the degree of "black box-character" they have. Furthermore, they can be classified according to more mathematical point of views, e.g. whether or not the models bear some stochastic fluctuations explicitly. Further classifications are possible referring to the numerical techniques to solve the equations. However, the last two aspects will be omitted within this text (Richter, 1987; Richter and Söndgerath, 1990; Richter et al., 1996).

V.3.2.3. Classification by the degree of sophistication

V.3.2.3.1. Evaluative models

The evaluative models tend to use a limited set of key transport processes. They often use empirical (regression) equations and/or restrictive boundary conditions to achieve a simplified model description. There are two reasons that may lead to a simplified model description. Firstly, the limited knowledge of the evolved processes and the limited data availability for non-key processes. Secondly, the purpose of the model, i.e. if the model is used as a screening model or a management model, it is not necessary that the model describes all evolved processes in detail. Often evaluative models are the basis for a comparative evaluation or a ranking of pesticides, as is described by Jury et al. (1983, 1984a–c) and Behrendt et al. (1997). Later, as one of the examples of evaluative models, the Jury model (Jury et al., 1983) will be discussed more deeply. Other examples of

evaluative soil transport models are the EXSOL model (EXposure in SOiL) (Matthies and Behrendt, 1991; Brüggemann et al., 1996; Brüggemann and Drescher-Kaden, 2003) and a derived version on a rather modern platform: SOIL (Trapp and Matthies, 1998).

V.3.2.3.2. Simulation models

Simulation models try to avoid the shortcomings of the evaluative models and tend to have a sounder physically based concept and less restrictive boundary/initial conditions. Hence, the simulation models are applicable to a wider range of scenarios. Although, in practice one may have difficulties to supply the huge amount of input data required for the simulation runs. Examples of soil exposure simulation models for organic compounds are the PRZM model (Dean et al., 1989), the LEACHP model (Wagenet and Hutson, 1997), the Boesten model (Boesten and van der Linden, 1991) and the SNAPS (Simulation model Network Atmosphere–Plant–Soil) model (Behrendt and Brüggemann, 1993; Behrendt, 1999). All four models have in common a deterministic description of the coupled chemical temperature and water transport processes in a 1D soil column. The simulation models are often used to answer a "what-if-scenario" in a high-dimensional parameter space (Boesten, 1991; Behrendt et al., 1995).

V.3.2.4. Classification by the characteristic scales

Evaluative and simulation models have to refer to the scale, for which they can be used. Thus it makes no sense to use a local model and to extend the results up to a regional scale. The reason is that the processes and the parameters needed to describe the processes depend on the spatial resolution. Typically for unsaturated soil zones are pores. If exclusively the transport within pores is to be described, processes and parameters differ from those which characterize the transport within the bulk system consisting of soil matrix and pores. (Dagan, 1989). Transport processes in pores may be one extreme; another extreme is the consideration of regional transport phenomena in catchment areas of rivers that can be exemplified in the MONERIS model (Behrendt et al., 2000). The consideration of scales is extremely important, when the water flow itself is to be modeled. Spatial and temporal averaging has to be in agreement with the spatial and temporal dimensions of the model. Newer approaches to derive model parameters use the fractal theory to transform distribution functions between different scales (Braun et al., 1996).

Even the use of empirical parameters, derived from soil properties, depends on the scale. Nevertheless here, local models on the scale, where the Darcy law of flow is valid, are introduced and discussed.

V.3.3. Examples of model architecture

V.3.3.1. Jury model

The Jury "screening" model (Jury et al., 1983) calculates the transport of a chemical (e.g. pesticide) in a 1D (vertical) semi-infinite homogeneous soil column. Transport processes

such as convection in soil water and diffusion in soil water and in soil air are included in the model. Existing applications of the Jury model are for example, the comparative evaluation of the transport of pesticides in the unsaturated upper soil zone (Jury et al., 1983; 1984a–c; Jury et al., 1987) and the evaluation of the volatilization sub-model in a field study (Jury et al., 1984a).

V.3.3.1.1. Equilibrium partitioning in soil

The chemicals concentration in soil is assumed to be low, e.g. the concentration in soil water is small compared to the water solubility of the chemical. Therefore, the chemicals (total) concentration in a soil volume C_T may be expressed by the quantities adsorbed to the soil matrix C_S, dissolved in soil water C_L and as a gaseous phase in soil air C_G:

$$C_T = \rho_b C_S + \theta C_L + a C_G \tag{V.3.1}$$

where ρ_b is the soil bulk density (g/m^3), θ is the soil water content (m^{3}water/m^{3}soil) and a is the soil air content (m^{3}air/m^{3}soil). Additionally, an equilibrium partitioning of the chemical in soil water, soil air and adsorbed on the soil matrix is assumed. Thus, the concentration in soil water and adsorbed on the soil matrix may be related by the linear equilibrium partition coefficient K_d (Thibodeaux, 1996):

$$C_S = K_d C_L \tag{V.3.2}$$

Analogously, the Henry's law coefficient K_{aw} may be used to relate the concentration in soil air and in soil water (Thibodeaux, 1996):

$$C_G = K_{aw} C_L \tag{V.3.3}$$

As the experimental determination of K_{aw} is difficult, it may be helpful to know how K_{aw} may be estimated from other substance properties. This can be found in an overview by Altschuh et al. (1999).

Using Equations (V.3.2) and (V.3.3), the concentration of the chemical in soil water, soil air, sorbed on the soil matrix and the total concentration in soil may be related by linear "capacity coefficients":

$$C_T = R_L C_L = R_S C_S = R_G C_G \tag{V.3.4}$$

where

$$\begin{aligned} R_L &= \rho_b K_d + \theta + a K_{aw} \\ R_G &= R_L / K_{aw} \\ R_S &= R_G / K_d \end{aligned} \tag{V.3.5}$$

V.3.3.1.2. Darcy water flow in soil

A time and depth constant vertical downward (or upward in the case of evaporation) water flux J_W is assumed, which obeys Darcy's law. Darcy's law states (Darcy, 1856) that the water flux J_W through a porous soil column is proportional to the gradient of the total water

potential H_T in soil, where K is the soil specific hydraulic conductivity (m/d):

$$J_W = -K\frac{\partial H_T}{\partial z} \tag{V.3.6}$$

Darcy's law applies to cases in which the Reynolds number of the fluid flow in soil is less than one (Marshall et al., 1996). Under these conditions the water flow is laminar and accelerations are unimportant. J_W is a macroscopic flow parameter, defined as the volume of water flowing through a cross-sectional area per time unit. Equation (V.3.6) was derived for saturated soil water conditions, but it may also be used for unsaturated conditions (Jury et al., 1991). The hydraulic conductivity K strongly depends on the pore size and the tortuosity and in the case of unsaturated conditions, also on the soil water content or the soil water matrix potential.

V.3.3.1.3. Convective transport in soil

The percolating water flux in soil may carry along dissolved chemicals (solutes) by a passive transport process "convection" (also called advection). One may observe a sharp boundary or interface zone of the concentration in the resident soil water and the concentration in the displacing soil water (Jury et al., 1991). In the latter case the transport process is also called a "piston flow" process. In mathematical terms we may write the convective mass flux in the vertical direction J_{LC} as:

$$J_{LC} = J_W C_L \tag{V.3.7}$$

V.3.3.1.4. Diffusion/dispersive transport in soil water and soil air

The "diffusive" flux of solutes in soil water results from the greater tendency to move from points of high concentrations to points of low concentration. Using Fick's first law, the diffusive flux J_{LD} is proportional to the concentration gradient (Equation (V.3.8)), where D_L is the diffusion coefficient of the solute in soil water (Jury et al., 1991):

$$J_{LD} = -D_L\frac{\partial C_L}{\partial z} \tag{V.3.8}$$

The diffusion coefficient of chemicals depends on the geometry of the water-filled pores of the soil. D_L is less than the molecular diffusion coefficient in free water $D_{L,bin}$. Using the empirical model of Millington (Millington and Quirk, 1961), we may calculate D_L from $D_{L,bin}$ the soil water content and the porosity of the soil:

$$D_L = \xi(\theta)D_{L,bin} = \frac{\theta^{3/2}}{\varepsilon^2}D_{L,bin} \tag{V.3.9}$$

In analogy of the diffusion in soil water, we write for the diffusive flux in soil air J_G (Jury et al., 1991):

$$J_G = -D_G\frac{\partial C_G}{\partial z} = -\xi(a)D_{G,bin}\frac{\partial C_G}{\partial z} \tag{V.3.10}$$

where $D_{G,bin}$ is the molecular diffusion coefficient in free air. The molecular coefficients $D_{L,bin}$ and $D_{G,bin}$ depend on the temperature, molar volume, and viscosity of the fluid

media. There exist empirical relationships that enable the calculation of the molecular diffusion coefficients from the molar mass, and from parameters of the structure of the molecule (for property estimation methods, see Baum, 1998). The molecular diffusion coefficients of organic pesticides are very similar, $D_{G,bin}$ is in the order of 0.1 m^2/d and $D_{L,bin}$ is in the order of 10^{-5} m^2/d (Jury et al., 1983). Thus, the diffusive transport in soil air is usually more effective than that in soil water. Convective transport in soil air is neglected here, as it is especially important for high-temperature gradients in soil and for chemicals with high vapor pressure (Cohen et al., 1988).

In soil column leaching experiments one often recognizes spreading of the transition zone between the displacing water and the resident water. This phenomenon is known as "hydrodynamic dispersion", which can be attributed to three mechanisms: the velocity distribution within a pore, the pore size distribution of the pores, and the fluctuating water flow path within the mean direction (Thibodeaux and Scott, 1985). The approximation of the convective mass flux on pore scale by a volume-averaged macroscopic flux in the 1D model results in the dispersive flux J_{LH} (Bear, 1972), where D_{LH} is the hydrodynamic dispersion coefficient.

$$J_{LH} = -D_{LH}\frac{\partial C_L}{\partial z} \tag{V.3.11}$$

In empirical models D_{LH} is often described as linear function of the pore water velocity v (see Equation (V.3.12)) (Klotz, 1980), where λ_{disp} is the dispersivity [L]:

$$D_{LH} = \lambda_{disp}|v| = \lambda_{disp}\left|\frac{J_W}{\theta}\right| \tag{V.3.12}$$

In soil column leaching experiments, the dispersivity is in the order of 1 cm (Beese, 1982), while in field studies D_{LH} is in the range of 10–100 cm and even higher values are found (Behrendt et al., 1994). In general, the diffusive flux J_{LD} is significantly lower than the dispersive flux J_{LH}, which is true except for low pore water velocities.

Within the Jury model, the dispersive contributions to the mass flux in the soil water phase is neglected, so that the total mass flux J_C is:

$$J_C = J_{LC} + J_{LD} + J_G = J_W C_L - D_L\frac{\partial C_L}{\partial z} - D_G\frac{\partial C_G}{\partial z} \tag{V.3.13}$$

V.3.3.1.5. Derivation of the transport equation

The law of conservation of mass states that any changes in the amount of solute in a given volume of soil must be due to convergence toward or divergence away from the soil volume (Thibodeaux and Scott, 1985). In mathematical terms this may be written as the solute conservation equation (V.3.14), where S_C is an additional source/sink term:

$$\frac{\partial C_T(z,t)}{\partial t} = -\frac{\partial J_C(z,t)}{\partial z} + S_C(z,t) \tag{V.3.14}$$

Using Equation (V.3.13) we arrive at:

$$\frac{\partial C_T(z,t)}{\partial t} = -\frac{\partial(J_W C_L(z,t))}{\partial z} + \frac{\partial}{\partial z}\left(D_L \frac{\partial C_L(z,t)}{\partial z}\right) + \frac{\partial}{\partial z}\left(D_G \frac{\partial C_G(z,t)}{\partial z}\right) + S_C(z,t) \tag{V.3.15}$$

Furthermore, we may use Equations (V.3.4) and (V.3.5) to derive the "convection–dispersion" equation:

$$\frac{\partial C_T(z,t)}{\partial t} = -\frac{\partial(V_E C_T(z,t))}{\partial z} + \frac{\partial}{\partial z}\left(D_E \frac{\partial C_T(z,t)}{\partial z}\right) + S_C(z,t) \tag{V.3.16}$$

$$V_E = \frac{J_W}{R_L} \tag{V.3.17}$$

$$D_E = (K_{aw} D_G + D_L)/R_L \tag{V.3.18}$$

Using the assumption that J_W, D_G, D_L and R_L do not depend on the soil depth, we arrive at:

$$\frac{\partial C_T(z,t)}{\partial t} = -V_E \frac{\partial C_T(z,t)}{\partial z} + D_E \frac{\partial^2 C_T(z,t)}{\partial z^2} + S_C(z,t) \tag{V.3.19}$$

V.3.3.1.6. Degradation in soil

The degradation rate of organic chemicals in soil depends on soil-specific parameters as pH, organic C content, clay content, temperature, soil water content, and nutrient supply, and on biotic parameters as amount and type of microorganisms (see for example in Valentine and Schnoor (1986) and Domsch (1992)). Here it is assumed, that we may specify a bulk first-order degradation rate μ ($1/T$), which is not dependent on the concentration of the chemical:

$$S_C(z,t) = -\mu C_T(z,t) \tag{V.3.20}$$

V.3.3.1.7. Boundary conditions

The upper boundary condition is determined by the transport of volatile chemicals from soil surface to free atmosphere, which often uses the concept of a mass transfer coefficient (Thibodeaux and Scott, 1985). The mass transfer coefficient k_A is defined by Equation (V.3.21), where J_A is the mass flux of the chemical perpendicular to the soil surface, C_A is the concentration in the air layer adjacent to the soil surface, and C_{A0} is the concentration in air far removed from the soil surface:

$$J_A = k_A(C_A - C_{A0}) \tag{V.3.21}$$

As it is discussed in detail by Thibodeaux and Scott (1985), the transfer coefficient k_A depends on the flow as related by the Reynolds number, the transport properties as related by the Schmitt number and on the geometry of the system as related to some length. Jury et al. (1983) made the assumption that J_A may be modeled by a diffusive transport through a stagnant air layer of depth d. Thus, a diffusive type boundary condition may be specified as:

$$J_C(0,t) = \left(V_E C_T - D_E \frac{\partial C_T}{\partial z}\right)_{t,z=0} = J_A = \frac{-D_G^A(C_G(0,t) - C_{A0})}{d} \tag{V.3.22}$$

In Equation (V.3.22) D_G^A is the diffusion coefficient in free air, and C_{A0} is the concentration in free atmosphere, which is assumed as zero. Jury et al. (1983, 1984a) estimated d from measured soil water evaporation rates and they recommend $d = 0.5$ cm.

The lower boundary condition uses the assumption that the concentration gradient is zero at the lower boundary of the semi-infinite soil column:

$$J_C(\infty, t) = V_E C_T(\infty, t) \tag{V.3.23}$$

As initial conditions, a constant concentration from soil depth $z = 0$ to $z = L$ is assumed. Using the boundary and initial condition an analytical solution may be derived for the transport equation (V.3.19) (Jury et al., 1983).

V.3.3.2. EXSOL model

The EXSOL model (EXposure in SOiL) (Matthies and Behrendt, 1991; Brüggemann et al., 1996; Brüggemann and Drescher-Kaden, 2003) calculates the transport of organic chemicals in soil by solving a convection–dispersion equation. The transport equation of the EXSOL model includes the dispersive flux J_{LH} (see Equation (V.3.11)) and additionally the model enables the definition of multiple soil horizons. Thus the transport equation of the EXSOL model is specific for each horizon of the soil profile, and the parameters D_E^i, V_E^i and μ^i depend on the soil horizon number i of the soil profile:

$$\frac{\partial C_T(z,t)}{\partial t} = -\frac{\partial (V_E^i C_T(z,t))}{\partial z} + \frac{\partial}{\partial z}\left(D_E^i \frac{\partial C_T(z,t)}{\partial z}\right) + \mu^i C_T(z,t) \tag{V.3.24}$$

The effective dispersion–diffusion coefficient D_E^i and the effective convection coefficient V_E^i are defined as:

$$D_E^i = (K_{aw} D_G^i + D_{LH}^i + D_L^i)/R_L^i \tag{V.3.25}$$

$$V_E^i = \frac{J_W}{R_L^i} \tag{V.3.26}$$

Furthermore, the upper boundary conditions may be specified as time-dependent. Time series of the precipitation rate P, the evapotranspiration rate E, and the surface run off R may be used to calculate the Darcy water flux rate J_W for each day of the simulation period:

$$J_W = P - E - R \tag{V.3.27}$$

A convective transport out of the soil column is assumed at the bottom of the soil column. The flux type boundary condition is defined as:

$$t \geq 0 \qquad z = Z_L \qquad J_C = \max(J_W C_L, 0) \tag{V.3.28}$$

Concentration gradients are assumed to be negligible at the depth Z_L of the soil column.

The transport equation (V.3.24) is solved by a numerical procedure. Applications of the EXSOL model include the analysis of soil column and field leaching studies (Behrendt et al., 1990; Schernewski et al., 1990), and assessment studies of groundwater contamination (Matthies and Behrendt, 1991; Altschuh et al., 1996).

V.3.3.3. SNAPS model

The SNAPS soil model "Simulation model Network Atmosphere–Plant–Soil" (Behrendt and Brüggemann, 1993; Behrendt, 1999) calculates the transport of organic chemicals in soil by solving a convection–dispersion equation, similar to the EXSOL model. Additionally, this model includes an explicit calculation of the water and heat transport in soil by solving the corresponding transport equations. The boundary condition at the soil surface, i.e. evaporation, transpiration and infiltration rates are determined from time series of climatic and plant specific parameters. The uptake of dissolved organic chemicals in soil water into plants is also included in the model. Furthermore, there exists an interface of the SNAPS soil model to the PLANTX model, which describes the transport and the partitioning of organic chemicals within plants (Trapp and Matthies, 1997). The SNAPS model was used for the interpretation of pesticide leaching studies (Behrendt et al., 1994), and in assessment studies of uptake of solutes in plant shoots (Behrendt and Brüggemann, 1993; Behrendt et al., 1995).

V.3.3.3.1. Water flow in soil

The water flow in soil is based on Darcy's law (Equation (V.3.6)), which we may write for unsaturated soil water conditions as:

$$J_W = -K(\psi_m)\frac{\partial H_T}{\partial z} = -K(\psi_m)\frac{\partial(\psi_m + z)}{\partial z} \tag{V.3.29}$$

In Equation (V.3.29) the total soil water potential H_T is defined as the sum of the soil matrix potential ψ_m and the gravitational potential. Contribution to the total soil water potential, as for example the osmotic potential, is neglected in Equation (V.3.29). Furthermore, the unsaturated hydraulic conductivity $K(\psi_m)$ is assumed to be a function of the soil matrix potential only. In the case of non-stationary water flow the transport equation may be derived by the combined use of the conservation equation for water in soil and of the Darcy equation (V.3.29):

$$\frac{\partial\theta(z,t)}{\partial t} = \frac{\partial}{\partial z}\left(-K(\psi_m)\frac{\partial(\psi_m + z)}{\partial z}\right) - S_w(z,t) \tag{V.3.30}$$

The sink term $S_w(z,t)$ accounts for the root water uptake by plants. Equation (V.3.30) may not be solved in the form it is, because it contains two unknowns $\psi_m(z,t)$ and $\theta(z,t)$. This difficulty may be overcome by using the water content matrix potential function $\theta(\psi_m)$:

$$c(\psi_m)\frac{\partial\psi_m}{\partial t} = \frac{\partial}{\partial z}\left(-K(\psi_m)\frac{\partial(\psi_m + z)}{\partial z}\right) - S_w(z,t) \tag{V.3.31}$$

$$c(\psi_m) := \frac{\partial\theta}{\partial\psi_m}$$

Equation (V.3.31) is the matrix potential form of the one-dimensional Richards equation, where $c(\psi_m)$ is the water capacity function. In Equation (V.3.31) it is assumed that there exists a continuous and differentiable function $\theta(\psi_m)$, which implies that hysteresis, as it is

observed in measured water content matrix potential relationships, is negligible (Jury et al., 1991). The SNAPS model uses the parameter functions of the Van Genuchten–Mualem model (Mualem, 1976; Van Genuchten, 1980) to describe the soil water content matrix potential function $\theta(\psi_m)$ and the hydraulic conductivity matrix potential function $K(\psi_m)$. The Van Genuchten–Mualem model has been found to be very useful in describing measured soil hydraulic properties for many soils (Van Genuchten and Nielsen, 1985; Woesten and Van Genuchten, 1988).

Initial values and boundary conditions have to be specified to derive a solution of the transport equation (V.3.31). As initial conditions, measured or estimated values of the soil matrix potential may be used. In the case of unsaturated soil water profile the equation (V.3.31) is a parabolic partial differential equation, this type of equations may be solved numerically by implicit finite differential methods (Knabner and Angermann, 2000).

V.3.3.3.2. Boundary conditions of the water flow in soil

At the lower boundary of the soil column it is assumed that the gradient of the matrix potential is zero, i.e. there is a free drainage of the soil water driven by the gravitational potential only. Using Equation (V.3.29) and the above assumption we arrive at:

$$|J_{Wn}| = K(\psi_m) \tag{V.3.32}$$

In mathematical terms we have a third-order type boundary condition, where $|J_{Wn}|$ is the normal flux at the lower boundary.

The boundary conditions for the atmosphere are determined by time series of climatic and crop-specific parameters on a daily basis. For each day of the simulation period the potential infiltration rate is calculated from the precipitation rate, the interception storage of the crop, and the potential evapotranspiration rate. The (positive) difference between potential and actual amount of water infiltrating the soil is accounted for the surface run-off. A reduced potential evaporation E_R is calculated according to the procedures of Ritchie (1972) and Feddes et al. (1978). The potential water flux at the soil surface q_{pot} is determined from a mass balance equation of the reduced potential evaporation E_R, the precipitation P and the crop interception storage E_i:

$$q_{pot} = E_R - (P - E_i) \tag{V.3.33}$$

By a set of inequalities the boundary conditions at the soil surface of the flux q_s and of the matrix potential ψ_s are defined: The Darcy flux q_s is limited by q_{pot} in the case of infiltration as well as in the case of evaporation.

In case of infiltration:

$$\psi_s \leq \psi_{pot} = 0, \qquad |q_s| \leq |q_{pot}|$$
$$\text{and} \quad (\psi_s - \psi_{pot})(q_s - q_{pot}) = 0 \tag{V.3.34}$$

If $|q_s|$ is less than $|q_{pot}|$, the difference between $|q_{pot}|$ and $|q_s|$ is accounted for the surface run-off.

In case of evaporation:

$$\psi_s \geq \psi_{pot} = \psi_{ad}, \qquad |q_s| \leq |q_{pot}|$$

$$\text{and} \quad (\psi_s - \psi_{pot})(q_s - q_{pot}) = 0 \tag{V.3.35}$$

where ψ_{ad} is the soil matrix potential for dry air. If the soil matrix potential is in equilibrium with the atmosphere, we may calculate ψ_{ad} from the relative humidity of the atmosphere (Campbell, 1985).

$$\psi_{ad} = \frac{RT}{Mg} \ln(rh_{ad}) \tag{V.3.36}$$

where R is the universal gas constant, T is the absolute temperature, M is the molar weight of water, g is the gravitational acceleration, and rh_{ad} is the relative humidity for dry air.

V.3.3.3.3. Water uptake by plants

The potential transpiration of the plants is determined by an energy balance equation according to Monteith and Ritjema (Feddes et al., 1978). Furthermore, the root length distribution is used to distribute the (potential) root water uptake along the soil profile. Root length distributions may be estimated from empirical relationships to soil texture and crop development stages (Wessolek and Gaeth, 1989). In the case of water stress of the plants, the potential root water uptake rate is reduced by an empirical function of the soil matrix potential $\alpha(\psi_m)$ (Feddes et al., 1978). Using the above assumptions, we may specify the sink term for root water uptake as:

$$S_W(z,t) = \alpha(\psi_m(z,t))S_p(z,t) \tag{V.3.37}$$

$$S_p(z,t) = T_p(t)\frac{w(z,t)}{\int_0^{zmax} w(z,t)dz} \tag{V.3.38}$$

where $S_P(z,t)$ is the potential root water uptake rate, and $w(z,t)$ is the root length distribution.

V.3.3.3.4. Heat transport in soil

Physical, chemical, and biological processes are influenced by soil temperature. Biological processes influencing the fats of organic chemicals in soil are strongly affected by soil temperature (Domsch, 1992). The soil temperature may significantly determine the (biotic) degradation rate in soil. Furthermore, it may also affect the transport of water and solutes in soil (Feddes et al., 1988), which is neglected here.

The following assumptions are used for the heat transport equations:

- the water transport affects the heat transport,
- the heat transport does not affect the water or solute transport in soil,
- there are no sinks or sources for heat transport in soil,
- the thermal conductivity is a function of the soil water content.

The assumptions above may be used to derive the following heat transport equation (Campbell, 1985):

$$\frac{\partial(C_v T)}{\partial t} = \frac{\partial}{\partial z}\left(\lambda(\theta)\frac{\partial T}{\partial z}\right) - C_{VW}\frac{\partial(qT)}{\partial z} \tag{V.3.39}$$

where T is the temperature in the soil, $\lambda(\theta)$ is the thermal conductivity in soil, and C_V and C_{VW} are the volumetric heat capacities for soil and water.

The transport parameter volumetric heat capacity C_V and thermal conductivity $\lambda(\theta)$ may be estimated by regression equation to soil texture and soil water content (Campbell, 1985).

As boundary conditions given temperatures at soil surface and at the bottom of the soil column in soil are used. The temperature at the bottom of the soil column is assumed to be time constant. The temperature at the boundary to atmosphere is estimated from the minimum and the maximum of the daily air temperatures. The estimation procedure assumes that the temperature is a quasi-period function of time with the maximum at 4.5 h before sunset and the minimum at 1.5 h before sunrise (Ca'Zorzi and Dalla Fontana, 1986). As in the case of the water transport equation, the numerical solution of the parabolic equation (V.3.39) is derived by an implicit finite differential method (Knabner and Angermann, 2000).

V.3.3.3.5. Solute transport in soil

As in the case of the Jury model, the linear partition coefficients (Equations (V.3.2) and (V.3.3)) are used to described the chemical mass balance in soil. Similar to the EXSOL model the processes convection in soil water, dispersion–diffusion in soil water, and diffusion in soil air are included within the transport equation of the chemical:

$$\frac{\partial C_T(z,t)}{\partial t} = -\frac{\partial(V_E(z,t)C_T(z,t))}{\partial z} + \frac{\partial}{\partial z}\left(D_E(z,t)\frac{\partial C_T(z,t)}{\partial z}\right) - S_{deg}(z,t) - S_{root}(z,t) \tag{V.3.40}$$

The effective convection coefficient V_E and the dispersion–diffusion coefficients D_E are both dependent on the time variable t and depth variable z as result of the time and depth-depended water flux $q(z,t)$ and the soil water content $\theta(z,t)$. The sink term S_{deg} accounts for the assumed biotic degradation in soil and the sink term S_{root} accounts for the uptake of solutes into the shoots of the plants.

V.3.3.3.6. Degradation in soil

Similar to the model of Boesten (Boesten and van der Linden, 1991), the biotic degradation of chemicals in soil is described by a first-order degradation rate for reference conditions μ_{ref} and additionally coefficients that account for the soil depth $f(z)$, and temperature in soil $g(T)$:

$$S_{deg}(z,t) = -g(T)f(z)\mu_{ref}C_T(z,t) \tag{V.3.41}$$

where μ_{ref} is the degradation rate at 20°C in the plow layer of the soil. The temperature correction $g(T)$ is defined as a numerically approximated Arrhenius equation:

$$g(T) = \exp[\gamma(T - T_{20°})] \qquad T \in [5°C, 30°C] \tag{V.3.42}$$

Boesten et al. (Boesten, 1986; Boesten and van der Linden, 1991) used data from 50 degradation studies with varying soils types, to specify $\gamma = 0.08 \pm 0.02\ K^{-1}$. The value of γ corresponds to mean activation energy of 55 kJ/mol. The depth-dependence of the degradation rate $f(z)$ is defined as 1 for the plow layer of the soil profile and decreases to zero for lower soil horizons. It is assumed, that $f(z)$ is correlated to the soil organic C-content of the soil horizons.

The sink term S_{root} describes the uptake of dissolved organic chemicals in soil water into the shoots of the plant. It is assumed that the uptake may be described as passive mass flux with the transpiration stream of the plant:

$$S_{root}(z,t) = \text{TSCF}(K_{OW}) S_W(z,t) C_L(z,t) \tag{V.3.43}$$

The transpiration-stream-concentration-factor (TSCF) is a chemical specific transmission coefficient, which accounts for the passage of the bio-membranes of the plant. For non-dissociating and non-polar organic chemicals, the empirical model of Briggs et al. (1982) may be used to correlate the TSCF to the octanol–water partition coefficient K_{OW}:

$$\text{TSCF}(K_{OW}) = 0.784 \exp\left(-\frac{(\log(K_{OW}) - 1.78)^2}{2.44}\right) \tag{V.3.44}$$

V.3.3.3.7. Boundary conditions

At the soil surface the diffusive–dispersive flux is neglected. In the case of infiltration, the input flux of the chemical is defined as the convective input flux with the infiltrating water:

$$t \geq 0 \qquad z = 0 \qquad J_C(t,z) = q_{inf} C_{inf} \tag{V.3.45}$$

where q_{inf} is the water infiltration rate and C_{inf} is the concentration in the infiltrating water. In the case of evaporation chemicals may be also transported from soil to atmosphere by diffusion through a stagnant air layer at the soil surface. This process is known as volatilization from soil to atmosphere (Korte et al., 1992), and may be modeled as in the case of the Jury model by a flux type boundary conditions (V.3.22). The SNAPS model neglects the volatilization transport process, which may be an acceptable approximation for low Henry's law coefficients ($<< 10^{-5}$) (Jury et al., 1984a). The boundary condition at the soil surface in the case of evaporation is defined as:

$$t \geq 0 \qquad z = 0 \qquad J_C(t,z) = 0 \tag{V.3.46}$$

As in the case of the EXSOL model a convective transport out of the soil column is assumed at the bottom of the soil column (see Equation (V.3.23)).

V.3.4. Inverse modeling

The fate of pesticides in the subsurface is based on the water movement in the unsaturated zone and in the aquifer and above all it depends on sorption and degradation processes.

Considering only the soil water flow non-linear functions describing the unsaturated hydraulic properties and, for the groundwater zone aquifer parameters as transmissivity and storability must be determined.

Traditionally, direct steady-state methods for the estimation of these parameters exist, but recently, transient experimental methods coupled with inverse modeling techniques have become more attractive (Kool et al., 1987; Nützmann et al., 1997). Less work has been done for simultaneous estimation of flow and solute transport parameters, i.e. sorption coefficients K_d and transformation rates μ.

Inverse modeling of the transport equation with respect to these parameters requires formulation of an objective function $O(v_A)$ as in the case of least-square optimization:

$$O(v_A) = \sum_{i=1}^{N} [c_i^* - c_i(v_A)]^T [c_i^* - c_i(v_A)] \tag{V.3.47}$$

where v_A is the vector of parameters, (K_d, μ), and c_i^* are the measured and $c_i(v_A)$ are the simulated concentrations. Other techniques are also used, like the maximum likelihood method, which allows inclusion of prior information about parameters quite easily (Medina and Carrera, 1996), or Bayesian statistics (e.g. Omlin and Reichert, 1999). This allows one to obtain not only the values of estimated parameters but also information about their certainty and facilitates the use of model selection criteria.

Solving the parameter estimation problem as formulated above the Levenberg–Marquardt algorithm could also be used to minimize the objective function. This was done to estimate coefficients of a non-linear sorption kinetic function for phosphorus migration in sandy soils (Pudenz and Nützmann, 1999). Without additional effort sensitivities with respect to the parameters are obtained from the first derivatives of $O(v_A)$ and therefore conditions of identification can be examined. This is advantageous to overcome the problem of ill-posed parameters in the estimation procedure. As reported by Marsili-Libelli (1992), the sensitivity functions can be related to parameter calibration accuracy and a numerical method for estimating the parameter error covariance matrix is to be used.

In a case study, Kluge et al. (1994) demonstrated that parameters depend on the site and the way of averaging the input data with respect to time. They concluded that the sensitivity and the number of required parameters decrease with increasing spatial and temporal averaging level. In general, it is more difficult to simulate single events or extreme values than averaged dynamics or trends.

V.3.5. Ranking as an example of model application

As an example, model calculations are performed to assess the accumulation potential in soil of several triazine herbicides and their metabolites. As a model the Jury approach is used. A dynamical calculation of the water and heat balance as done in SNAPS is not needed, because the environmental conditions can be held constant in order to perform comparisons of the chemicals under a given environmental scenario. The degradation of the chemicals was estimated with help of the program EROS, "elaboration of reactions for organic synthesis" (Gasteiger et al., 1995, 1997). Details of the calculation of the fate descriptors by the combined use of the Jury model and of the program EROS are shown elsewhere (Behrendt et al., 1997, 1999).

It is known that the water flux boundary conditions may significantly determine the dominating transport process of a chemical in soil (Jury et al., 1984a). Therefore three descriptors D_E, D_T, and D_{Lea} were defined from the results of the Jury model calculations to quantify the accumulation potential in soil for the boundary conditions, such as: downward water flux, transpiration or evaporation. Each of the descriptors D_E, D_T, and D_{Lea} gives the time in days until the chemical's concentration in soil is reduced to 50% of the initial concentration. The descriptor D_E accounts for boundary conditions with evaporation and without transpiration, the descriptor D_T accounts for boundary conditions with transpiration and no evaporation, and the descriptor D_{Lea} accounts for boundary conditions with downward water flux and transpiration. The definition implies that chemicals resting in soil and degrading slowly have a high accumulation potential and vice versa. In addition to the descriptors defined from the Jury model results, the natural log of the chemical's concentration time integral of the EROS model run (the persistence) is defined as an accumulation potential descriptor D_P. The descriptor D_P is intended to account for the parent–daughter relationships of the chemicals.

Each descriptor aggregates deterministically a large amount of information, valuable for priority setting procedures and for sustainable development of new chemicals on the market ("ecodesign"). To come up to a ranking without an arbitrary aggregation of these four descriptors to get a ranking index, the theory of partially ordered sets is applied. The main idea is, how to compare objects (here: chemicals), if they are characterized by a list of properties. Here is no space to explain the rather extensive theory (see for e.g. Brüggemann and Halfon, 1997; Brüggemann et al., 2001); the results in a graphical form of a Hasse Diagram are given in Figure V.3.1.

Note that classified data, not the original numerical values, were used to construct this diagram. The numerical range of each descriptor was divided into three classes: 0 not relevant, 1, relevant, 2 very relevant. The diagram shows that there are long sequences of triazines that are mutually comparable. The least hazardous chemical with respect to the fate, given by the four descriptors is AO10 and the most hazardous chemical is TB4, which is a metabolite of terbutylazine (TBA) and which is in all four aspects more hazardous than TBA. The diagram shows also two groups of chemicals separated, on the right-hand-side chemicals with high descriptor D_P and on the left-hand-side chemicals with intermediate or low descriptor D_P. Furthermore, there are metabolites of TBA, which are not comparable to each other. For example AO6 and AZ2 and AO9 and AZ2 are non-comparable to each other due to contradictions between the descriptors D_T and D_P.

A full Hasse diagram is shown in another publication (Behrendt et al., 1997). Here the example shows, how a model calculation can help to combine pure substance properties with that of a specific scenario and to derive a hazard assessment, specified by the chosen descriptors.

Similarly waste disposals should be evaluated by model calculations, descriptors should be defined and a ranking developed, based on the techniques briefly outlined here. In any case, a decision should be based on validated models, accommodated to the specific questions, scales and data availability. The manifoldness of model results should not be masked in an aggregation just to perform a ranking, but should also apply rather modern mathematical tools, as shown here by the Hasse diagram technique. As regulators often do not feel comfortable by this use of graph theory, the recent development aims at a

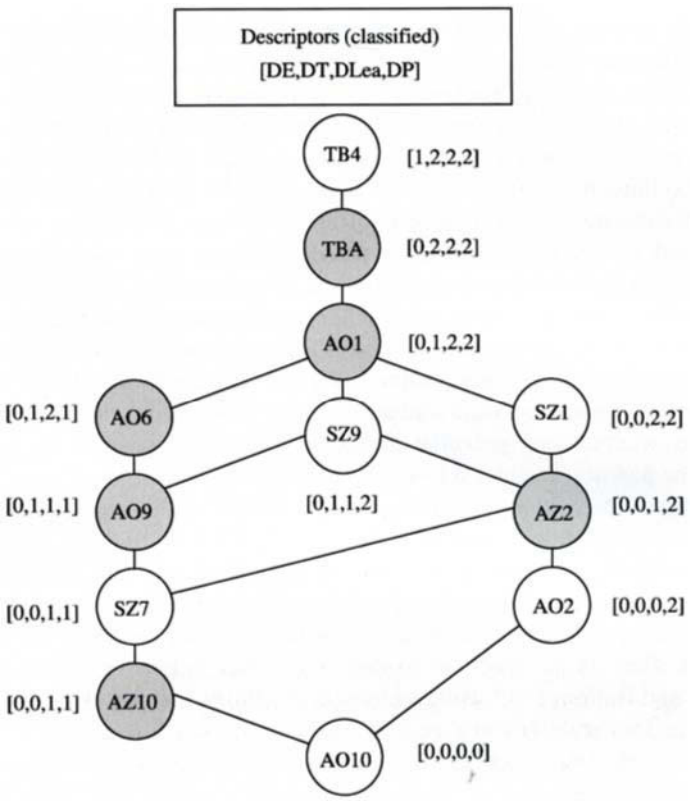


Figure V.3.1. Hasse diagram of those triazines (and their metabolites) that are comparable with terbutylazine (TBA). Shaded circles: TBA and metabolites of TBA. Further explanation: see text.

probabilistic extension: a linear rank is derived, however, a probability distribution of the ranks is added (e.g. Sørensen and Lerche, 2002, and references cited therein).

Nomenclature

C_A concentration in atmosphere ($\mu g/m^3$)
C_G concentration in soil air ($\mu g/m^3$ air)
C_{inf} concentration in infiltrating water at the soil surface ($\mu g/m^3$)
C_L concentration dissolved in soil water ($\mu g/m^3$ water)
C_S concentration adsorbed on the soil matrix ($\mu g/g$ soil)
C_T total concentration soil ($\mu g/m^3$ soil)
C_V volumetric heat capacity of soil ($J/m^3/K$)
C_{VW} volumetric heat capacity of water ($J/m^3/K$)
D_E effective diffusion coefficient in soil (m^2/d)
D_G diffusion coefficient in soil air (m^2/d)
$D_{G,bin}$ molecular diffusion coefficient in free air (m^2/d)

D_{LE} effective dispersion–diffusion coefficient (m^2/d)
D_{LH} hydrodynamic dispersion coefficient (m^2/d)
D_L diffusion coefficient in soil water (m^2/d)
$D_{L,bin}$ molecular diffusion coefficient in free water (m^2/d)
E evaporation rate (m/d)
E_i crop interception storage (m/d)
E_R reduced evaporation rate (m/d)
H_T total water potential in soil (m)
J_G diffusive flux in soil air ($\mu g/m^2/d$)
J_A mass flux of the chemical from soil air to atmosphere ($\mu g/m^2/d$)
J_L total mass flux in soil water ($\mu g/m^2/d$)
J_{LC} vertical convective mass flux ($\mu g/m^2$ soil/d)
J_{LD} diffusive flux in soil water ($\mu g/m^2/d$)
J_{LH} dispersive flux in soil water ($\mu g/m^2/d$)
J_W Darcy water flux in soil ($m^3/m^2/d$)
K hydraulic conductivity (m/d)
K_{aw} air–water partition coefficient (–)
K_d linear equilibrium partition coefficient soil matrix/soil water (cm^3/g)
K_{ow} octanol–water partition coefficient (–)
M molar weight of water (kg/mol)
P precipitation rate (m/d)
R universal gas constant (J/mol/K)
R surface run-off (m/d)
R_L capacity coefficient soil water (–)
R_S capacity coefficient soil matrix (g/m^3)
R_G capacity coefficient soil air (–)
S_{deg} sink term for biotic degradation in soil ($\mu g/m^3$ soil/d)
$S_P(z,t)$ potential root water uptake rate (m/d)
S_{root} sink term for uptake of solutes into plants ($\mu g/m^3$ soil/d)
S_w root water uptake rate (m^3 water/m^3/d)
T absolute temperature (K)
$TSCF$ transpiration stream concentration factor (–)
V_E effective pore water velocity (m/d)
Z_L depth in soil of the bottom boundary of the soil column (m)
a soil air content (m^3/m^3)
c soil water capacity (m^{-1})
$f(z)$ empirical function of soil depth (–)
g gravitational acceleration (m/s^2)
$g(T)$ temperature dependence of the degradation rate in soil (–)
k_a mass transfer coefficient for volatilization (m/d)
q_{inf} water infiltration rate at the soil surface (m/d)
rh_{ad} relative humidity for dry air (–)
t time (d)
v pore water velocity (m/d)
$w(z,t)$ root length distribution (m/m^3)
z depth in soil (m)

α empirical function (–)
μ first-order degradation rate (d^{-1})
μ_{ref} first-order degradation rate at reference conditions 20 °C and 70–100 kPa soil water matrix potential in the plow layer (d^{-1})
ε soil porosity (m^3/m^3)
ψ soil matrix potential (m)
θ soil water content (m^3water/m^3)
$\xi(\cdot)$ tortuosity factor (–)
$\lambda(\theta)$ thermal conductivity in soil (W/°K/m)
ρ_b soil bulk density (g/m^3)

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V.4
Evaluating the susceptibility of aquifers to pollution

Klaus-Peter Seiler

V.4.1. Introduction

The largest reservoirs on earth are formed by groundwater, the oceans, and the atmosphere; for the most part, the groundwater and the atmosphere are transient depots and the oceans are final depots for pollutants.

On many continents, groundwater is the only resource available for irrigation, for manufacturing industrial products, for producing energy, and also for drinking water. This is especially true for semi-arid and arid regions and all regions with extremely high permeable rocks (e.g. soluble rocks and Quaternary gravels).

A review of the average distribution of water on the continents is given in Table V.4.1. Comparing the groundwater quantities with the annual discharge from the continents (Table V.4.1) and assuming that all of the groundwater participates evenly in the water cycle, the minimum turnover time would be 180 years. In other words, the average groundwater outflows on the continents would not yet show significant effects of the pollutants released since the start of the industrial age. Although this holds true for certain regions of the continents, in general this is not the case. Groundwater responds to instantaneous, short-term and to long-term contamination impacts as well.

The causes for this are diverse and lie in the sensitivity with which the groundwater in the aquifer systems reacts to any substance input in undesired concentrations (pollution). These reaction mechanisms have their roots

- in the intensity, with which the groundwater is incorporated in the water cycle and used by people,
- in the transport potential of the different discharge components,
- in the hydrodynamic properties of aquifers and aquifer systems, and
- in microbiological activities in the aquifers.

V.4.2. Importance of groundwater

The importance of groundwater becomes obvious, if one looks at its usage in the different continents (Table V.4.2); surface water usage is also included in this account. Table V.4.2 shows that in the developing countries the demand for irrigation water is the highest. In the industrialized nations, however, the demand for water for energy and industrial production

Table V.4.1. Review of the average distribution of waters on the continents. Ice distribution is not considered.

Groundwater	8,000,000 km^3
Lake water	226,000 km^3
Soil moisture	62,000 km^3
Air humidity	15,000 km^3
River water	1000 km^3
Discharge from the continents	45,000 km^3

is the highest. Worldwide, the water use for household purposes, including drinking water, is the lowest for all countries. The average total water demand of about 3000 km^3/year (1990) amounts to only 6.6%, the drinking water demand to only 0.5% of the average discharge from the continents. Of course, these statistics do not incorporate the uneven distribution of renewable water resources in the different climatic and geological zones on earth. It indicates, however, that the water quantities as an average will actually not be a predominant problem.

Demands on groundwater quality are the highest for drinking water as well as for waters for food processing and much lower for all the other water usages. Water quality is primarily dependent upon geogenic factors and nowadays is also strongly influenced by anthropogenic factors. Worldwide, this has led to a decrease of water quality on the continents, especially in the urban areas and in the coastal regions. As a result, actual availability of groundwater mostly depends less from renewable water, but from water quality.

In many regions of the world, the high demand for water for non-household uses has drawn away attention from maintaining groundwater quality and that way led to an unequilibrated competition between maintaining the natural ecological elements and functions for self-purification processes and water usage for production purposes.

By nature, groundwater is poor in nutrients that promote self-purification processes in surface waters. Due to anthropogenic impacts, groundwater can suffer considerable losses

Table V.4.2. Water demand statistics for individual regions in km^3 (1990). Till 1995 the world water demand has increased to about 5000 km^3.

Regions	Irrigation	Energy production	Industrial production	Household use	Total
Asia	1400	68	31	98	1597
Africa	61	11	4	12	88
Australia	13	8	6	2	29
South America	35	6	4	11	56
North America	205	232	77	38	552
Europe	116	176	184	40	516
Total	1830	501	306	201	2838

in quality. Generally, these appear only slowly underground and once begun, these processes require much more time to fade away than they needed to build up.

Today's increased technical possibilities for using groundwater, the prevailing production-oriented usage of groundwater, and the lack of sewage water treatment in many countries have led to a reduction in the amount of water in some developing countries available for household use and food processing. Therefore, it has become crucial to evaluate the susceptibility of the groundwater reservoirs with regards to its vulnerability to contamination, when developing, exploiting, and managing the aquifers.

V.4.3. Dynamics of groundwater within the water cycle

Only a small portion of the existing groundwater (Table V.4.1) is directly recharged by precipitation (infiltration) or undergoes indirect recharge (bank filtration, artificial groundwater recharge). The majority of the groundwater acts as a long-term reservoir. Only the recharged portion of groundwater is available for management purposes and contributes simultaneously to important ecological functions of the surface water. Any management of the long-term resources that started recently in developing and industrialized countries presents on a long run irretrievable groundwater consumption.

Groundwater recharge occurs in all regions of the continents; the desert regions receive very small amounts (<5 mm/a) very irregularly, the tropical regions receive an annual amount of less than 150 mm and the humid regions an annual amount of less than 1000 mm. Recent investigations have shown that groundwater recharge occurs even in permafrost regions, albeit only little.

However, this groundwater recharge, which can also transport pollutants into the underground, does not flow through the entire thickness of the aquifer. Instead, it mainly flows through the aquifer system near the surface (Seiler and Lindner, 1995).

The groundwater flows in aquifers and each aquifer has its individual hydraulic properties. In unconsolidated aquifers, the hydraulic conductivity and porosity generally decrease with increasing depth and statistically, the hydraulic conductivity of the fissures decreases too with increasing depth in consolidated, fissured aquifers; only in areas with deep reaching tectonic faults do the hydraulic conductivity of the fissures often reach a depth of several thousand meters.

The bedding of aquifers and the general and discontinuous decrease of the hydraulic conductivities with depth are the major reasons that the groundwater recharge is not distributed equally among all the aquifers.

To present the quantitative turnover of groundwater recharge in the individual sections of the aquifer systems (Fig. V.4.1), the groundwater movement in a section of an aquifer system between the undergroundwater divide and the receiving stream with layers of different hydraulic conductivity has been simulated numerically in two dimensions; the groundwater surface receives a recharge of 150 mm/a, the groundwater flows through all the layers and finally reaches the receiving stream as a surface discharge. The numerical simulation of scenarios with generally known hydraulic conductivity/depth distributions (Fig. V.4.2) and the calculated amounts of groundwater turnover in the individual layers (in percent of groundwater recharge) leads to the conclusion that generally more than 85%

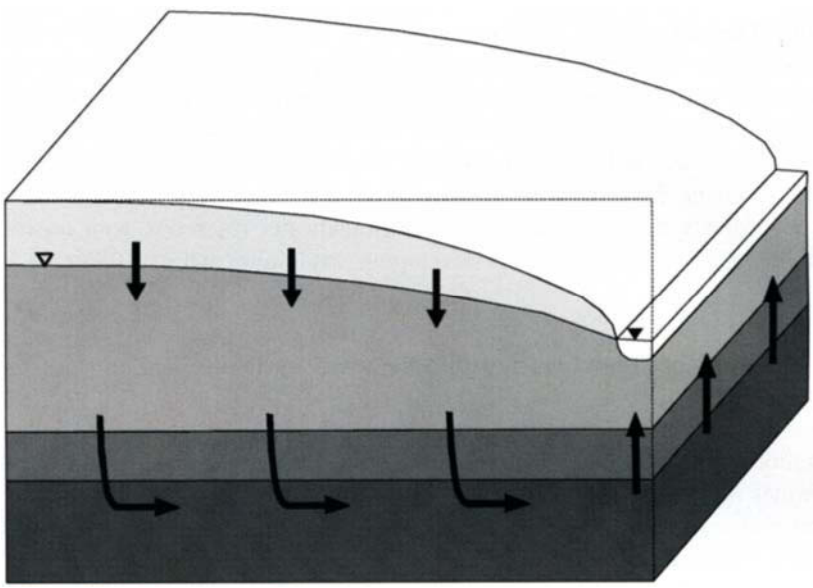


Figure V.4.1. The two-dimensional modeling plane presenting the influence of conductivity distributions in sediments upon the distribution of the groundwater recharge in the individual layers. A groundwater recharge of 150 mm/a was assumed with no overland discharge or interflow and no groundwater underflows the receiving stream.

of the groundwater recharge occurs in near surface layers and that less than 15% of the groundwater recharge reaches also deep lying aquifers.

Thus, the groundwater recharge is divided in an active, near surface zone with young groundwater (< 50 years old) and a passive, deep groundwater recharge zone (Fig. V.4.3) with water ages exceeding 50 years and reaching many thousand years (see below). Both of these groundwater recharge zones occur worldwide.

- In semi-arid to arid regions, the active groundwater recharge zone has a thickness of a few decimeters or meters, increases in the tropics to decameters and is in humid areas are less than 100 m thick; its thickness depends on the recharge and storage properties (hydraulic conductivity and effective porosity) of the system.
- The passive groundwater recharge zone can achieve a thickness of several hundred meters and is underlain by the connate groundwater (Engelhardt, 1960), i.e. from groundwater that did not return to the biosphere for millions of years (Fig. V.4.3).

The interface between the active and passive recharge zone can be identified in depth profiles by sudden changes in the age of the water and in part also by changes in the water quality. If isochrones are incorporated in the numerical simulation of the scenarios of the groundwater recharge (Fig. V.4.4), it can be seen that the age of the water at the base of the active groundwater recharge zone in effect increases very rapidly to several hundred to thousand of years. If the natural depth distribution of ^{3}H, ^{14}C, and e.g. ion exchange waters (Fig. V.4.5) are considered, it is obvious that the tritium content does not gradually decrease with depth, but instead suddenly. The ^{14}C-concentrations also show a similar

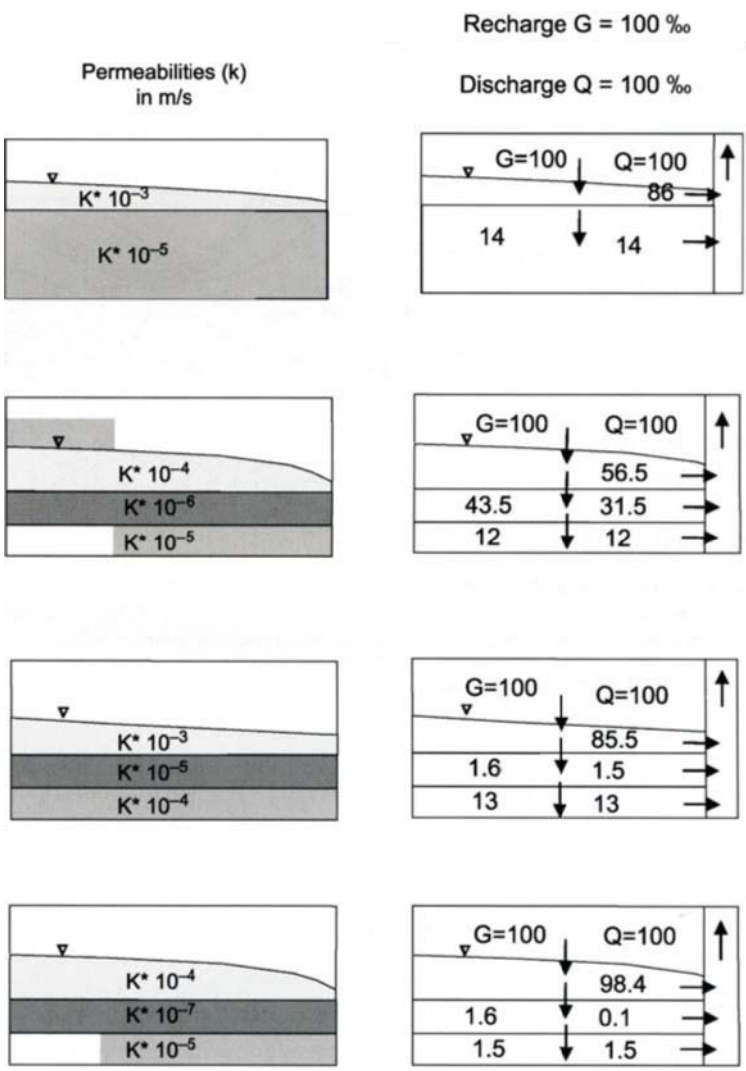


Figure V.4.2. Hydraulic conductivity series, as seen frequently in nature (left columns) and the percentage of the groundwater recharge in the individual layers (right columns). G = recharge (100%), Q = discharge (100%).

sudden decrease and also the ion exchange waters occur clearly more frequently below this depth. It has been proven practicable to define the boundary between the active and passive groundwater recharge areas with the radioactive environmental isotope ^{3}H. To do this, the tritium naught line (TNL) is defined, an interface below which the tritium concentrations have fallen to values under the detection limit in routine measurements (Seiler and Lindner, 1995). Frequently, this boundary is also defined with the salt water/fresh water interface under the continents (Richter and Lillich, 1975). This requires, however, that salt

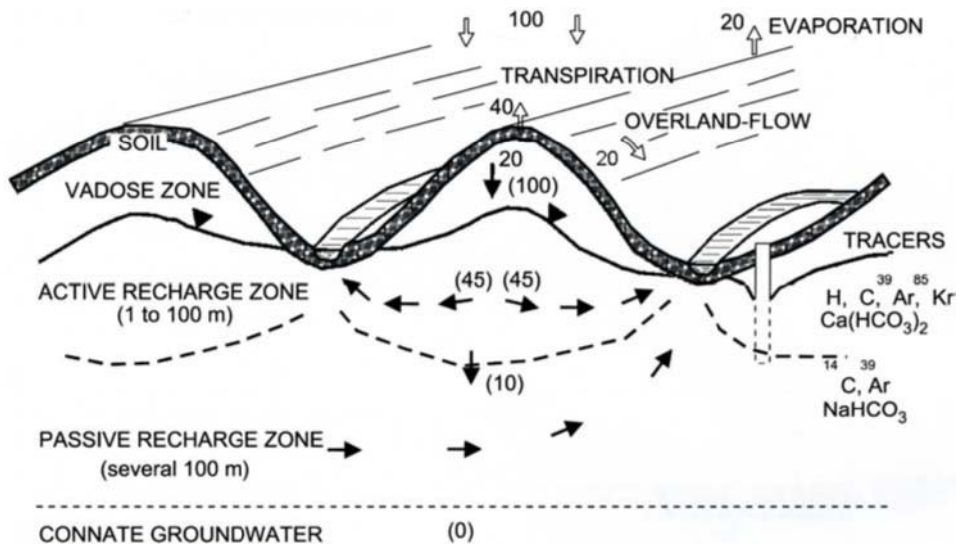


Figure V.4.3. The subdivision of the aquifer systems in active and passive groundwater recharge zones and connate groundwater; not to scale. Without brackets = precipitation and the discharge components related to precipitation; in brackets = groundwater recharge and its subsurface distribution related to groundwater recharge.

rocks are present within the rock sequence and reach to the active groundwater recharge zone. Tritium is an environmental tracer and is introduced in considerable concentrations only through the water cycle. It occurs worldwide in precipitation, albeit in different concentrations (Moser and Rauert, 1980; Mook, 2000) and has a half-life of 12.34 years. It can be measured routinely with an accuracy of ± 0.5 TU and is produced by the interaction of cosmic rays with ^{14}N in concentrations between 5 and 15 TU (1 TU = 0.113 Bq/l or $^3H/^1H = 1/10^{18}$).

The active groundwater recharge zone is thin (< 100 m) and has high groundwater flow velocities (> 0.1 m/d). The passive groundwater recharge zone is much thicker (> 300 m) and has groundwater flow velocities under 0.01 m/d. Due to the high dilution volume, which results from the low groundwater flow velocities and the large groundwater thickness, the passive groundwater recharge zone reacts much slower to pollutant inputs than the active groundwater recharge zone. Only the connate water stays free of pollutants – in principle. Connate groundwaters (Engelhardt, 1960) are usually not used as drinking or industrial water due to their chemical composition; however, they can be and are used in balneology.

Following the development of water supply in the last 100 years, it turns out that in many countries at the beginning river waters, later waters of springs and shallow wells, and finally of deep wells that penetrate the passive groundwater recharge zone, have been used for water supply. The reason for this development was, among others, impairment of the groundwater quality for drinking water purposes. Mostly the sources of contamination have been disregarded and the water quality problems have been solved by digging deeper

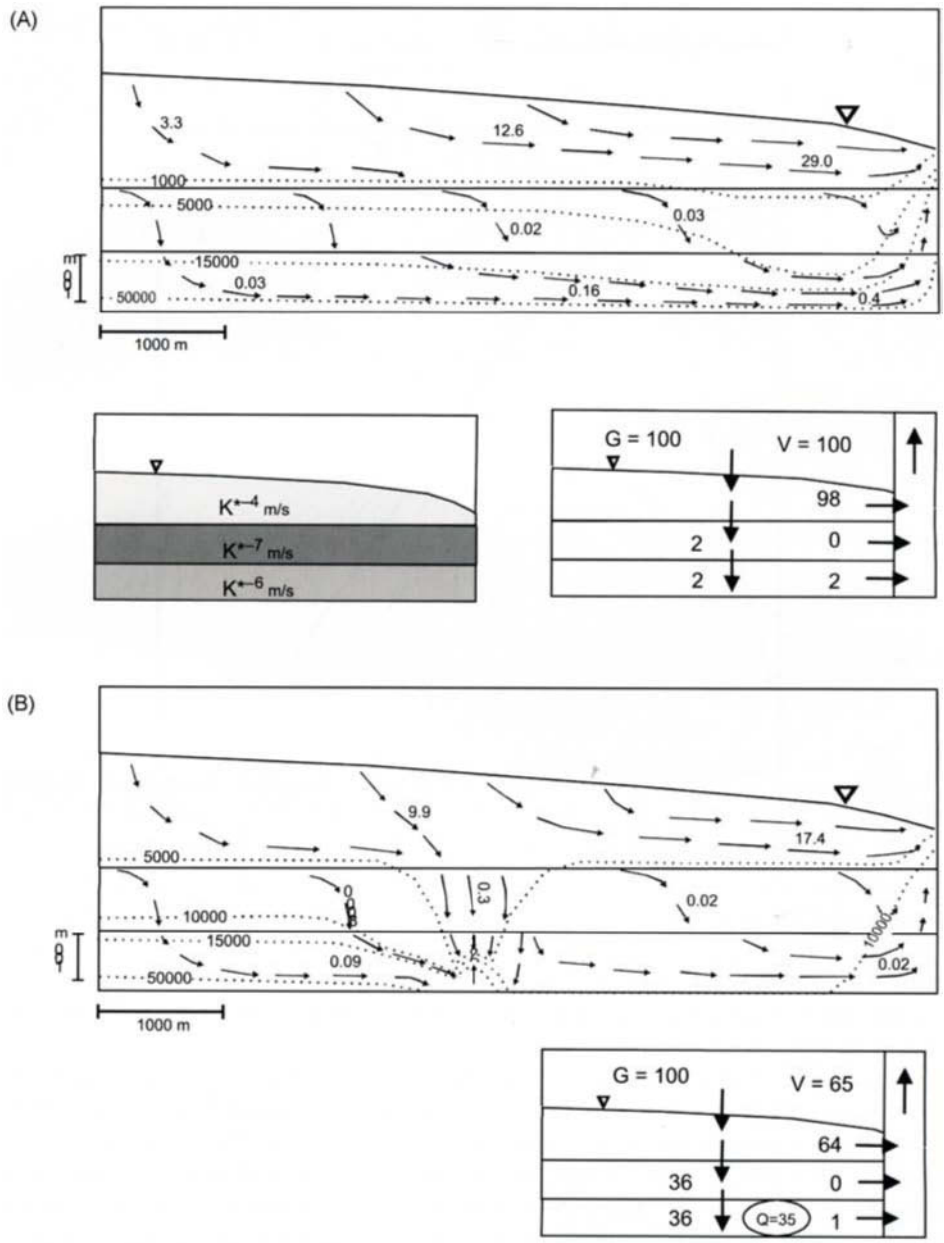


Figure V.4.4. Flow paths and velocities (m/d) and age distribution (years) in the groundwater at certain hydraulic conductivities (m/s) in the aquifer systems: (A) without; (B) with a groundwater withdrawal from the passive recharge zone of 35% recharge.

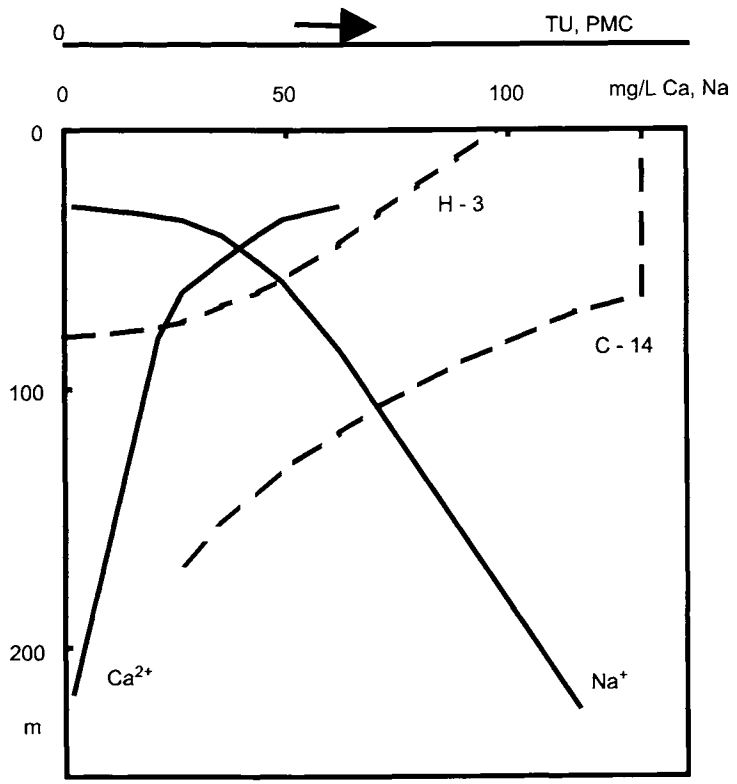


Figure V.4.5. Changes in ^{3}H-, ^{14}C-, Ca^{2+}- and Na^{+}-concentrations with groundwater depth; ^{3}H-concentrations in TU, ^{14}C-concentrations in pmc (percent modern carbon).

wells or providing bigger dilution volumes. However, this only produces an increase of dilution for the pollutants, but will not prohibit a long-term contamination of the groundwater of the passive recharge zone.

Groundwater exploitations from the passive groundwater recharge zone have generally not been based on the low, yet available groundwater recharge ($<15\%$). Instead, they are based on the calculated groundwater recharge for the landscape. The impact of such groundwater withdrawals from deeper layers was also calculated in the scenarios (Fig. V.4.4). Thereby, it was shown that such exploitations will lead to hydraulic short-cuts between the different zones, if the groundwater exploitation is higher than the natural, respective to the aquifer related yield. The resulting groundwater deficit must then be compensated (DVWK, 1983, 1987). This compensation process can last for several years to decades and keeps the hydrodynamic system for a long run in transient conditions. Thus, it appears that a quantitatively and qualitatively secure water supply from the passive zone was available if applied in accordance to the aquifer specific recharge else leads to a long-term contamination input into a groundwater zone that would have been naturally protected in the long run.

V.4.4. Transport potential of discharge components

Discharge comprises three major components (Fig. V.4.6):

- overland discharge,
- interflow, and
- base flow from groundwater recharge.

All of these flow components can transport pollutants, either by erosion or dissolved or particle favored and achieve quite different impacts on ground- and surface water. Solid wastes either disposed in the landfills, or spread on the land surface as dry and wet particulate deposition or in purpose as excessive agrochemicals or common fill used in civil engineering, are ultimate sources of contaminants leached and transported to groundwater by infiltrating precipitation waters. The main pools of contaminants for these discharge components are the land surface and the effective root zone (Luckner, 1994).

Overland discharge and interflow only originate in sediments and rocks of hilly terrains with limited infiltration capacity. Normally, they do not occur in plains. Both of these discharges develop flow velocities of several kilometers and meters per day, respectively. Contrary groundwater recharge in non-fissured sediments has flow velocities of less than 0.02 m/d.

Interflow, which develops in hilly terrains out of bypass flow (Seiler, 1997), can wash a considerable amount of pollutants out of the effective root zone and thus contributes to the groundwater protection (Hellmeier, 2001). On the other hand, such a discharge of pollutants during precipitation (Fig. V.4.7) leads to main shock impacts

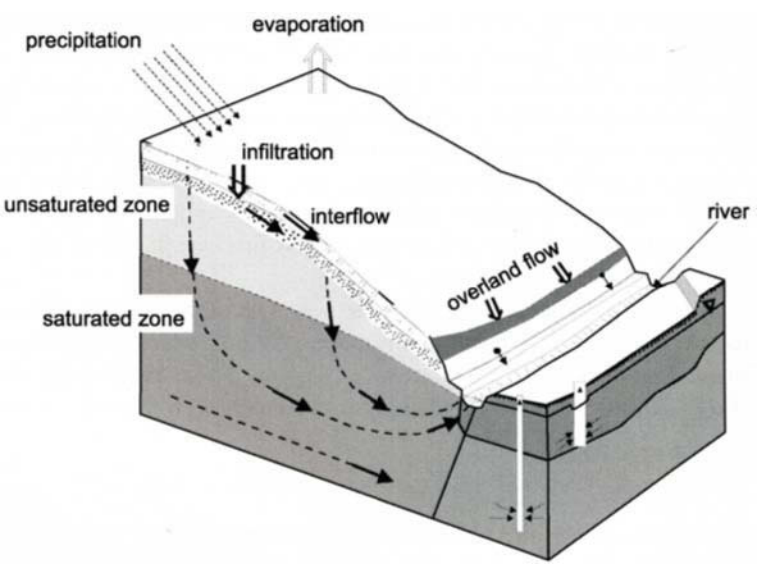


Figure V.4.6. Block diagram of a landscape with the three most important discharge components.

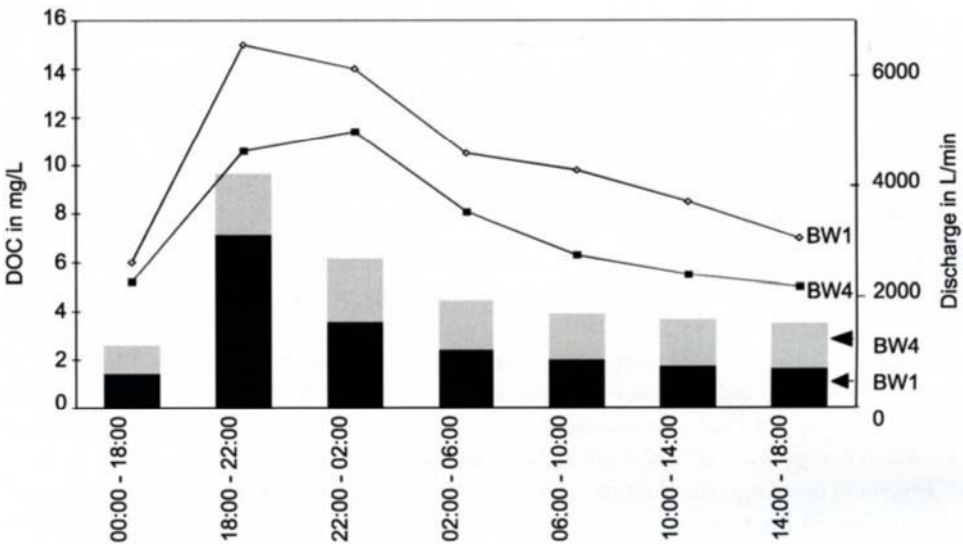


Figure V.4.7. DOC discharge after precipitation. BW1 = area with 100% firs, BW4 = forested area, about 20% used agriculturally. The DOC-concentrations in the discharge during precipitation are higher in the surface runoff than in the unsaturated zone under the effective root zone.

- to rivers, ponds, and lakes in hilly terrains and
- to groundwater in plains.

Mechanical filtration occurs in both saturated and unsaturated flow and impeded particle favored transport much more in the unsaturated zone. This is certainly a major reason why, e.g. DOC occurs in much larger concentrations in the seepage waters of the effective root zone (Fig. V.4.8) than beneath and therefore charge interflow much more than groundwater recharge (usually less than 3 mg/l) as far as these aquifers are free of fossil organic matter. This distribution of organic matter in discharge components is due as well to the mechanical filtering as a selective, slow sorption of DOC onto rocks; this sorption occurs onto clay-free sediments as well as onto clayey–silty sediments and also favors the co-precipitation of other pollutants, such as, e.g. certain heavy metals and pesticides. DOC sorption, however, would reach rather quickly sorption capacity if microbiologic activities would not disintegrate it; this process, however, also deliberates contaminants sorbed on DOC surfaces.

The importance of the pore geometries of the flow path of the water for the mechanical filtering processes is given for specified substances, e.g. in Seiler (1985), Matthess et al. (1991), Kim et al. (1994), and in Chapter V.2 of this book. Hence, the soil and the unsaturated zone provide a certain protection for aquifers and groundwater from pollution

- due to their storage capacity and
- due to the diversion of matter flow from vertical to lateral directions.

Both of these impacts prohibit short-term pollutant input into the groundwater, favor a momentary dilution of the pollutants, but can lead to long-term unwanted background levels of pollutants that may reach groundwater.

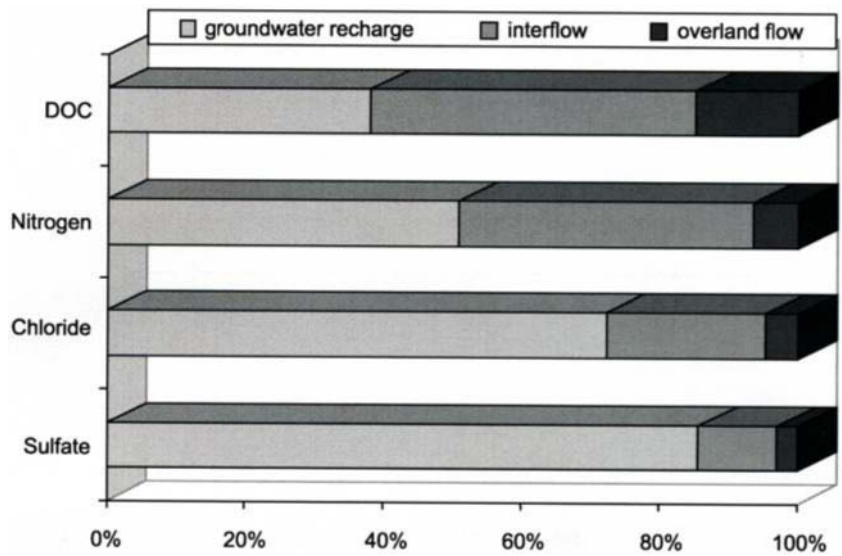


Figure V.4.8. DOC distributions as compared to nitrogen, chloride, and sulfate concentrations in groundwater recharge, interflow and overland flow (from left to right) in tertiary sediments of a hilly area (Scheyern, Germany). Chlorides and sulfates are transported as dissolved matter and the distributions in the three discharge components are in the same relations as the three discharge components itself. DOC transport differs significantly from this pattern because it is mechanically filtered within the effective root zone and does not reach groundwater as much as directly surface water through interflow; nitrogen shows a transient behavior as it is transported partially by DOC, partially as dissolved matter (Hellmeier, 2001).

V.4.5. Rock properties and the susceptibility of aquifers to contaminants

Water bearing rocks are called aquifers and normally they are subdivided into unconsolidated and consolidated aquifers. Unconsolidated aquifers are generally porous and do not have a secondary porosity such as fissures. Consolidated aquifers, on the other hand, were physically or chemically solidified after sedimentation (sedimentary rocks) or crystallized (crystalline rocks) by metamorphic processes; fissures provide a secondary porosity. In easily soluble rocks, the fissures can be widened into solution cavities. Some of the consolidated aquifers can also have a primary porosity, such as, e.g. many sandstones, carbonate reefs, or Cretaceous chalks. Such rocks with fissures and matrix pores belong to the heterogeneous-porous media, because their flow velocities are not continuous, but have usually a bimodal or polymodal frequency distribution.

The importance of rock porosities (pores, fissures, solution cavities) with regard to pollutant behavior and thus the susceptibility of the aquifers to pollution is closely connected with the groundwater flow velocities and the hydrodynamic dispersion:

- The movement of the groundwater is positively correlated with the size of the rock pores. In general, the hydraulic conductivity of the rock changes proportionally to the square of the porosity. The proportionality constant is closely coupled with the sediment genesis and the diagenesis of the rock. Figure V.4.9 shows a broad review of rock hydraulic conductivities.

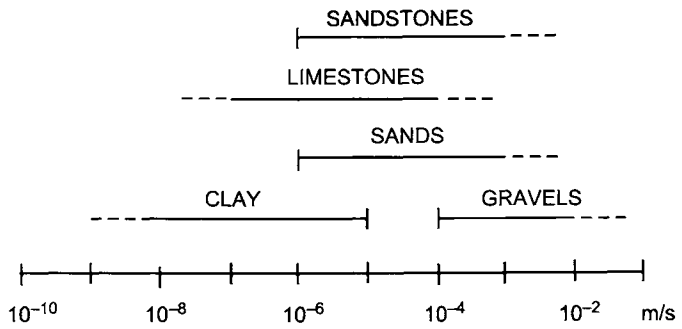


Figure V.4.9. Hydraulic conductivities of sediments and rocks.

- The groundwater flow velocity depends on the rock hydraulic conductivity and the groundwater recharge as well.
- The larger the rock pores are, the lower are the lateral and transverse hydrodynamic dispersion, i.e. the dilution, and most groundwater flow velocities will increase. Examples for the hydrodynamic dispersion of non-reactive tracers are shown in Figure V.4.10 (Lallemand-Barres and Peaudecerf, 1978; Freeze and Cherry, 1979; Seiler, 1985; Seiler et al., 1989; Glaser, 1997).

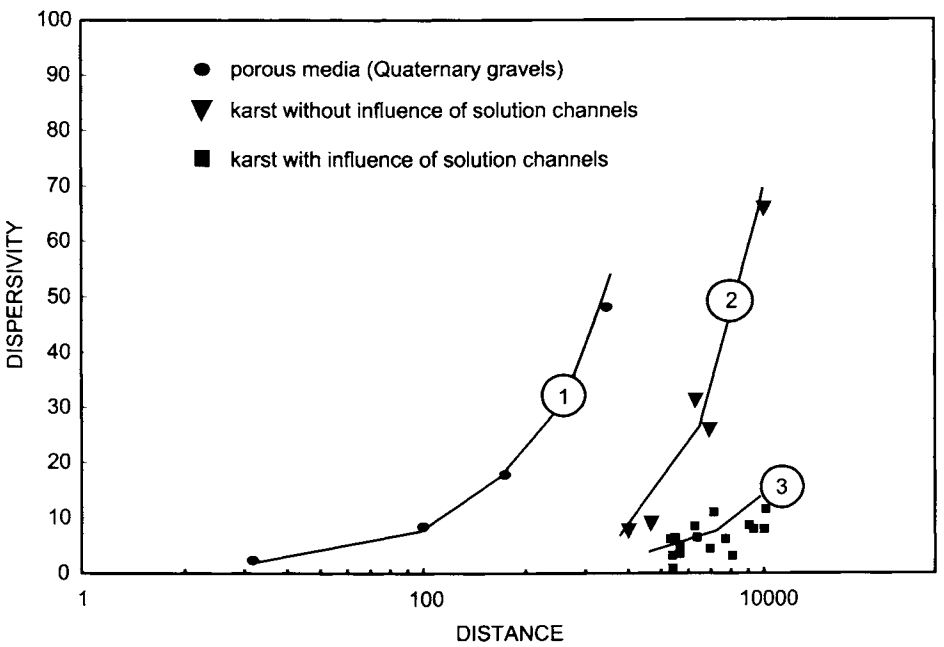


Figure V.4.10. Dispersivity of non-reactive tracers in solution cavities (curve 3), in gravels (curve 1), and in fissured bedded rocks with low matrix porosity (curve 2).

In biporous media, in addition to the hydrodynamic dispersion, there is also a preferential lateral dilution component (Sudicky and Frind, 1981) due to molecular diffusion (Fig. V.4.10, top curve). This increases the dilution process,

- as long as a concentration gradient exists between the draining (e.g. fissures) and storing section (e.g. porous matrix) in heterogeneous-porous media,
- dead end fissures favor the transition of fissure flow into matrix flow, and
- the larger the spacing of fissures, respectively, the longer the flow distances within the matrix are getting.

These geological boundary conditions in fissured rocks with matrix porosity can lead to a creeping pollutant charge in the rock matrix with low hydraulic conductivity, which mostly cannot be discovered in time with conventional monitoring methods for ground- and drinking water.

Typical examples for heterogeneous-porous media are the reef rocks from the Upper Jurassic of the Franconian Alb. They have fissure porosities of less than 2 vol.% with hydraulic conductivities around $10^{-3}-10^{-4}$ m/s (Seiler et al., 1991) and matrix porosities between 5 and 10 vol.% with hydraulic conductivity under 10^{-7} m/s (Weiss, 1987). In the same area there are also bedded rocks without matrix porosity and with the same fissure porosity and hydraulic conductivity as the reef rocks. Here it was shown by tracer experiments that

- 5 kg of non-reactive tracers, injected instantaneously into the groundwater, were diluted in the reef rocks after flow distances of 2 km to concentrations under their detection limit (2–20 ng/l). In contrast, in the neighboring bedded facies with less than 4 vol.% of matrix porosity, the tracer was still detected in high concentrations after a flow distance of more than 10 km and 50–100% of the injected tracer was recovered.
- In cases of heterogeneous-porous media, the tracer can also reach springs that discharge old water. Here, young and old waters get mixed along the fissure pathway.

In the investigated case, the pollutant input into both aquifer types was the same as the amount of the infiltrating water. Due to the mentioned differences in the rock properties, the groundwater from the bedded facies has clearly higher pollutant concentrations than the groundwater from the reef facies (Fig. V.4.11). The aquifer without matrix porosity shows the current pollution situation, whereas the aquifer with matrix porosity is not yet fully charged with pollutants, i.e. is creepingly charged, as long as microbiological processes in the rock matrix do not decay the pollutants (Seiler et al., 1996a,b).

In heterogeneous-porous media, through a suitable combination of classical hydrogeological, geochemical, and isotope investigation methods, the process of charge of the matrix with pollutants can be determined and process-orientated numerically modeled (Seiler et al., 1991; Seiler, 1997). In the case mentioned above, the mean residence time of the groundwater was determined in the rock matrix by sampling under dry-weather flow conditions for the environmental tracer ^{3}H; as a result residence times of several decades to a few centuries (Fig. V.4.12) were determined (Seiler et al., 1996a,b); the determination of the groundwater flow velocities in the fissures of the same aquifer (0.5–1 km/d) was done with fluorescent tracers and was coupled with a tracer balance (less than 1% recovery). Tracer balance and flow velocity provide quantitative information about the extent of the tracer exchange between the fissures and the porous rock matrix.

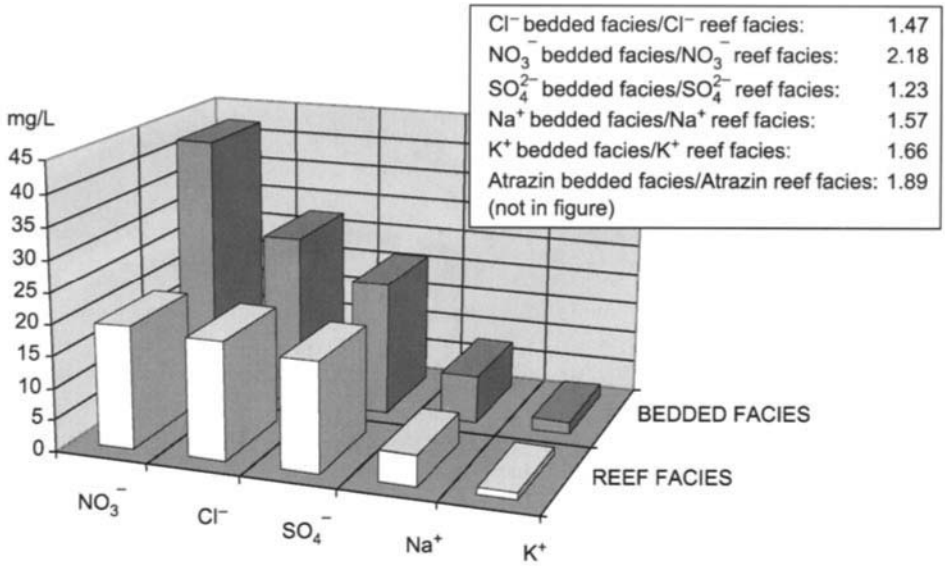


Figure V.4.11. Average concentrations of agrochemicals in groundwater from aquifers without (bedded facies) and with matrix porosity (reef rocks) in the Franconian Alb, Germany (after Glaser, 1997).

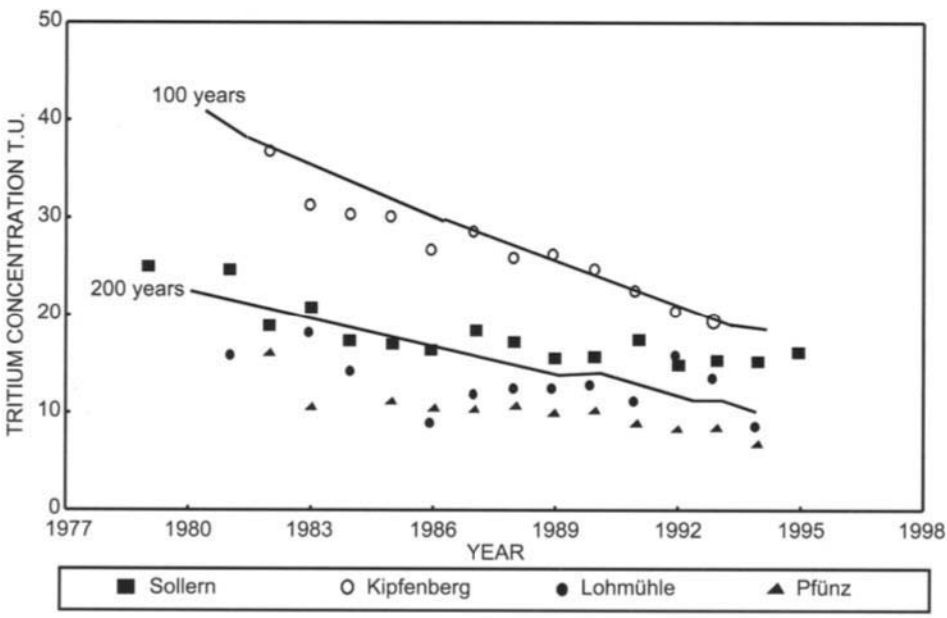


Figure V.4.12. Tritium concentrations and mean residence times of some groundwaters from the Franconian Alb.

Together with physical investigations of the rocks on determination of matrix porosities, pore sizes and matrix hydraulic conductivity, these data provide the basis for a numerical simulation of the pollution charge of the rock matrix, which can be compared with the measured values of the pollution charge in the groundwater form this heterogeneous-porous media.

V.4.6. Microbiological activities in aquifers

Common scientific teaching states that aquifers are poor in microorganisms, which catalytically influence chemical reactions. In contrast, the soil zone with abundant organic matter has a very high microbiological disintegration potential.

It is known from past investigations that microbiological activity occurs in confined aquifers with slow groundwater movement (Rietti-Shati et al., 1996) and in ore mines; however, in open aquifers, such reactions were rarely recognized up to now.

Recent microbiological–hydrochemical investigations have shown, however, that microbiological reactions in unconfined and even in heterogeneous-porous aquifers take place more often than previously assumed (Seiler et al., 1996a,b; Seiler, 1997).

Most aquifers appear to have a natural small microbiological population density, which can increase as a whole or selectively, as soon as nutrients (carbon, phosphate, nitrogen) and sufficient energy sources are available. This can happen, e.g. through the influx of organic pollutants that are easy to decay and will start after a certain incubation time needed to increase the microbiologic population. An example of this process can be taken from the fissured-porous rocks of the Upper Jurassic Limestones in the Franconian Alb. Here it was demonstrated (Seiler et al., 1996a,b) that under agriculturally used land, higher counts of colony forming microorganisms appear than under forest areas (Fig. V.4.13). The groundwater under the agricultural areas has a high (Fig. V.4.14), and the biofilms in these rocks have an even higher denitrification capacity. In comparison, the groundwater and biofilms under forest areas have a much lower denitrification potential. In the unfrosted areas of these regions, household sewage water and agrochemicals infiltrate into the soil. Under the forests, only atmospheric pollutants infiltrate the soil via interception.

The microbiologically effective colonization of the limestones of the Upper Jurassic is efficient solely in the fissured-porous media. Their matrix porosity is 5–10 vol.% and the pore openings are large enough for microbiological colonization (>5 μm). The importance of the differences in the microbiological colonization of the rocks with (reef facies) and without matrix porosity (bedded facies) is shown by a statistical comparison of some pollutants in the reef facies and the bedded facies (Fig. V.4.11). The nitrate, chloride, sodium, potassium, and sulfate concentrations (Seiler, 1997) correspond in the bedded facies to that calculated from the releases of agrochemicals and sewage waters in landscapes as compared to the groundwater recharge. In the reef facies, however, these values are generally low, because the rock matrix with porosities between 5 and 10 vol.% produces a higher dilution of the pollutants than the facies without the matrix porosity, but simultaneously increases a creeping storage of pollutants. This charging process began about 40–50 years ago with the increased use of agrochemicals. For sodium, potassium, chloride, and sulfate, the average concentration ratio in the groundwater from the reef and bedded facies is 1:1.5 and reflects the slow storage of pollutants in the matrix; yet for

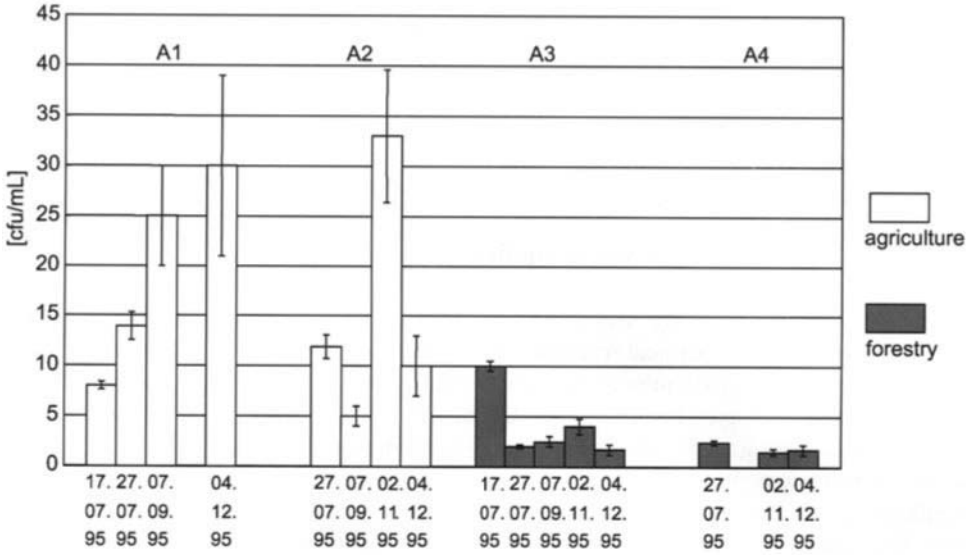


Figure V.4.13. Colony forming units (cfu) in groundwaters under agriculture (left two column groups) and forest areas (next two columns) in the reef facies and in a mixed reef/bedded facies (right columns).

nitrate it is 1:2. This is undoubtedly due to the decay process in the facies with the matrix potential, which is – as shown above – microbiologically controlled and which works against the pollutant storage in the rock matrix. Such a microbiological decay also appears to be present for atrazine.

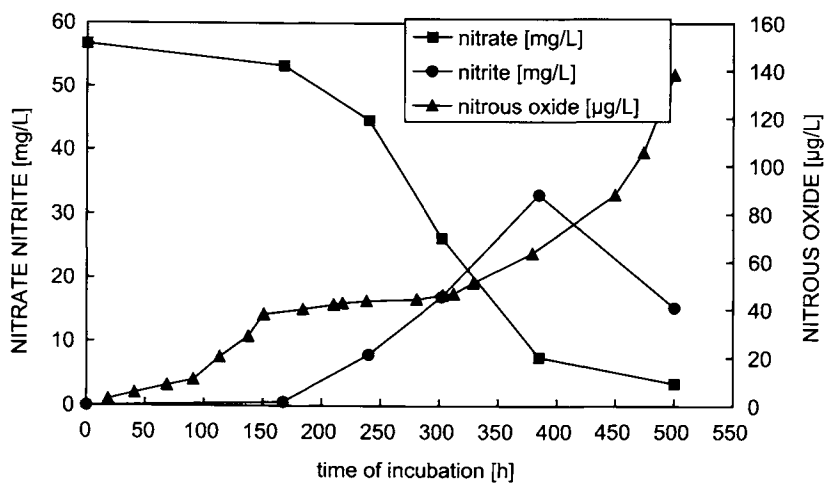


Figure V.4.14. Denitrification in a karst groundwater, which was dosed with 50 mg/l nitrate. NO_2 and N_2O gas form subsequently. The N_2-production could not be measured and was not prohibited.

An example that shows how fast microbiological populations in aquifers can increase as a result of pollutant input can be seen in the Caracas Aquifer under the city area of Caracas, Venezuela. Up to about 50 years ago, the city only covered the western part of the confluence of the Guaire and Valle rivers (Fig. V.4.15) but has since expanded astronomically over to the eastern part. The city receives its drinking water from nearby surface water reservoirs. The influx amounts to 17 m^3/s, and 0.9 m^3/s (Seiler, 2000) are lost into the groundwater due to leaks in the water supply systems under the city area. These losses are a significant source of the groundwater recharge under the city (Seiler, 1997).

The sewage water from Caracas is collected in a sewage system, which also leaks. Therefore, under the old and new city areas (Seiler, 1997) the chloride content in the groundwater is higher than in the imported drinking water, which percolates into the ground, and in the natural groundwater recharge. However, the nitrate content in the groundwater under the old parts of the city amounts to only a few milligrams per liter and the water contains some nitrite and ammonium; however, the groundwater under the new city has higher nitrate contents than in the drinking water. This proves qualitatively that denitrification processes effectively occur in the groundwater under the old city and that it has not yet started underground the new city, in spite of comparable pollutant inputs. Obviously, here an incubation time of a few decades is needed to increase the microbiological populations to a degree that considerable denitrification may occur. In both parts of the city area, the mean residence times of the groundwater are consistently around 4–5 years.

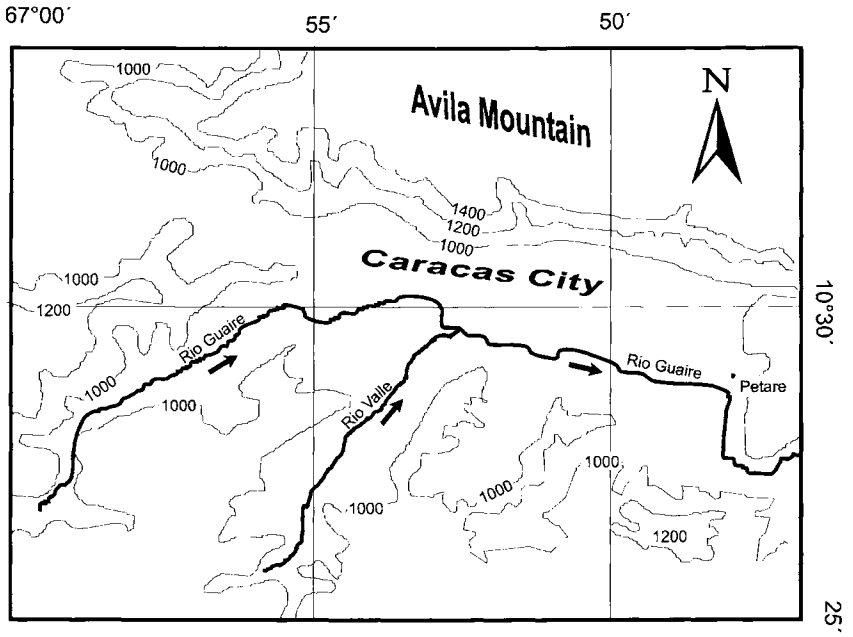


Figure V.4.15. Map of the city of Caracas in Venezuela. The old city lies in the west and the new city in the east.

Both of the examples described above prove that microbiological reactions in groundwater and in aquifers may increase the resilience of the underground system in its decay of pollutants after a specific, yet still not precisely known incubation time. The extent of this resilience will probably

- reflect the intensity of the land use and
- will get limited by too high concentrations of pollutants and an unfavorable chemical environment as well (e.g. low pH).

V.4.7. Concluding remark

The renewable groundwater resources are particularly vulnerable to contamination from anthropogenic sources: nowadays, in parallel with fast growing demand, reduction of drinking water availability due to deterioration of groundwater quality became a serious problem of immediate concern. Solid waste disposal, non-disposal use of chemicals and waste materials on the surface of the land, and long-term wet and dry deposition from high and low emitters are the major categories of sources of groundwater contamination. Soils appear to be not capable enough of binding and holding chemicals applied to their surfaces directly or leached from waste. Where concentrations of leached substances have been encountered in groundwater, they have been orders of magnitude higher than those found in surface water. Their dilution and removal is also much slower than in surface water and may render the groundwater non-potable for the foreseeable future. To safeguard groundwater resources from deterioration, the methods of waste and man-made chemicals management and use have to be thus judicious and effective.

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V.5
Regional prediction of the transport of contaminants from the flotation tailings dam: a case study

Robert Duda

V.5.1. Introduction

General misunderstanding of the groundwater nature and of the impact on its quality, which leachate from bulk industrial waste may cause, has subjected the vast groundwater resource to contamination by many past actions involving the disposal of these wastes on and in the land. The unlined dumping sites/landfills of bulk industrial wastes were predominantly located without any concern about groundwater quality, frequently on sites that are vulnerable to groundwater contamination problems. Over the last decades of the 20th century, reports of groundwater contamination from surface impoundments and landfills had been growing. This has been drawn to the attention of public and environmental agencies of all levels to these sources as areas where the effective control measures are needed. Currently, parallel with efforts to minimize future adverse impacts of industrial waste landfills on groundwater resources, we have to assess and manage environmental consequences associated with past wrong decisions and activities that have long-lasting negative implications.

In the presented case study, these problems are exemplified in the Zelazny Most dam, the biggest industrial landfill (dump) under operation in Europe that for 25 years serves for disposal of copper ore flotation tailings. The area of the dam is 14 km^2, volume, 315×10^6 m^3, and final volume up to 1000×10^6 m^3. A 2D hydrological model for the vicinity of the tailings dam was used as a basic tool for environmental impact assessment, prediction of groundwater pollution and evaluation of methods developed for restricting movements of pollutants and groundwater protection.

V.5.2. Hydrogeological characteristic of the dam area

Tailings from the flotation of copper ores in the Lubin-Glogow Copper District are being collected in the Zelazny Most dam, the biggest industrial waste dump in Europe. It was constructed in 1977 as a field, open and unsealed dam, located in a natural depression within the Dalkowskie Hills (Fig. V.5.1). The hills are a frontal moraine and the

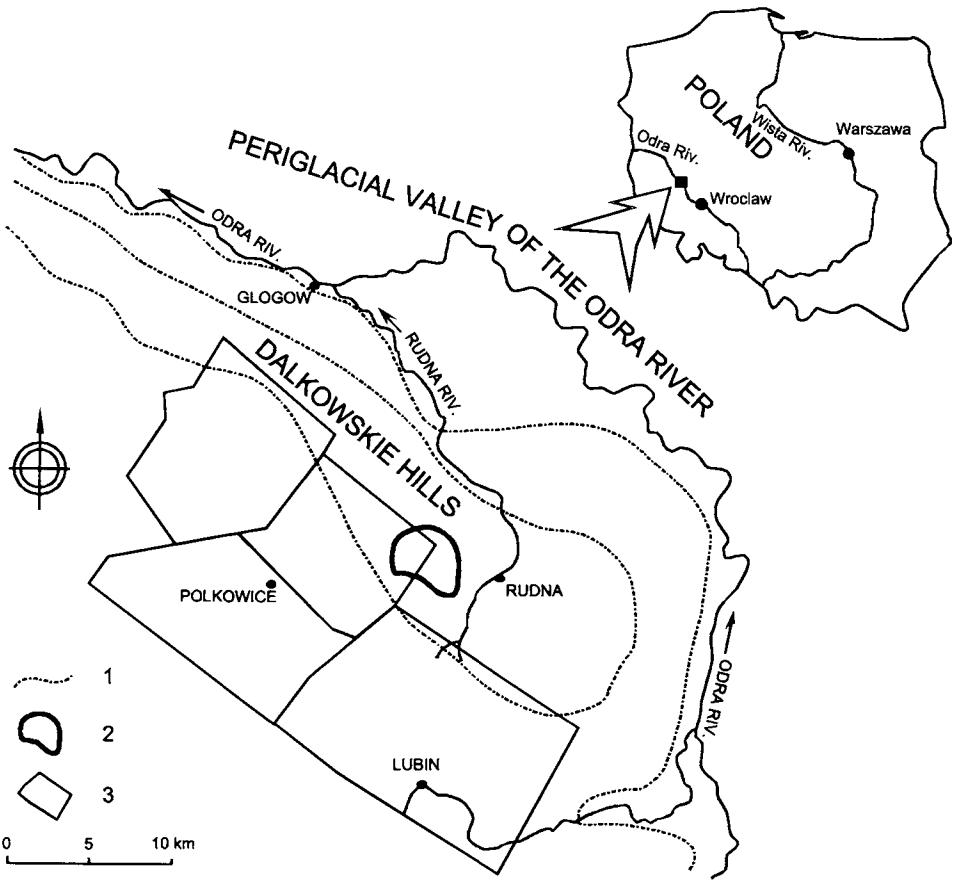


Figure V.5.1. Localization of the Zelazny Most flotation tailings dam. 1 – extent of geographical units, 2 – tailings dam, 3 – extent of mining fields.

depression, which is a melt structure, formed during the glacier recession. Immediately south of the dam area, there is a hill range that is a piled frontal moraine. North of the depression the dam is bordered by glacitectonically piled hill ranges (Fig. V.5.2), separating it from a periglacial valley of the Odra River, further north.

The flotation tailings dam is located on land that was used for agriculture and forestry. The area of a hydrogeological model close to the dam belongs wholly to the left-bank catchment of the Rudna River (Fig. V.5.3), a left-bank tributary of the Odra River.

The surroundings of the tailings dam consist of two areas with different types of geological structure:

- An upland area, situated within the zone of glacitectonic disturbances, confining quaternary and tertiary strata, which form an immediate bedrock of the dam.
- A periglacial valley area, which is probably a glacitectonic depression, later filled by melt and river waters.

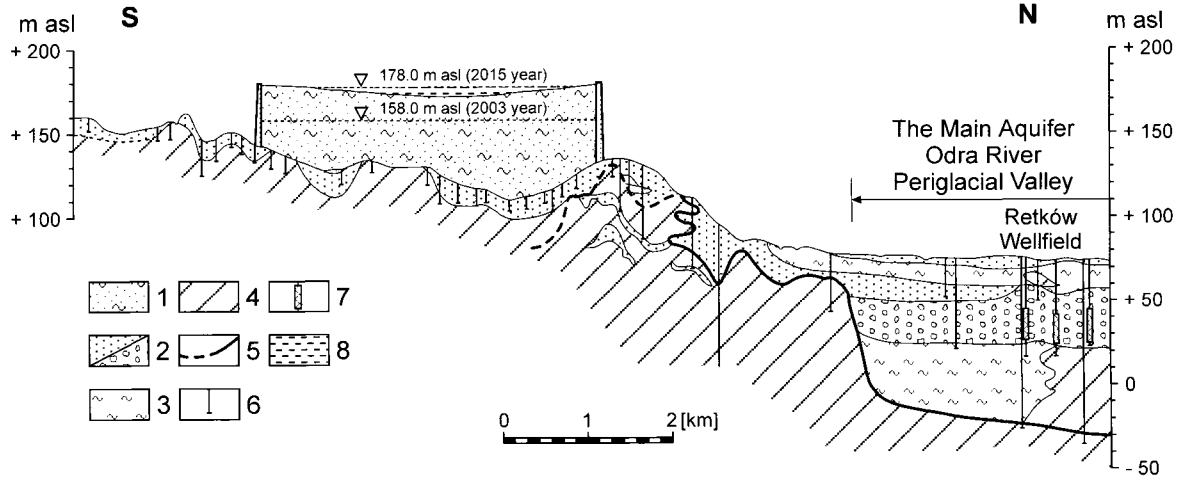


Figure V.5.2. Simplified geological cross-section S-N (the line of cross-section marked in Fig. V.5.3.). 1 – flotation tailings (silts, sandy silts), 2 – permeable rocks (sands, sands and gravels), 3 – semi-permeable rocks (silty and loamy sands, sandy silts), 4 – low-permeable rocks (loamy silts, sandy loams, boulder clays, clays), 5 – inferred boundary of the top of tertiary clays, 6 – piezometers and observation boreholes, 7 – wells of the Retkow well-field, 8 – pond

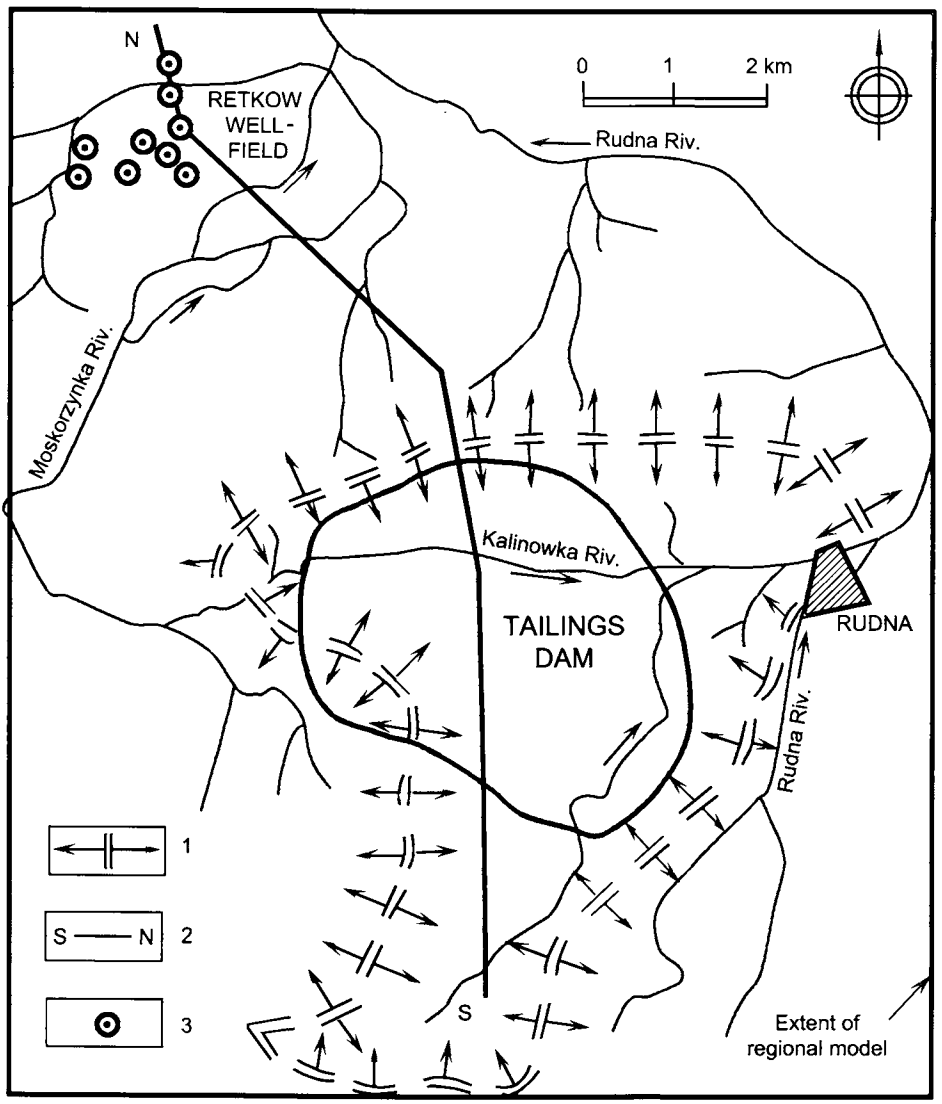


Figure V.5.3. Range of the regional model of groundwater flow in the dam area against hydrographic sketch. 1 – position of a local watershed prior to the construction of the dam, 2 – the line of a simplified geological cross-section S-N from Figure V.5.2., 3 – wells of the Retkow well-field.

Glacitectonic forms are very different, from regular folds to scales and caps, composed both of quaternary and tertiary strata (Fig. V.5.4). Due to the glacier position, their general strikes follow the E–W trend.

The quaternary strata are represented by Pleistocene fluvioglacial deposits and Holocene river and valley sediments. Within the upland area, the Pleistocene deposits are considerably differentiated in their thickness and lithology. They may be from a few to almost 100 m thick (the latter thickness in local potholes), on an average

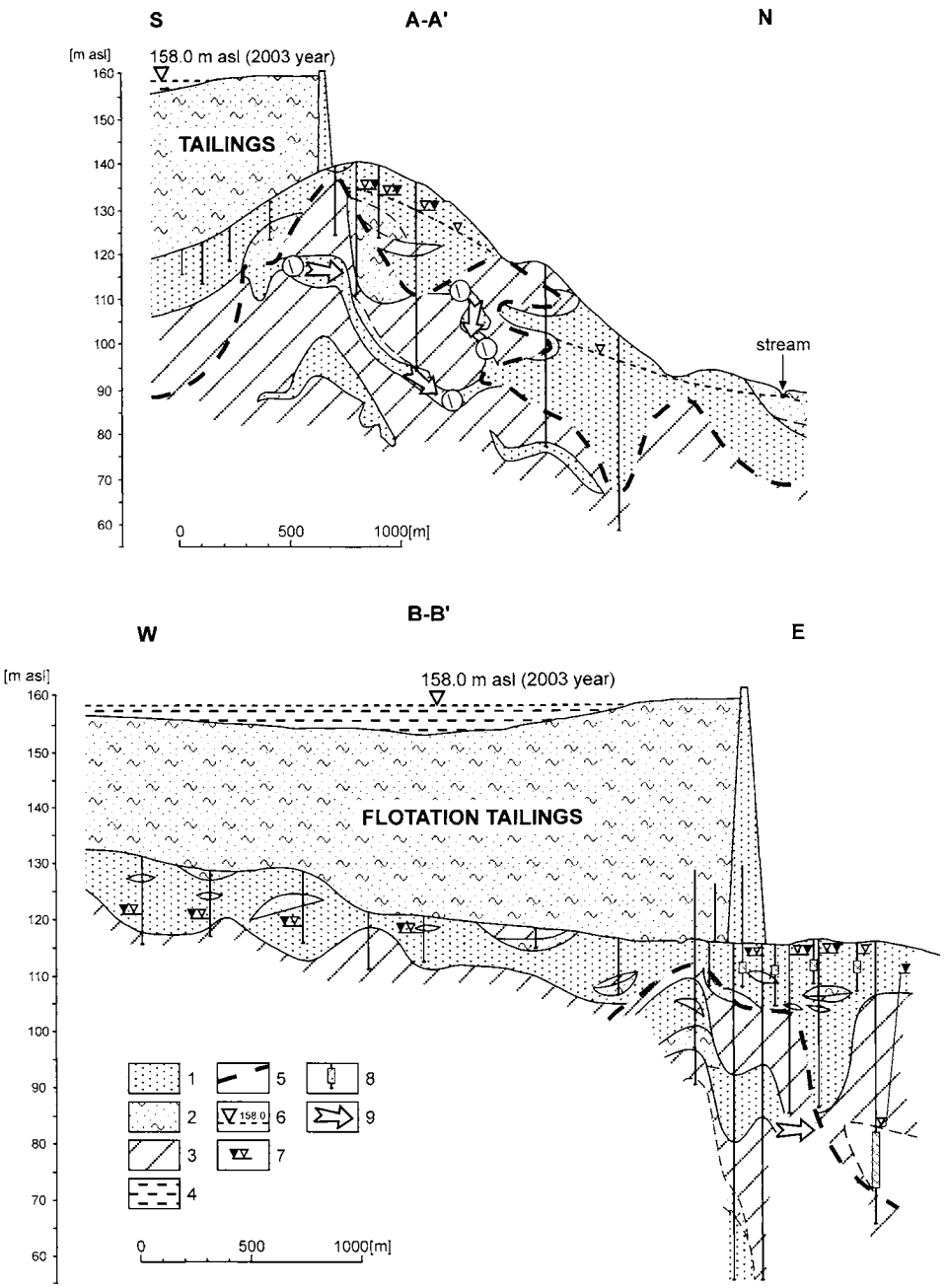


Figure V.5.4. Hydrogeological cross-sections A – A' and B – B' (the lines of cross-sections marked in Fig. V.5.6.). 1 – permeable rocks (sands, sands and gravels), 2 – semi-permeable rocks (silty and loamy sands, sandy silts), 3 – low-permeable rocks (loamy silts, sandy loams, boulder clays, clays), 4 – pond, 5 – inferred boundary of the top of tertiary clays, 6 – datum of the pond lifting, 7 – static and dynamic piezometer head, 8 – piezometers, 9 – supposed paths of groundwater flow.

20–30 m. Boulder clays and fluvioglacial sands and gravels are dominant, while in the periglacial valley the major rocks are sands and gravels 30–40 m thick. The thickness of the tertiary strata is variable, from 160 to 400 m, and consists of muds, clays, sands and gravels, with big lenses and layers of brown coal. The Pliocene strata with a thickness up to 150 m rests on top and generally are developed as clays. In the tailings dam area they are strongly disturbed by glacitectonic movements and can be seen out cropping on the surface or close to it.

In the flotation tailings dam area there are two aquifers: the quaternary, and the tertiary. The aquifers in question are separated by quaternary low-permeable strata, developed as boulder clays, or by Pliocene clays. The continuity of the clays may be glacitectonically interrupted and then an immediate hydraulic contact of the two aquifers is possible. In turn, extrusions of the clays, as well as older boulder clays, on the surface disturb the continuity of the permeable quaternary strata. These phenomena result in a relatively strong differentiation of hydrogeological conditions in most important, with respect to the flotation tailings dam, quaternary aquifer.

Conditions of water migration within the quaternary strata are strongly differentiated on a regional scale. In the periglacial valley there occurs a big and regular basin of groundwater, recognized as one of the major groundwater basins (MGWB) in Poland, i.e. the MGWB No. 314—the Odra River Periglacial Valley, which should be under special protection (Kleczkowski, 1990). It is composed of an aquifer, 30–40 m thick, underlain by almost impermeable strata. The aquifer is built of sands and gravels with high permeability. The mean hydraulic conductivity is 26.4 m/d. The water-bearing layer is directly recharged by infiltrating rainwater plus surface and underground run-offs from the upland area on the south.

In the area of the moraine upland, lithological variations are complicated by glacitectonic disturbances. As a result, irregular water basins with a variable thickness and shapes of glacial troughs, oval ponds and big lenses have been formed. Part of the water flows in a cascade-like manner through successive basins down to the Odra periglacial valley. A continuous aquifer with a thickness up to 35 m, one of a few in the dam area, may be distinguished in the valley, in which the Kalinowka River flowed, prior to the construction of the dam.

The water of the quaternary aquifer, in the dam area is utilized locally as a source of potable and industrial waters. The most important well field (Retkow) is localized within the Odra periglacial valley and has exploitation reserves of 370 m^3/h.

The range of chemical contaminants, penetrating from the Zelazny Most flotation tailings dam to groundwater may be determined if natural, i.e. original, and current, i.e. anthropogenically modified, hydrogeochemical baseline of this groundwater are established. Prior to the construction of the dam, the chemical composition of the quaternary aquifer water was typical for zones with an active water exchange. The characteristic range for the natural baseline of chlorides was 2–10 mg Cl/l, and the total dissolved solids amounted to 200–600 mg/l. Chlorides have been selected as a contamination tracer because of their conservative character; they are neither sorbed nor enter into chemical reactions with the surrounding environment of an aquifer, and thus migrate with the actual velocity of the groundwater flow. Characteristic levels of the current hydrogeochemical baseline for the chloride concentrations in groundwater have been distinguished; they depend on the land use, and range from

20 mg Cl/l for a forest area to 50 mg Cl/l for an agricultural land, and to 85 mg Cl/l for a residential area.

V.5.3. Characteristics of the flotation tailings dam as a source of groundwater contamination

Earth embankments of a local gravel-sandy material were raised in the first phase of the flotation tailings dam construction. They are currently overbuilt with properly selected, coarser sandy fractions of the flotation tailings. In addition to the flotation tailings, copper smelter slag has been used in construction of parts of the dam since 1990. The highest part of the embankment, some 45 m above the local surface level, is situated in the center of the eastern dam section. The exploitation of the Zelazny Most flotation tailings dam is planned to cease with the cessation of copper mining in the Lubin-Glogow Copper District. The flotation tailings dam will then have a volume of 1 billion m^3, i.e. 1 km^3 of disposed tailings. The essential technical characteristics of the dam, in selected time spans, are presented in Table V.5.1 to visualize the rate of its continued filling and the scale of the object.

The dam is filled with silt- and sand-size fractions of flotation tailings, disposed in the form of a pulp with a density of 180–200 g/l. The pulp is discharged from pipes, situated along the dam embankment. Each of the sections forms a discharge zone some 500 m long (Fig. V.5.5), with a beach, composed of the coarsest fractions; some part of the discharged water may infiltrate through the beach. Such a technique creates a pond in the central part of the dam over finer, semi-permeable and low-permeable flotation tailings.

Along the base of the embankment on its outer side, a drainage system was installed to control outflow of excess water seeping through the embankment and the dam bedrock. The system is composed of dewatering ditches (horizontal drainage), supported (since 1996) by a barrier of dewatering wells (vertical drainage). Overflow water is reversed in a hydrotransport circuit, and part of it is periodically discharged to the Odra River.

The overflow water represents saline waters of $Cl–SO_4–Na–Ca$ type, with total dissolved solids content from 15,000 up to 22,000 mg/l. Chlorides, sulfates and sodium are the major components leached from the flotation tailings dam to the water environment. In 2000, the mean concentration of chlorides in leachate was 8800 mg/l, of sulfates 2900 mg/l, and of sodium 5500 mg/l. Such high concentrations of major ions in water

Table V.5.1. Technical characteristics of the Zelazny Most flotation tailings dam.

Parameter	1988	1994	2000	2003	2015
Volume of tailings disposed (10^6 m^3)	144.2	241.3	315.0	350.0	600.0
Dam area (km^2)	11.9	14.0	14.0	14.0	14.0
Overflow pond area (km^2)	6.0	6.1	7.3	≈6.5	≈6.5
Volume of pond water (10^6 m^3)	13.5	10.7	7.5	≈10.5	≈10.5
Datum of the pond lifting (m asl)	140.5	148.2	154.6	158.0	178.0

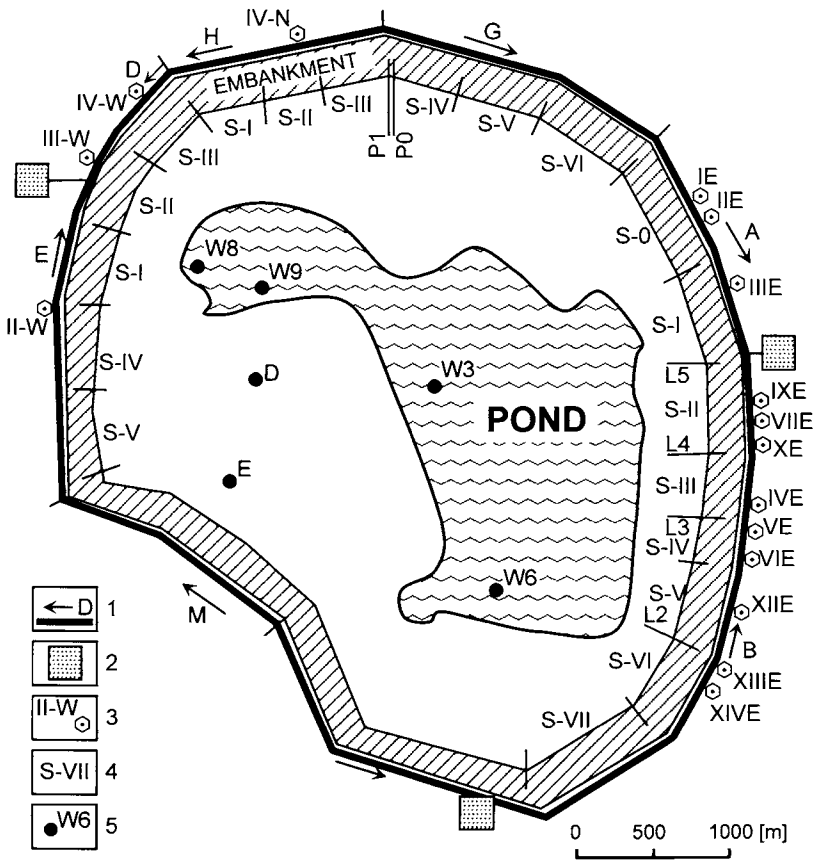


Figure V.5.5. Sketch of the dewatering installation of the dam. 1 – dewatering ditch (arrows indicate water flow direction), 2 – pump stations with water reservoirs, 3 – wells of the vertical drainage, 4 – pipe sections discharging flotation tailings, 5 – overflow spill-towers.

migrating toward the foreground of the dam significantly threaten the quality of the quaternary aquifer whose total dissolved solids content is 200–600 mg/l. The presence of heavy metals in the overflow water is an additional hazard, somewhat retarded due to sorption. The water also contains microelements and contaminants associated with processing of copper ores, and their amounts exceed permitted levels. These substances include detergents, phenols, cyanides, and xanthenes.

The flotation tailings dam also threatens the water environment through infiltration of overflow water with the dissolved chemical substances to the dam bedrock, and further migration of the water toward the dam foreground. The infiltrating saline water degrades the quality of fresh groundwater and also subsequently, surfacewater. The contaminated streams will become a secondary source of groundwater contamination, particularly around the Retkow well field (Duda and Witczak, 1994; Duda et al., 1997).

Saline water migrates within the dam foreground first of all through the uppermost aquifer, although recently a migration through lower lying aquifers has also been noted.

Migration of saline water is the fastest along preferential flow paths in parts of an aquifer with the highest conductivity. Additionally, the spatial distribution of chloride concentration (Fig. V.5.6) results from mixing of the leachate infiltrating from the dam, with the fresh groundwater flowing through the bedrock from hills south of the dam. The

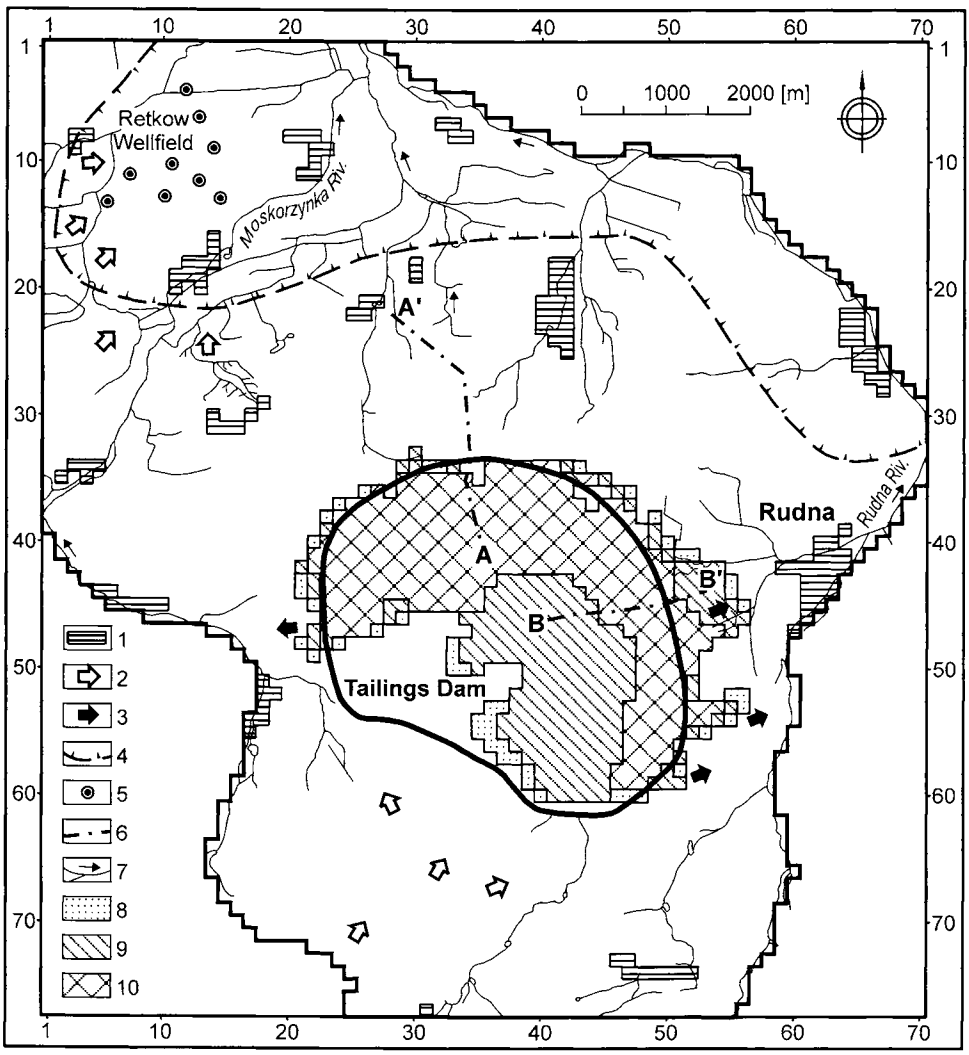


Figure V.5.6. Spatial distribution of the chloride concentration in groundwater assumed in the current prediction for the calibrated (1988) regional model of the dam area. 1 – residential area, 2 – directions of fresh groundwater flow, 3 – directions of contaminants migration from the dam, 4 – the range of the MGWB No. 314 - the Odra River Periglacial Valley, 5 – wells of the Retkow well-field, 6 – lines of hydrogeological cross-sections from Fig. V.5.4., 7 – streams and rivers, 8–10 – spatial distribution of chlorides in groundwater: 100–300 mg/l (8), 300–3,000 mg/l (9), >3,000 mg/l (10).

extent of water contamination in the dam foreground has been determined from chloride concentrations in groundwater. The boundary isopleth has been established at 100 mg Cl/l, i.e. the chloride content in groundwater exceeding the value of the current hydrogeochemical baseline.

The year 1996 has been accepted as a time marker for calibration of a groundwater flow and of a mass transport. At that time the saline water reached a distance from some tens of meters to ca. 900 m from the dam. The extent of the contaminated zone generally agreed with predictions, and was confirmed during monitoring aimed at checking earlier predictions (Duda and Witczak, 1994). The model described here is the fourth attempt to determine the hydrodynamic field in the vicinity of the dam. Such a procedure called a post-audit analysis is indispensable in evaluation of the quality of permanent hydrogeological models.

Within the northern dam foregrounds the propagation of contaminants in groundwater appeared to be smaller than the earlier predictions. But one cannot exclude waters infiltrating from the dam that may appear somewhere further, if remote zones of preferential conductivity are reached. Such a case is quite probable because of a complicated geological structure of the area. If the favorable hydraulic link does exist, a fast water flow to the north must be assumed, as hydraulic gradients along this direction are significant (Fig. V.5.4, $A'-A'$ section).

V.5.4. A model of groundwater flow in the area of the flotation tailings dam

A model of groundwater flow has been created for the area that can be affected by the flotation tailings dam. Two separate problems have been given special attention:

- formation of water seepage through the tailings and into the dam bedrock from the pond and from the beaches;
- a pattern of a regional hydrodynamic field around the dam.

Numerical solution of a differential equation, describing the groundwater flow in a porous medium (Harbaugh, 1992), has been found by a finite difference method (FDM). The applied solution has many references, e.g. Spitz and Moreno (1996) and ASTM (1999). As a tool in preparation and calibration of a hydraulic field model, a MODFLOW program has been selected. This modular, 3D, finite-difference groundwater flow model developed by US Geological Survey has become the most popular hydrogeological model in the world and since 1988 underwent several revisions, MODFLOW-96 (McDonald and Harbaugh, 1996; Harbaugh and McDonald, 1999), and consecutively MODFLOW-2000 (Harbaugh et al., 2000; Hill et al, 2000; Clement, 2001; Mehl and Hill, 2001; Zheng et al., 2001) being the latest versions by 2002.

For this model, a number of groundwater modeling software packages and graphical user interfaces have been elaborated (e.g. Chiang and Kinzelbach, 1998). To use this model, complementary papers about the methodology were also published (Prudic, 1989; Goode and Appel, 1992; Hsieh and Freckleton, 1993). The most recent release based on the MODFLOW model is an integrated Visual MODFLOW Pro 3.0 package that integrates several tools extending calibration techniques, and visualization and animation

capabilities of the model (Waterloo Hydrogeologic, 2003). It has been continuously developed and upgraded, though the basic features of this core, 3D groundwater flow and contaminant transport model remain unchanged.

The MODFLOW is particularly useful in modeling water flow between the cells of a grid, discreting the modeled region in the dam area. Its advantage is in averaging of the hydraulic conductivity values in adjacent cells of the grid as harmonic means (Goode and Appel, 1992). The use of the harmonic means makes possible the best projection of sudden conductivity changes of an aquifer between adjacent cells of the model and of the presence of low-permeable rocks, breaking the continuity of an aquifer within a filtration field.

The 2D, permanent regional model of the dam area with unconfined/confined conditions of the groundwater pressure has been formed for a land tract with a surface of 121 km^2 (10.5 × 11.5 km). This area has been described with a grid of square cells composed of 77 lines and 70 columns; the size of a single cell was 150 × 150 m.

Creation of a conceptual model required certain schematization of the geological structure and hydrogeologic conditions in the vicinity of the dam as well as of technical and technological parameters of its exploitation. A part of the grid cells has been utilized in setting outer and inner boundary conditions. Along the most sections of rivers within the model area, as well as along the girdling ditches, a head-dependent boundary condition has been set, i.e. the condition taking into account the filtration resistance of a stream bottom. The outer boundaries of the area under modeling have been set in some of the cells on distant rivers as a general-head boundary. Along some river sections a constant-head boundary has been set.

The thickness of the quaternary aquifer has been accepted from a geological survey with some modifications in these regions where further hydrogeological or geophysical surveys or observed behavior of groundwater originated from earlier predictions. The thickness of the aquifer has been generally determined as effective, as it is the thickness interpreted without insets of low permeable strata that is partly corrected for non-homogeneity of hydraulic conductivity along the vertical profile of the aquifer. The thickness in question ranges from 1 to ≈ 30 m.

The hydraulic conductivity of sands and gravels of the quaternary aquifer varies from 0.3 m/d to over 20 m/d. These values have been arrived at by a calibration of the transmissivity of the aquifer on the model, the distribution of computed hydroisopleths (groundwater contours) on the model corresponded well with the distribution observed in the field. Basically, the model has not been calibrated through modification of the hydraulic conductivity of aquifers as the latter parameter affects the velocity of a groundwater flow, and – in consequence – also the velocity of contaminant migration.

The transmissivity of the aquifer has been assumed as a product of a mean hydraulic conductivity and an effective thickness of water-bearing strata in each of the cells of the model. A probable distribution of transmissivity of an aquifer over the whole area of the model has been obtained. The hydraulic transmissivity of the aquifer varies from 1 m^2/d to over 300 m^2/d.

The data in the case of an unconfined/confined aquifer have been assumed as:

- data for the surface level in the areas of unconfined conditions; it means that the top of permeable rocks is situated above a stabilized groundwater table;

- data for the bottom of an impermeable horizon, overlaying an aquifer, in the areas of confined conditions.

Recharging of groundwater by rainwater has been calculated for the model from a long-term, mean annual rainfall, being 592 mm for the catchment area of the Rudna River. It has been assumed that introduction of such a long-term means is justified as the model will also be used for long-term predictions. In the model, zones with differentiated permeability of bedrock, morphology and land use have been distinguished. Using a calibration method, it has been assumed that within the upland area composed of rocks with low permeability, about 10% of annual rainfall infiltrates, while this value is about 25% within the flat area composed of permeable rocks and covered with woodlands and meadows. Also some transition regions, with infiltration values between the two mentioned above, have been distinguished.

One of the main criteria of model fitting, understood as a validation analysis of a numerical model quality in respect to field conditions, is a comparative balance of water amounts: those filtrating through tailings accumulated in the dam to those flowing out through girdling ditches and dewatering wells. Also a comparison of amounts of water penetrating into a dam foreground, calculated from the model, with field hydrogeological observations coupled with measurements of a flow velocity rate of saline water infiltrating from a dam outside is an important element of model validation.

The balance of outflow from the embankment drainage and girdling ditches has indicated that approximately 90% of water infiltrating through tailings collects in the ditches (horizontal drainage of the tailings dam). Hydrogeological data have been accepted as reliable for the model validation because water infiltrating into the dam bedrock must appear in proximal or more distant rivers within the boundaries of the catchment area being modeled. The estimated amounts of overflow water infiltrating into the dam bedrock have been compared and balanced against the amount of flow in the drainages and the increased outflow from partial catchments, draining the dam foreground (Table V.5.2, Fig. V.5.7). The total flow in streams in the dam foreground, which is a real measure of the water volume penetrating from a dam into its foreground, has increased at 5024 m^3/d. The correctness of the whole regional model of a hydrodynamic field is reflected in the balance of groundwater computed for the calibrated model (Table V.5.3).

V.5.5. Model of Contaminant migration

In construction of the model of contaminant mass migration in the vicinity of the dam, the modified method of characteristics (MMOC) by Zheng (1993) was selected. The FDM was rejected because of a high probability that a phenomenon of numerical dispersion in the model could occur – a Peclet number was 3.5. The next reason of selection of the MMOC is its good performance in models where a Peclet number ranges from several to some tens, i.e. for the problems with a significant contribution of hydrodynamic dispersion in a solute transport in groundwater (Zheng and Bennett, 1997. The calculations were carried out using MT3DMS – a modular 3D multispecies transport model designed by

Table V.5.2. Model-computed balance of the amounts of overflow saline water and loads of chlorides migrating into the dam foreground.

Datum of the overflow pond lifting		150.2 m asl (in 1996)		158.0 m asl (predicted for 2003)					
Computing scenario		Calibrated model		Scenario A) without the additional vertical drainage		Scenario B) with the additional vertical drainage		C) Difference B − A	
		m^3/d	kg Cl/d	m^3/d	kg Cl/d	m^3/d	kg Cl/d	m^3/d	kg Cl/d
Q_1	Seepage of overflow water into the dam bedrock	21,788	123,102	23971	135,436	25,588	144,572	1617	9136
Q_3	Water drainage by girdling ditches	15,039	–	10,732	–	10,282	–	−450	–
Q_4	Water drainage by supporting system of vertical wells	4030	–	12,746	–	16,237	–	3491	–
Q_5	Ditches and wells recharging from a dam foreground	2306	–	2502	–	2594	–	92	–
Q_6	Amount of saline water migrating into a foreground	5024	28,386	2995	16,922	1095	6187	−1900	−10,735

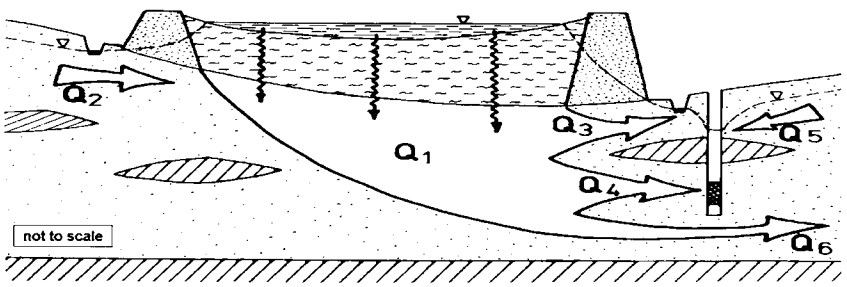


Figure V.5.7. Conceptual model of groundwater flows in the immediate vicinity of the dam. Q_1-Q_6 – water inflows balanced during calibration of the permanent regional model (Table V.5.2.)

Zheng and Wang (1998) and linked with MODFLOW. MT3DMS has been revised; the last upgraded one is MT3D99 (Zheng et al., 2001).

Setting of initial conditions in a mass migration model equals fixing an initial concentration of a tracer in all the cells of a grid at a time for which a model is calibrated. Within the range of observation wells in the dam foreground, the concentration of chlorides has been determined according to field investigations from 1996. In the areas outside the range of the wells, the concentrations of chlorides at the level of the current hydrogeochemical baseline have been assumed, depending on land use (forest, agricultural or residential areas).

In the model of contaminants migration in the vicinity of the dam, only a boundary condition based on a tracer injection concentration was set in those cells where the water flow into the model was known to be positive. It is the inflow computed for the model of groundwater flow from: infiltration of rainwater, seepage of overflow water through tailings, into the dam bedrock, infiltration from rivers into groundwater, and from outer inflows into the model.

The fundamental parameter of migration that characterizes broadening of the front of the contamination plume in a flow of groundwater, i.e. longitudinal dispersivity, was initially determined for the area of the Zelazny Most flotation tailings dam on a basis of an analytical method at 8 m (Maloszewski 1978). Later, an average flow velocity of

Table V.5.3. Groundwater balance for the regional model (relative error = 0.04%).

Balance components	Inflow into the model (m^3/d)	Outflow from the model (m^3/d)
Infiltration of rainwater	20,010	–
Yield of wells exploited within the area	–	4030
Flow across the borders of the model	3850	17,450
Seepage from the dam and into streams and drainage ditches	24,040	26,400
Total	47,900	47,880

groundwater was estimated at 44 m/year and dispersion at 43 m (Szczepinski, 1993). Considering an irregular structure of the aquifer in question, the value of transverse hydrodynamic dispersivity has been assumed as 10% of longitudinal dispersivity.

The value of effective porosity of the sandy strata through which mass migration takes place has been assumed as constant for the whole model and equal to 30%. The value of $R = 1$ for the retardation factor of mass transport has been accepted, while parameters characterizing chemical reactions have been neglected because conservative chloride ion only has been used as a tracer in the current prediction.

A calibrated model of migration of the contaminants tracer in groundwater in the vicinity of the flotation tailings dam can be validated quantitatively in the form of the following mass balance with a relative error of 0.1%:

- injection of a mass into the model – 115,671,769.0 g/d,
- increase of a mass in the model – 16,107,564.0 g/d,
- outflow of a mass from the model – 99,678,312.0 g/d.

V.5.6. Prediction of contaminant migration

Seepage of water into bedrock through the flotation tailings accumulated in the dam is one of the fundamental elements of the model. This process has been modeled considering:

- the durations of tailings discharge and the ranges of a shoreline of the overflow water pond during exploitation of the dam in 1985–1996,
- a 2D profile model of water seepage through the flotation tailings, combined with a water flow through an unsaturated zone as a basis of assumptions, to construct a regional model as the part of the dam itself.

The relationships and processes obtained for the profile model of water infiltration into flotation tailings and for its seepage through the tailings into an aquifer (Fig. V.5.8) indicate an important role of filtration through the most permeable part of a beach being formed. The seepage into bedrock has been simulated accepting head-dependent boundary conditions.

The whole process of seepage of overflow water through flotation tailings into the dam bedrock can be subdivided into three components:

- infiltration of pond water (i.e. overflow water) through the bottom of the pond;
- infiltration of water discharged together with tailings through the beach being formed;
- infiltration of rainwater through beaches during breaks between successive tailings discharges.

Infiltration is more intensive close to the embankment where the hydraulic conductivity is the highest. The beach is being formed through sedimentation and the coarsest fractions gather near the outlets of the discharging pipes. However, the process is additionally complicated by a continuous growth of a tailings pile, at about 1.3 m per year, and the resulting consolidation. The permeability of tailings decreases in deeper parts of the dam, and an excess of pore water is being squeezed out of the accumulated tailings.

Besides technological parameters, infiltration of water from the dam surface through tailings depends on the random character of natural conditions. The flow in the Odra River,

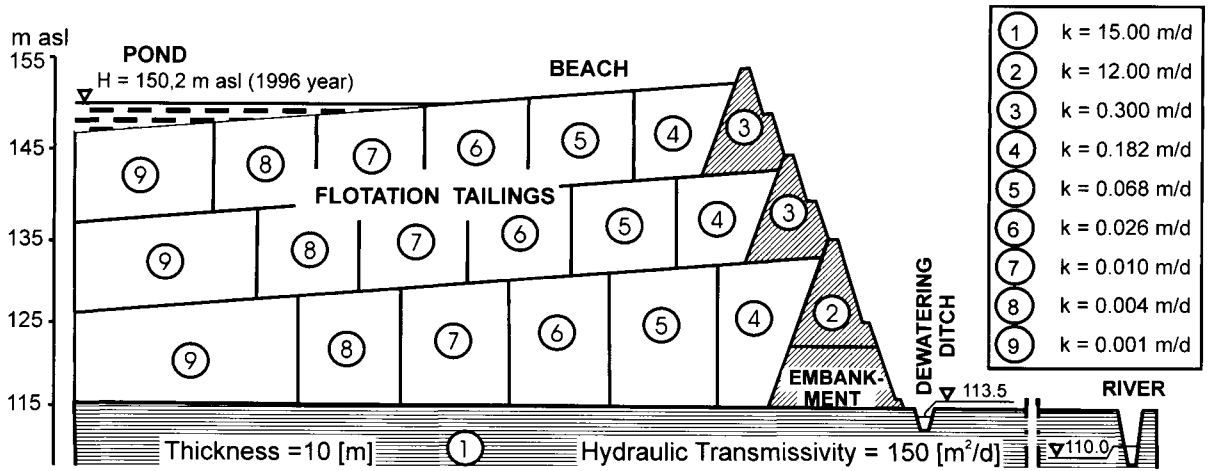


Figure V.5.8. Conceptual model of the hydrodynamic field within a part of the flotation tailings dam and its bedrock created for modelling of overflow infiltration trough the vadose zone in the tailings. 1 – hydraulic conductivity of an aquifer in the dam bedrock, 2–3 – hydraulic conductivities of materials, used in the construction of embankments, 4–9 – hydraulic conductivities of flotation tailings.

which controls the discharge of overflow saline water from the Zelazny Most dam, depends randomly on meteorological conditions. Low river water levels make impossible discharging of higher amounts of water from the dam, lifting in consequence the datum of the pond. As a result, the beaches are inundated and more water seepages into the dam bedrock. The shoreline of the dam is also of random character. This means that technological processes within the dam, despite their controlled regime, may and should be treated as random variables in a prognosis because it is not possible to accept that the shoreline will be maintained in a constant distance from the embankments. The distribution of changes of the shoreline (Fig. V.5.9) indicates that the horizontal range of beaches oscillates from -270 to $+270$ m around a mean value with a probability of 90%.

The probability cited on the axis of ordinates may be treated as a fraction of time during which a given part of the beach is inundated. The distribution obtained for selected cells of the model which simulate the Zelazny Most dam, has allowed determination of the fraction of time when water infiltrates through the cell surface into the bedrock. As it is a random process, a mean annual infiltration resulting from oscillations of the shoreline may be computed in the same way as the rainfall: by multiplying the infiltration rate by a relative time during which a single cell of the model is inundated. The predicted range of the pond has been averaged from the mean water levels, observed every 6 months during 1985–1996.

Seepage of water during discharges of tailings into the dam is more complex. Water freely flows along the surface of the beach, fully wetting its surface but not exerting any overpressure. Vertical modeling of the dam in a period of such a discharge indicates that infiltration of water into the bedrock is particularly intensive, in beach zones situated close

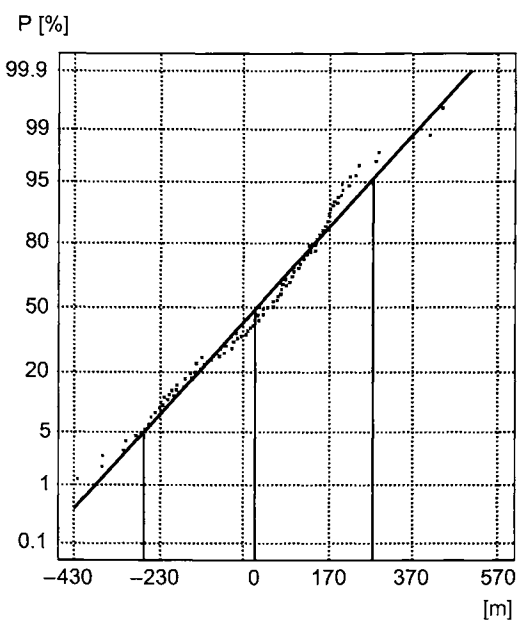


Figure V.5.9. Probability graph of deviation of a shoreline of the pond from the mean value for individual sections.

to the embankments, as the hydraulic conductivity of the tailings is the highest in this area. Predictive computations have been carried out, with a certain simplification, assuming that all the discharging sections were active during the same time, i.e. 8 weeks in a year.

Seepage of rainwater into sediments within a beach zone takes place effectively only during a period between successive discharging campaigns. The value of this infiltration is many times smaller from infiltration of water discharged in the form of a tailings pulp. Therefore, the rainfall infiltration has been disregarded in calculations, assuming that it does not exceed the limits of the computing error. Therefore, two superimposing processes have been modeled:

- water seepage through the bottom of the pond, periodically inundating the beaches of the Zelazny Most dam;
- water infiltration through the beach being formed, i.e. during tailings discharges.

These processes are time-variable, therefore it has been assumed that the cells of the model that are inundated for more than 50% of time are treated in calculations as permanently covered by water, while the cells inundated for less than 50% of time as permanent beaches.

The hydrodynamic field has been predicted in the model for steady-state conditions, associated with the assumed data of pond lifting. It is a simplification, as – in fact – conditions of a pond lifting and collecting of tailings within the dam area are not transient, accepted as permitted with regard to small changes of the hydrodynamic field within the foreground of the dam in the prognosed time span. Such a situation is caused by the drainage around the dam embankments, which collects approximately 90% of water infiltrating from the dam into its bedrock.

In the prediction, the hydrodynamic field from the year 1996 has been calibrated for a pond lifting datum of 150.2 m asl. According to a current extension variant of the Zelazny Most tailings dam, a predicted pond lifting datum of 158.0 m asl for the year 2003 has been accepted.

The following concentrations of chloride injection have been assumed when predicting mass migration of the contaminant:

- within the area of seepage of overflow water into the dam bedrock – 7000 mg Cl/l;
- within the areas of infiltration of rainwater through the soil and vadose zone – 20 mg Cl/l for forested land, 50 mg Cl/l for an agriculturally used land, and 85 mg Cl/l for a residential area,
- within the areas of water infiltration from streams into an aquifer in the Retkow well field region – the value calculated from a mass balance of contaminants being transported in proximal rivers.

The process of mass migration of contaminants in groundwater has been simulated as a transient one on a basis of a steady-state hydrodynamic field. As the changes of the hydrodynamic field pattern within the dam foreground were small, the process, which in fact is transient, has been split into two periods, each treated as one with a steady-state hydrodynamic field. The prediction has been calculated for two scenarios: with and without a supportive vertical drainage in the form of dewatering wells.

The Zelazny Most flotation tailings dam has got real chances to be a dump with a closed circulation of technological water because of a natural flow pattern toward the dam and

along its embankments (Fig. V.5.3). Thus, it is necessary to strengthen the drainage close to the embankments in such a way that the natural flow directions of groundwater in the area is reconstructed and maintained (Witczak and Duda, 1995). This may be accomplished through keeping a proper level of the groundwater table in the immediate foreground of the dam, i.e. the level that was observed in the area of the dam embankments prior to their construction in 1977. Among some technical means to lower the water table, a supportive vertical drainage with dewatering wells has been recognized as the most suitable. It is an active method of controlling migration of contaminants outside a dam area (Nawalany et al., 1992).

The error that results from splitting of a longer time period, during which migration is transient, into two shorter, steady-state periods is reflected by the shape of breakthrough curves for chlorides. The curves, observed in points localized along particularly important migration paths within a model, depart from smoothed lines (Fig. V.5.10). However, the general trend of chloride concentrations growing in time is preserved with accuracy. The predictive simulation gives also visualization of a spatial distribution of a tracer concentration until the year 2003 (Fig. V.5.11).

Predictive simulations for the scenario without an additional vertical drainage have shown that infiltration of overflow saline water into a tailings dam foreground at a datum of 158.0 m asl will be equal to 2995 m^3/d (Table V.5.2, Fig. V.5.7). Most of the water will be collected by the horizontal drainage of the embankments supported by system of vertical wells, thus lowering the hazard of groundwater contamination. Infiltration into a foreground will decrease to 1095 m^3/d for the scenario with an additional vertical drainage. The relatively biggest outflows should be expected in the areas where a bedrock aquifer close to the embankments is contained by low permeable rocks, making the drainage by girdling ditches ineffective.

Water migrating into the dam foreground, particularly through such zones of ineffective drainage, may be captured substantially by the vertical drainage system, as it has been simulated in the second scenario. The vertical drainage will also eliminate artesian conditions in the bedrock that are unfavorable for the stability of embankments and hinder possible use of the dam foreground because of bottom flooding. However, most of the saline water that reached the foreground before the vertical drainage barrier was active, will not be stopped and will flow away according to a pattern of groundwater movement. Another advantage of the dam vertical drainage will result in lowering of the range and concentration of secondary contamination sources. This problem is particularly important for the Retkow well field, threatened by secondary contamination by pollutants carried by rivers.

According to predictive simulation for both scenarios, migration of contaminants from the Zelazny Most tailings dam should not directly pollute the Retkow well field unless its groundwater is extensively exploited. More hazardous for the well field is a secondary contamination from surfacewater, as a substantial amount of the Retkow water reserves is formed by infiltration from proximal streams and rivers. The computation has shown that the Moskorzynka River, close to the intake area, will be saline at the mean low streamflow, i.e. the one used in the prediction of contamination: for the first scenario at 2630 mg Cl/l, and for the second one at 1030 mg Cl/l. One of the tributaries of the Moskorzynka River flows across an area reached by migrating saline waters from the tailings dam.

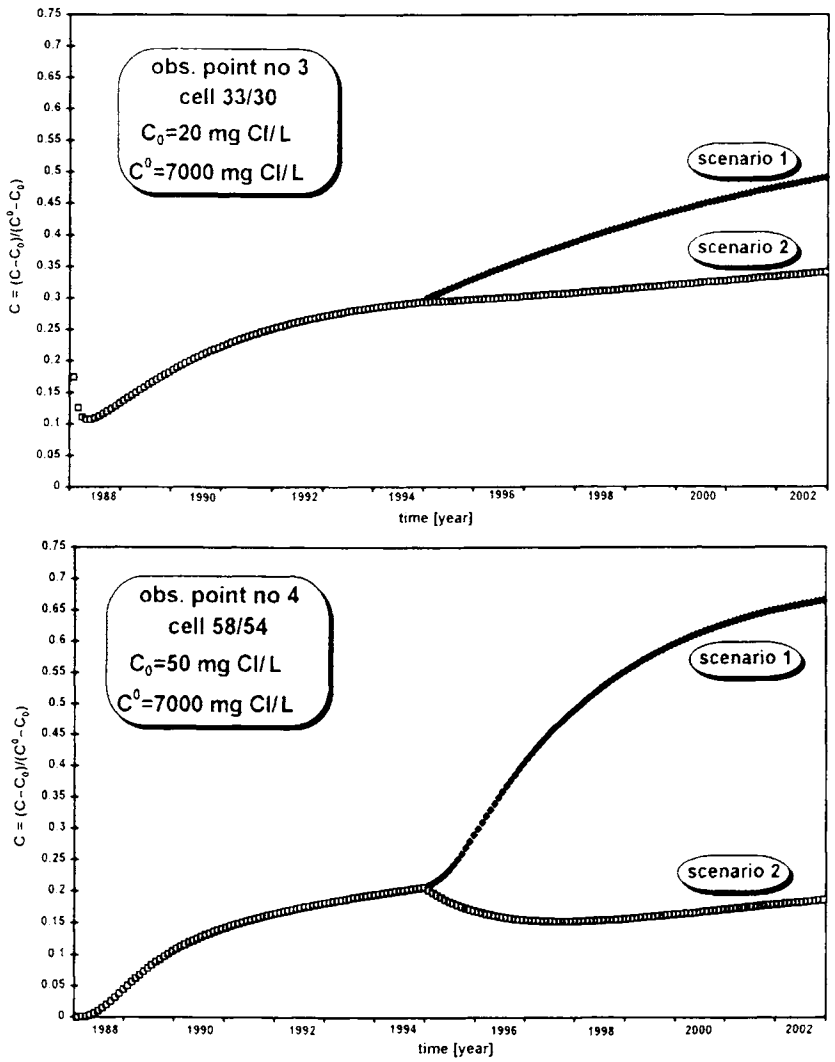


Figure V.5.10. Predicted changes in the concentration of a chlorides in the years 1988–2003 in the selected observation points (localization of the points indicated in Fig. V.5.11.). C_0 – concentration of chlorides for the current hydrogeochemical baseline, C^0 – concentration of a chloride injection.

The likelihood of the hazard predicted for the Retkow well field depends on the proper recognition of water pathways within the western foreground of the flotation tailings dam. The prediction is based on the assumption that within semi-permeable and low-permeable rocks dominating in the area, there are permeable zones facilitating migration of saline waters from the dam. Hydrological measurements have indicated an increased discharge from springs and flow in streams, both observed during calibration of the model and later

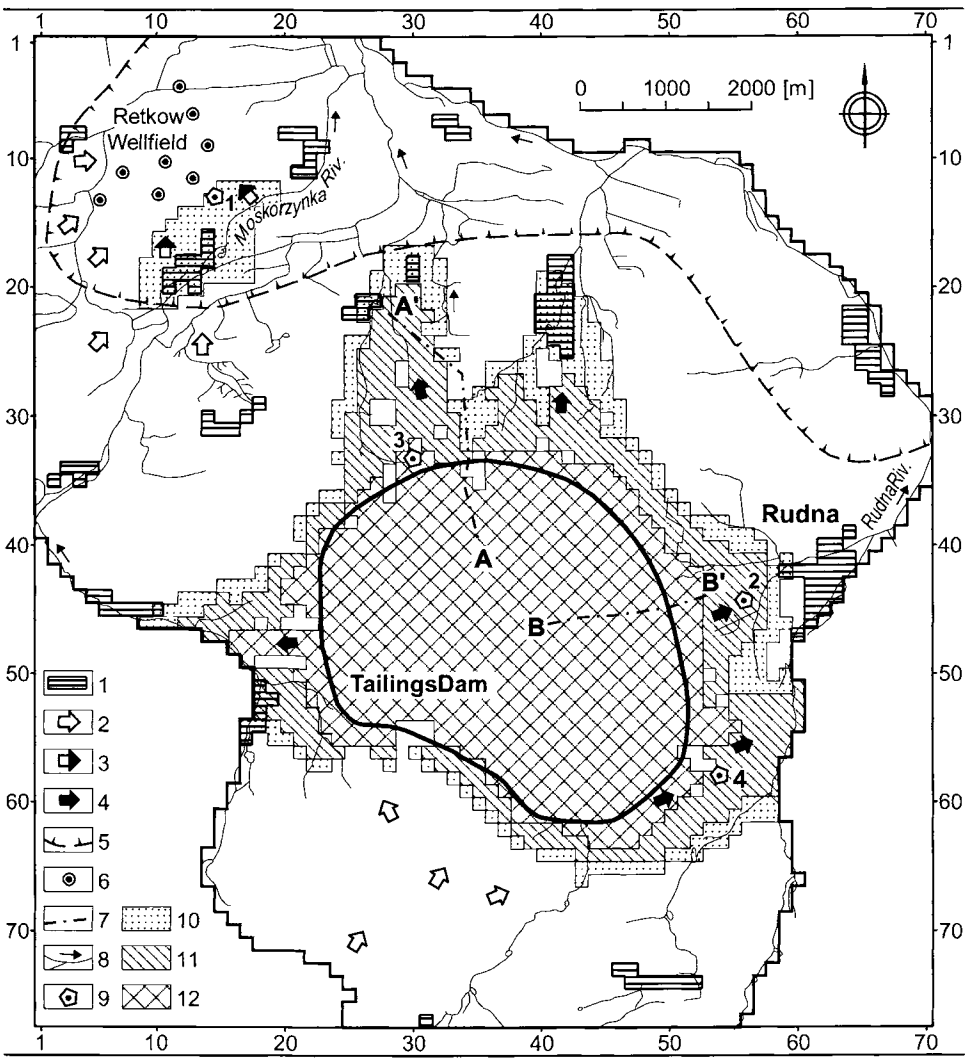


Figure V.5.11. Prediction of chloride migration in groundwater in the dam area for the year 2003 (datum of the pond 158 m asl); the scenario assuming an additional vertical drainage. 1 – residential area, 2 – directions of fresh groundwater flow, 3 – directions of migration from secondary contaminant sources (rivers carrying contaminants originating at the dam), 4 – directions of contaminant migration from the dam, 5 – the range of the MGWB No. 314 – the Odra River Periglacial Valley, 6 – wells of the Retkow well-field, 7 – lines of hydrogeological cross-sections from Figure V.5.4., 8 – streams and rivers, 9 – localization of the observation points from Figure V.5.10., 10-12 – predicted spatial distribution of chlorides in groundwater: 100–300 mg/l (10), 300–3,000 mg/l (11), > 3,000 mg/l (12).

on. The effect has been accepted as resulting from migration of saline water from the dam. Saline Water migrating northward from the flotation tailings dam, may probably contaminate fresh water within a south part of the groundwater basin No. 314 – the Odra River Periglacial Valley.

V.5.7. Conclusion

The presented prediction of contaminants migration in the area of the Zelazny Most flotation tailings dam indicates that only lowering of the groundwater table level close to the dam embankments, resulting from vertical drainage by dewatering wells, may limit propagation of contaminants in groundwater around the dam. This limiting will be based on reconstruction of watersheds existing there prior to the construction of the dam, and on directing the groundwater flow toward the dam or along its embankments, as the two processes will cause that the hydraulic system of circulation of technological water will be closed. The dam itself is and will remain, however, a permanent source of contamination, hazardous directly for groundwater of the region and indirectly for stream waters.

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Twardowska, Allen, Kettrup and Lacy (Editors)
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V.6

Design of a groundwater protection system at an inactive hazardous waste disposal facility: a case study

Amar C. Bumb

V.6.1. Introduction

Once contamination is discovered, various remedial alternatives are evaluated for protection of human health and the environment, cost effectiveness, implementability, short-term and long-term efficiency, permanence, and public acceptance. One of the major pathways for contaminants to reach receptors is to be leached out of waste and reach groundwater, which is then consumed by the receptors. Other pathways may include direct contact, ingestion, and inhalation. This chapter describes an improved containment and capping remedy to protect groundwater where a secondary slurry wall, called curtain wall, was used to reduce overall remediation costs by approximately $1.7 million over the conventional remedy.

Remedial alternatives considered at a hazardous waste landfill to protect groundwater typically include natural attenuation (i.e. no further active remediation), containment and capping, excavation/treatment/disposal, *in situ* treatments, or a combination of these options. Natural attenuation may include a long-term monitoring program to ensure that groundwater is protected. Containment and capping protects groundwater by reducing rainfall infiltration and isolating wastes by placing hydrologic barriers between waste, groundwater, and receptors. The excavation/treatment/disposal alternative requires excavation and treatment of waste to achieve waste acceptance criteria of the disposal facility or backfilling before final disposal. A number of treatment technologies are available based on the contaminants of concern. Treated waste may be disposed off-site or on-site. *In situ* treatment may include technologies such as solidification/stabilization, vitrification, geochemical treatment, soil vapor extraction, air sparging, enhanced bioremediation, and soil washing.

Modeling can be used to determine remedial goals protective of groundwater, evaluate future effectiveness, and design selected remedial actions. Modeling can involve evaluation of hydraulics of groundwater flow alone (Dorrance and Chang, 1991; Bumb et al., 1996a) or performing coupled fate and transport analysis (Berglund and Cvetkovic, 1995; Johnson and Rogers, 1995; Bumb et al., 1996a,b). This chapter uses evaluation of groundwater hydraulics to design a groundwater protection system at an inactive hazardous waste landfill in Northeast United States of America where containment and

Groundwater Flow
N
Subdrain pipe
2000 ft
Perimeter slurry wall
Extent of contamination
DNAPL
DNAPL
DNAPL
DNAPL
DNAPL
600 ft
600 ft
200 ft
Curtain wall
Current Shoreline
Groundwater Collection Trench
Wet well
River

Figure V.6.1. S

capping was the selected remedy. Only a simplified general layout is shown in Figure V.6.1 to avoid revealing the location of the site.

V.6.2. Background and assumptions

The remedial objective of containment/capping is to protect groundwater and direct contact with waste and contaminated water. Design of a containment/capping remedy to be protective of groundwater is illustrated by the following example. Figure V.6.1 shows the general layout of an inactive landfill and groundwater flow patterns. The uncontrolled landfill is approximately 600 m × 240 m (2000 ft × 800 ft) in size and is located just north of a river. Site investigation revealed that the landfill was used to dispose industrial waste containing chlorinated hydrocarbons, pesticides, PCBs, and metals. Dense non-aqueous phase liquids (DNAPLs) were found within the landfill at local depressions in the underlying confining unit, a clay aquitard (see a generalized cross-section in Figure V.6.2). Distribution of DNAPL and extent of contamination as determined from site investigations are shown in Figure V.6.1. Design is based on the results of site investigation.

Shallow groundwater flows from north to south and discharges into an adjacent river. The saturated thickness of the aquifer at the site ranges from 3 to 4.6 m (10–15 ft). The top of the clay aquitard (clay) is relatively constant with some local depressions. All elevations are referred with respect to the average elevation of the top of the clay under the landfill (see Figure V.6.2). The clay aquitard is relatively thick and has low permeability. Site investigations indicated that contaminants have not migrated more than 0.3 m (1 ft) into the clay.

The basic elements of a typical containment/capping remedy at a hazardous waste landfill include a cap over the landfill, a soil/bentonite[1] perimeter slurry wall keyed into the underlying impermeable layer, and a groundwater collection system. The objectives of a groundwater collection system were to create and maintain an inward gradient across the perimeter slurry wall at the landfill, minimize the potential for off-site migration of contaminated groundwater through the perimeter slurry wall, and minimize the potential for contaminant migration through underlying formations. A secondary slurry wall, referred to as "curtain wall", has been added in this remedy to more effectively create and maintain an inward gradient across the perimeter slurry wall and to reduce the volume of groundwater that is recovered and treated.

The inward gradient across the perimeter slurry wall could be achieved by reducing the static groundwater level inside the perimeter slurry wall and the curtain wall to at least 0.3 m (1 ft) below the minimum river elevation and the natural groundwater levels outside the perimeter slurry wall. Once this level is attained, inflow will consist of water from the following sources:

- precipitation infiltration through the landfill cap,

[1] Bentonite is highly colloidal, plastic clay first found near Fort Benton, WY, in cretaceous beds. It has unique characteristic of swelling to several times its original volume when placed in water and it forms thixotropic gels with water.

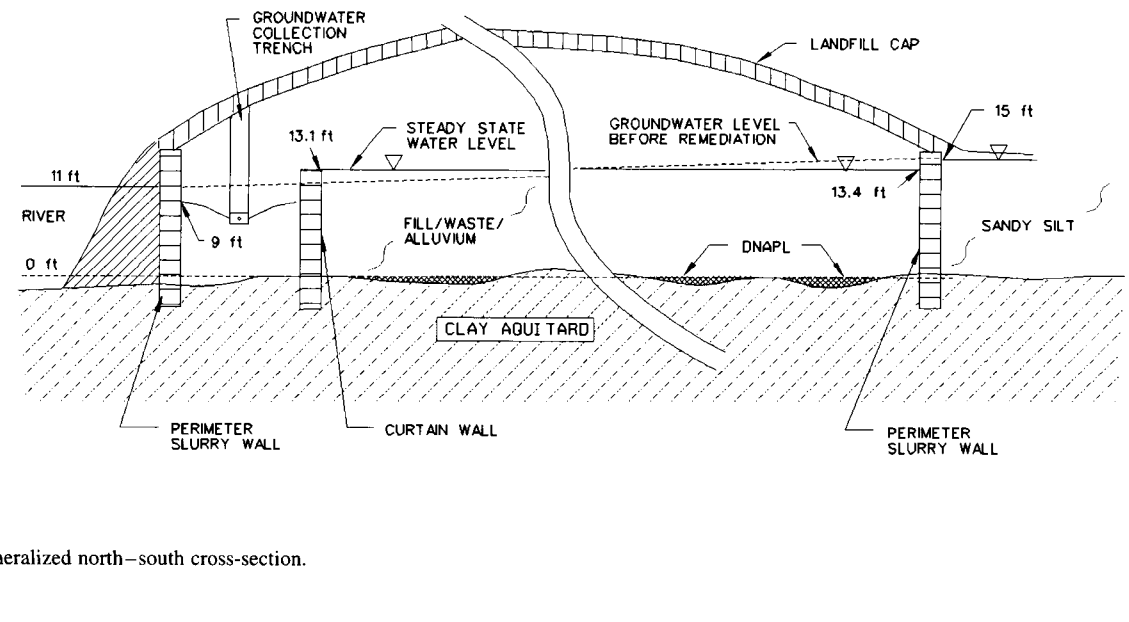


Figure V.6.2. Generalized north–south cross-section.

- groundwater infiltration through the perimeter slurry wall, and
- groundwater infiltration through the clay under the perimeter slurry wall.

A volume of water equal to the infiltration listed above must be pumped to maintain these steady-state water levels. Each of the water sources must be evaluated to estimate steady-state pumping requirements. Conservative assumptions are typically made to estimate maximum infiltration. The following assumptions were used in the calculations:

- The average width of the perimeter slurry wall is 0.9 m (3 ft).
- The average hydraulic conductivity of the perimeter slurry wall is 1×10^{-7} cm/s.
- The average hydraulic conductivity of the underlying clay is 2×10^{-7} cm/s.
- The minimum river elevation is 3.0 m (10 ft) with respect to the top of clay.
- The average river elevation is 3.35 m (11 ft) and significant extended variations from this level do not occur.
- A minimum of 0.3 m (1 ft) differential in water levels should be maintained across the perimeter slurry wall. This essentially means that water level elevations between the perimeter slurry wall and the curtain wall should be maintained at approximately 2.75 m (9 ft).
- The area enclosed within the perimeter slurry wall is approximately 149,000 m^2 (1.6 million square feet).

Installation of the perimeter slurry wall will change the groundwater flow pattern outside the encapsulated landfill and result in groundwater level increase just north of the landfill. The extent of the groundwater mounding was evaluated with the help of a finite-difference model based on the United States Geological Survey modular flow model, known as MODFLOW (McDonald and Harbaugh, 1999; Harbaugh et al., 2000; Mehl and Hill, 2001; Zheng et al., 2001; see also Chapter V.5). Calculations indicated that significant mounding could take place. A subdrain pipe (Fig. V.6.1) was added to the remedy to relieve groundwater mounding north of the landfill.

V.6.3. Curtain wall

If a perimeter slurry wall alone is installed and groundwater is pumped to maintain an inward gradient, water levels within the landfill will continue to decline until steady-state water levels (approximately 2.75 m (9 ft)) are attained. A curtain wall has been included in the remedial design to reduce water recovery and treatment, and to minimize contaminant concentrations in the extracted water by isolating DNAPL contaminated soils.

To maintain the inward gradients across the perimeter slurry wall, water levels between the perimeter slurry wall and the curtain wall will be maintained approximately 0.3 m (1 ft) below the lowest river elevation and the natural groundwater levels outside the perimeter slurry wall. Water levels within the curtain walled area may remain at a higher elevation. This will reduce water treatment requirements.

A minimum distance of 9 m (30 ft) is required between the perimeter slurry wall and the curtain wall to allow construction of the groundwater recovery system. Therefore, the curtain wall is located 9 m (30 ft) north of the south slurry wall. The top of the curtain

wall, 4.0 m (13 ft), is set at the average water level between the south curtain wall (3.4 m (11 ft)) and the north slurry wall (4.6 m (15 ft)) so that all the water initially in the area contained within the curtain wall will stay in that area. Once all the remedial actions have been implemented, water levels within the curtain walled area should equilibrate to a nearly flat surface due to the bathtub effect (see Appendix A). Water levels north of the perimeter slurry wall are approximately 4.6 m (15 ft). Therefore, a curtain wall is not required on the north side. Similarly, the curtain wall is not required for the northern 60 m (200 ft) segments of western and eastern parts of the slurry wall. The proposed location of the curtain wall is shown in Figure V.6.1.

V.6.3.1. Reduction in initial water treatment requirements

The alluvium and fill in the landfill will gravity drain from initial water level to final water level after the perimeter slurry wall, curtain wall, and cap are constructed. Water content of the drained alluvium and fill will decrease from full saturation (total porosity) to the field capacity. The difference between total porosity and field capacity is the specific yield. The specific yield of the alluvium/fill was assumed to be 25%. Therefore, the volume of groundwater to be pumped initially, in excess of additional infiltration, to achieve steady-state groundwater levels is calculated by:

$$\text{Volume} = (\text{Area}) \times (\text{Average Head Difference}) \times (\text{Specific Yield})$$

Note that this estimate does not include infiltration to the encapsulated landfill as calculated later.

If curtain wall is not installed, the average water level of 3.96 m (13 ft) inside the perimeter slurry wall would be reduced to the steady-state water level of 2.75 m (9 ft). The total area enclosed within the slurry wall is 149,000 m^2 (1,600,000 ft^2). Therefore, the total volume of water to be pumped to achieve steady state is then estimated to be 45,400 m^3 (12,000,000 gal).

When the curtain wall is installed, all the groundwater initially in the area contained within the curtain wall will stay in that area (as per the design of the top of the curtain wall). Therefore, only groundwater in areas on the south, east, and west between the curtain wall and the perimeter slurry wall needs to be lowered to 2.75 m (9 ft). It represents an area of 9000 m^2 (94,000 ft^2) and amount of water to be pumped to achieve steady state is estimated to be 1700 m^3 (460,000 gal). Therefore, installation of the curtain wall results in reducing initial water treatment requirements from 45,400 m^3 (12 million gallons) to 1700 m^3 (0.46 million gallons), i.e. a reduction of 43,700 m^3 (11.5 million gallons) or a 96% reduction. Using calculations similar to that presented later, it can be shown that 16% reduction in steady-state water treatment requirements is also achieved as gradients across the perimeter slurry wall are reduced.

Using a water treatment cost of $53 per cubic meter (20 cents per gallon), reduction of groundwater pumping by 43,700 m^3 (11.5 million gallons) results in reducing water treatment costs by $2.3 million. The cost of installing a 957 m (3140 ft) long by 5 m (16.4 ft) high curtain wall (including 1 m tie-in) is estimated to be approximately $600,000. Therefore, a net cost reduction of $1.7 million is achieved by installing the curtain wall.

V.6.4. Water balance within the curtain wall

The inflow to the area within the curtain wall then consists of:

- surface water infiltration through the cap,
- groundwater infiltration through the northern portion of perimeter slurry wall, and
- groundwater infiltration beneath the northern portion of perimeter slurry wall.

The outflow from the curtain walled area consists of movement through and under the curtain wall and any overflow.

V.6.4.1. Infiltration through the cap

Infiltration through the cap was estimated using the Hydrologic Evaluation of Landfill Performance (HELP) model (Schroeder et al., 1988; Scientific Software Group, 2003) for two landfill cap designs shown in Figure V.6.3. Both designs are similar except "Alternate A" incorporates a 30 cm (12 in.) silty clay layer under a 60 mil very low density polyethylene (VLDPE) or equivalent liner while "Alternate B" uses a prefabricated geosynthetic clay liner, with maximum permeability of 1×10^{-9} cm/s, under a 40 mil VLDPE or equivalent liner. The "topsoil" was simulated as sandy loam, "select fill" was simulated as silty loam, and the geotextile/geonet layer was simulated as a 2.5 cm (1 in.) layer of coarse sand with a hydraulic conductivity of 1×10^{-2} cm/s. Soil properties were taken from Rawls et al. (1982) and the HELP model documentation. A hydraulic conductivity range of 10^{-5}–10^{-6} cm/s was used for the silty clay layer.

An intact liner does not allow any water to infiltrate. However, liners are known to develop small leaks during installation and due to differential settling over its life. The number of leaks is a function of the method of installation, construction material used, waste in the landfill, and quality assurance/quality controls used. Thick liners are expected to develop a smaller number of leaks than thin liners. The "Alternate B" liner was assigned a leakage factor of 0.01 (maximum value of typical range), which corresponds to leaks in the liner on an approximately 15 m (50 ft) square grid. This is a conservative assumption that results in overestimating the seepage through the cap. The 60 mil VLDPE liner ("Alternate A") was assumed to develop fewer leaks and therefore was assigned a leakage factor of 0.003, which corresponds to leaks on an approximately 30 m (100 ft) square grid. Average climatological data for the local area were used as input to the HELP model. The area enclosed by the curtain wall is approximately 140,000 m^2 (1,506,000 ft^2).

For "Cap Section – Alternate A" (Fig. V.6.3), the HELP model calculated infiltration of 8300 liters per day (l/d) (2200 gallons per day (gpd)) through the cap using a hydraulic conductivity of 10^{-5} cm/s for the silty clay layer below the 60 mil VLDPE liner. If 10^{-6} cm/s hydraulic conductivity of silty clay layer could be achieved, the infiltration through the cap is estimated to be 844 l/d (223 gpd). In comparison, if the leaks in the 60 mil VLDPE liner occur on an approximately 15 m (50 ft) square grid, then the infiltration is estimated to be as high as 25,700 l/d (6800 gpd).

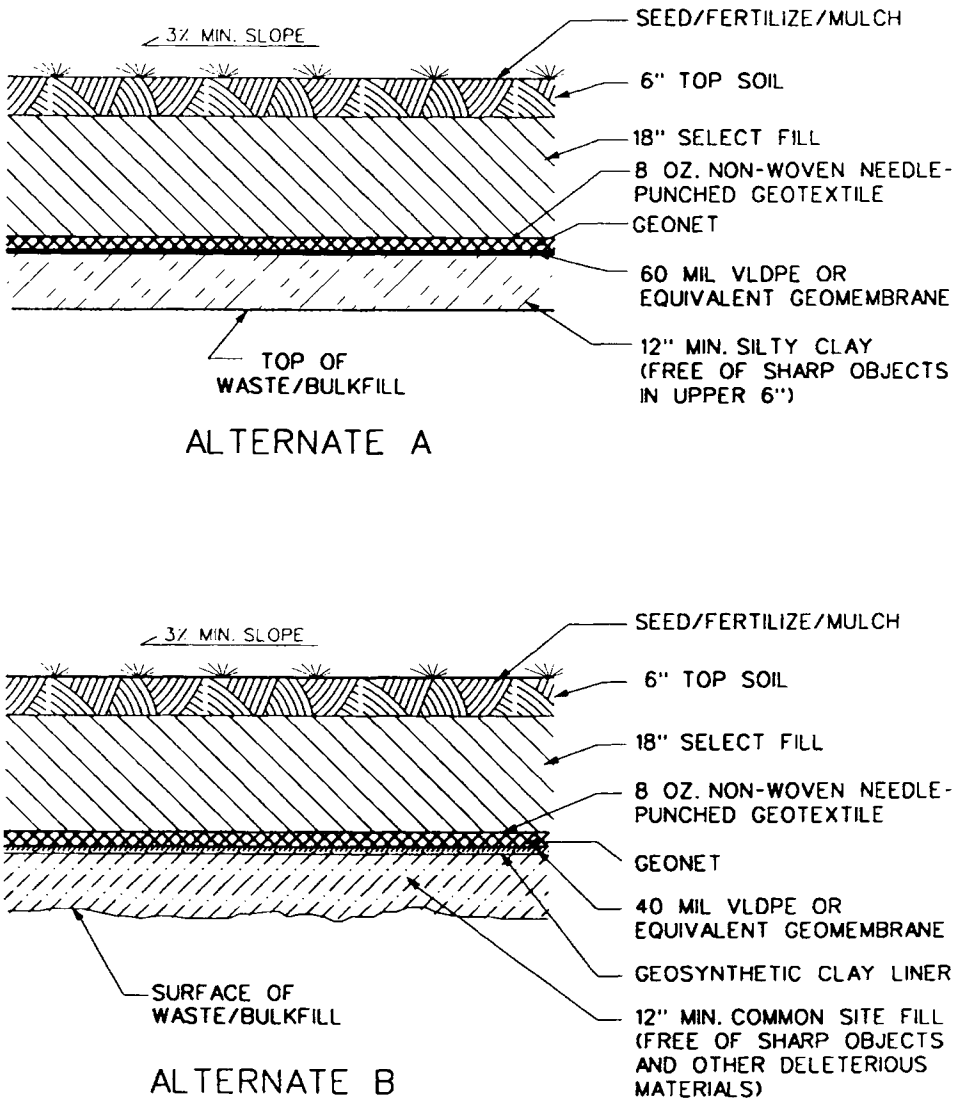


Figure V.6.3. Alternate landfill cap sections.

For "Alternate B" cap (Fig. V.6.3), the HELP model estimated infiltration to be 606 l/d (160 gpd) through the cap. Note that the liner in "Alternate B" cap was assumed to develop leaks on an approximately 15 m (50 ft) square grid.

Based on these cap design calculations the "Alternate B" cap design would allow less infiltration than the "Alternate A" cap design. Additionally, it may be difficult to install a 30 cm (12 in.) silty clay layer ("Alternate A") and obtain the desired hydraulic conductivity of 10^{-6} cm/s, which is required to obtain performance essentially equal to that of "Alternate B" cap design. Therefore, "Alternate B" cap design was selected, and will be used in the remainder of this chapter.

V.6.4.2. Groundwater infiltration through perimeter slurry wall

It was assumed that the saturated thickness on the north side will not change appreciably, from the data presented in Figures V.6.1 and V.6.2, once the subdrain pipe to control groundwater mounding is in place. Overall steady-state flow rate is not very sensitive to small changes in the saturated thickness as infiltration under and through the slurry wall is small compared to the total inflow to the landfill. The average head difference across the northern perimeter slurry wall was estimated to be 0.6 m (2 ft). Infiltration is calculated using Darcy's Law:

$$Q = KiA = K\left(\frac{\Delta h}{W}\right)A \qquad \text{(V.6.1)}$$

where:

A = saturated area of the perimeter slurry wall, 2790 m^2 (30,000 ft^2),
i = hydraulic gradient across the perimeter slurry wall,
K = hydraulic conductivity of the perimeter slurry wall, 1×10^{-7} cm/s,
Q = infiltration through the perimeter slurry wall,
W = perimeter slurry wall thickness, 1 m (3 ft), and
Δh = average head difference across the perimeter slurry wall.

The calculations shown in Table V.6.1 indicate that the infiltration through the perimeter slurry wall to the curtain wall enclosed area is approximately 184 l/d (49 gpd).

V.6.4.3. Groundwater infiltration under the perimeter slurry wall

The perimeter slurry wall will be keyed into the confining clay layer. Flow paths may be created beneath the wall and into the encapsulated landfill area, driven by the head differential across the perimeter slurry wall. Along the north side and 60 m (200 ft) sections of east and west sides, infiltration under the slurry wall will be to the curtain walled area. The remaining infiltration, along the south side and three-fourths of east and west sides, under the perimeter slurry wall is isolated from the area contained by the

Table V.6.1. Infiltration under and through the slurry wall to the area contained by the curtain wall.

Side	Length, m (ft)	Average saturated thickness, m (ft)	Average head difference, m (ft)	Infiltration, l/d (gpd)	
				Through slurry wall	Under slurry wall
North	610 (2000)	4.6 (15.0)	0.61 (2.0)	160.5 (42.4)	32.2 (8.5)
East	61 (200)	4.4 (14.5)	0.46 (1.5)	11.7 (3.1)	2.3 (0.6)
West	61 (200)	4.4 (14.5)	0.46 (1.5)	11.7 (3.1)	2.3 (0.6)
Total	732 (2400)			183.9 (48.6)	36.8 (9.7)

curtain wall. The infiltration rate for this source is estimated using Darcy's Law:

$$Q = KiA = K\left(\frac{\Delta h}{L_f}\right)(L_s W_f) = K\Delta h L_s\left(\frac{W_f}{L_f}\right) \tag{V.6.2}$$

where:

A = cross-sectional area for flow path under the perimeter slurry wall,
i = hydraulic gradient across the perimeter slurry wall,
K = hydraulic conductivity of the clay, 2×10^{-7} cm/s,
L_f = length of flow line (across which head difference is used),
L_s = length of the perimeter slurry wall,
Q = infiltration under the perimeter slurry wall,
W_f = width of flow zone under the perimeter slurry wall, and
Δh = head difference across the perimeter slurry wall.

Flowlines under the slurry wall have to at least traverse the flow width twice, once going down and once coming up. Therefore, a conservative estimate of 1/2 for the ratio of flow width to flow length is used. Total infiltration under the perimeter slurry wall to the area contained by the curtain wall is estimated to be approximately 37 l/d (10 gpd) (Table V.6.1).

V.6.4.4. Groundwater movement through a curtain wall

At steady state, water levels in the area enclosed by the curtain wall should be 3.96 m (13 ft) and the water level between the curtain wall and the perimeter slurry wall should be 2.75 m (9 ft). Therefore, the head difference across the curtain wall is calculated to be 1.2 m (4 ft). The hydraulic conductivity of 1×10^{-7} cm/s was used for a 1 m (3 ft) wide soil/bentonite curtain wall, and groundwater movement is estimated using Darcy's Law:

$$Q = KiA = K\left(\frac{\Delta h}{W}\right)A \tag{V.6.3}$$

where:

A = saturated area of the curtain wall, 3792 m^2 (40,800 ft^2),
i = hydraulic gradient across the curtain wall,
K = hydraulic conductivity of the curtain wall, 1×10^{-7} cm/s,
Q = water movement through the curtain wall,
W = curtain wall thickness, 1 m (3 ft), and
Δh = average head difference across the curtain wall, 1.2 m (4 ft).

The estimated groundwater movement through a soil/bentonite curtain wall is 435 l/d (115 gpd).

V.6.4.5. Groundwater movement under the curtain wall

The curtain wall will be keyed into the confining clay layer. Flow paths may be created beneath the wall, driven by the head differential across the curtain wall. Water movement

rate under the curtain wall is estimated using Darcy's Law:

$$Q = KiA = K\Delta h L_s\left(\frac{W_f}{L_f}\right) \tag{V.6.4}$$

where:

A = cross-sectional area for flow path under the curtain wall,
i = hydraulic gradient across the curtain wall,
K = hydraulic conductivity of clay, 2×10^{-7} cm/s,
L_f = length of flow line (across which head difference is used),
L_s = length of the curtain wall, 957 m (3140 ft),
Q = water movement under the curtain wall,
W_f = width of flow zone under the curtain wall, and
Δh = head difference across the curtain wall, 1.2 m (4 ft).

Flowlines have to at least traverse the flow width twice, once going down and once coming up. Therefore, a conservative estimate of 1/2 for the ratio of flow width to flow length was used. The estimated water movement under the soil/bentonite curtain wall is 98 l/d (26 gpd).

V.6.4.6. Inflow vs. outflow from the area contained by the curtain wall

Estimated total inflow to the area contained by the curtain wall is:

Through the cap "Alternate B"	606 l/d	160 gpd
Through the perimeter slurry wall	184 l/d	49 gpd
Under the perimeter slurry wall	37 l/d	10 gpd
Total inflow	827 l/d	219 gpd

Estimated total outflow from the area contained by a soil/bentonite curtain wall is:

Through the curtain wall	435 l/d	115 gpd
Under the curtain wall	98 l/d	26 gpd
Total outflow	533 l/d	141 gpd

The estimated potential total outflow from a soil/bentonite curtain wall is smaller than the estimated inflow to the area contained by the curtain wall. Therefore, excess groundwater will flow over the top of the curtain wall and be collected in the groundwater collection system.

V.6.5. Steady-state groundwater pumping requirements

To achieve the purpose of the groundwater collection system, it will be necessary to create and maintain inward gradient across the perimeter slurry wall. This could be achieved by

reducing the static groundwater level inside the area between the perimeter slurry wall and the curtain wall to approximately 0.3 m (1 ft) below the river elevation and the natural groundwater levels outside the perimeter slurry wall. Once this level is attained, infiltration will consist of water from the following sources:

- inflow to the area contained by the curtain wall,
- precipitation infiltration through that portion of the cap, which overlies the area between the perimeter slurry wall and the curtain wall,
- groundwater infiltration through the perimeter slurry wall, and
- groundwater infiltration beneath the perimeter slurry wall.

An equivalent volume of water must be pumped to maintain steady-state water levels.

V.6.5.1. Inflow to the area contained by the curtain wall

Total inflow to the area contained by the curtain wall was estimated to be 827 l/d (219 gpd) (see calculations in the preceding section). All the inflow to the area contained by the curtain wall will eventually drain to the groundwater collection system either as flow under, through, or over the curtain wall.

V.6.5.2. Additional infiltration through the cap

In the previous section, it was shown that the average infiltration through "Alternate B" cap over 140,000 m^2 (1,56,000 ft^2) area was approximately 606 l/d (160 gpd). The area between the curtain wall and the perimeter slurry wall is approximately 9000 m^2 (94,000 ft^2). Therefore, the average infiltration through the cap over this 9000 m^2 area is estimated to be 38 l/d (10 gpd).

V.6.5.3. Groundwater infiltration through the perimeter slurry wall

The saturated area of the perimeter slurry wall, through which water may infiltrate, varies around the site with the elevations of the top of the confining clay layer and the water table. For illustration purposes, average elevation of the top of the clay layer is used. An inward head difference of 0.3 m (1 ft) across the slurry wall on the south side (near the river) is the controlling factor in selecting water levels in the encapsulated landfill area because the river is on the downgradient side. Water levels inside the perimeter slurry wall are designed to be maintained at 2.75 m (9 ft). Average water level data, on the east, west, and south sides were used to determine the steady-state gradients. Infiltration was estimated using Darcy's Law identically as it was used in the calculations in groundwater infiltration through the perimeter slurry wall described in the previous section (see Equation (V.6.1)). Table V.6.2 shows that the total infiltration through the perimeter slurry wall to the area between the perimeter slurry wall and the curtain wall is estimated to be 257 l/d (68 gpd).

Table V.6.2. Infiltration through and under the perimeter slurry wall to the area contained by the perimeter slurry wall and the curtain wall.

Side	Length, m (ft)	Average saturated thickness, m (ft)	Average head difference, m (ft)	Infiltration, l/d (gpd)	
				Through slurry wall	Under slurry wall
South	610 (2000)	3.35 (11.0)	0.61 (2.0)	117.3 (31.0)	32.2 (8.5)
East	183 (600)	3.81 (12.5)	1.07 (3.5)	70.0 (18.5)	17.0 (4.5)
West	183 (600)	3.81 (12.5)	1.07 (3.5)	70.0 (18.5)	17.0 (4.5)
Total	976 (3200)			257.3 (68.0)	66.5 (17.5)

V.6.5.4. Groundwater infiltration under the perimeter slurry wall

The perimeter slurry wall will be keyed into the confining clay layer. Flow paths may be created beneath the wall and into the encapsulated landfill area, driven by the head differential across the perimeter slurry wall. The infiltration rate for this source is estimated using Darcy's Law analogously as it was shown in the previous section (see Equation (V.6.2)). Calculations for infiltration under the perimeter slurry wall are summarized in Table V.6.2. Total infiltration under the perimeter slurry wall is estimated to be 66 l/d (18 gpd).

V.6.5.5. Total flow into the groundwater collection trench at steady state

Sources of inflow to the encapsulated landfill area and related rates based on the "Alternate B" cap design are summarized in Table V.6.3. A conservative estimate of total water inflow of less than 1500 l/d (400 gpd) into the groundwater collection trench is anticipated at steady state. These numbers are based on an annual average basis. The actual daily inflow will vary with fluctuations in river elevation, seasonal water table, and changes in rainfall and climatologic conditions.

Table V.6.3. Sources of water to the groundwater collection system.

Source	Inflow rate, l/d (gpd)
Total inflow to (outflow from) area contained by the curtain wall	827 (219)
Infiltration through cap between the curtain wall and the perimeter slurry wall	38 (10)
Infiltration through the perimeter slurry wall	257 (68)
Infiltration under the perimeter slurry wall	66 (18)
Total	1188 (315)

V.6.6. Groundwater collection system

The groundwater collection system can consist of vertical wells, horizontal wells, or a trench with a number of wet wells. Use of both the vertical wells and trench with wet wells to recover groundwater and control gradients are proven technologies. However, due to low permeability of silty sand near the river and small saturated thickness at this site, a large number of vertical wells would be required to ensure minimum of 0.3 m (1 ft) inward gradient along the southern section of the slurry wall. Therefore, vertical wells were eliminated in favor of the trench and wet well system. Horizontal wells have gained popularity in last few years. However, it may be difficult to install horizontal wells in an uncontrolled landfill containing construction debris. A trench can be installed by conventional excavation technology with side slopes followed by installation of a perforated pipe in a pea gravel bed and backfilling. A trench can also be installed by use of biodegradable slurry to keep a small trench open while the perforated pipe is installed. Use of biodegradable slurry is preferred, as this will minimize contact with potentially contaminated soils and groundwater. Therefore, a groundwater collection trench installed using biodegradable slurry was selected for this application. Three wet wells, as shown in Figure V.6.1, at low points in the groundwater collection trench will be used to pump the contaminated water and maintain inward gradients.

Anticipated groundwater mounding within the enclosed landfill area is minimal (see Appendix A). Therefore, the trench along the full length of the perimeter slurry wall on the east and west sides is not required. As shown in Figure V.6.1, the groundwater collection trench will extend 60 m (200 ft) on east and west sides.

V.6.7. Summary

A curtain wall has been added to a typical remedy to reduce the total volume of groundwater that will be recovered and treated, to maintain groundwater levels within the curtain wall at current levels, and to minimize migration of DNAPL to the groundwater collection trench. Installation of a curtain wall is expected to save approximately $1.7 million in remediation costs.

The "Alternate A" cap design uses a 30 cm (12 in.) silty clay layer beneath a 60 mil VLDPE liner while "Alternate B" uses a geosynthetic clay liner beneath a 40 mil VLDPE or equivalent liner. The "Alternate B" cap design has been shown to be more effective in reducing rainfall infiltration and was selected in the remedial design.

A conservative estimate, i.e. more than anticipated, of total water inflow of less than 1500 l/d (400 gpd) into the landfill area is estimated at steady state for cap design "Alternate B". These numbers are based on annual averages. The actual daily inflow will vary with fluctuations in river elevation, seasonal water table, and bedrock head potential, and changes in rainfall and climatologic conditions.

Approximately 1900 m^3 (500,000 gal) of groundwater will be pumped out of the landfill before a 0.3 m (1 ft) head differential across the perimeter slurry wall and a steady-state infiltration and pumping requirement of less than 1500 l/d (400 gpd) is achieved.

Appendix A: Maximum mounding within the area contained by the curtain wall

Maximum groundwater mounding within the area contained by the curtain wall is estimated using the equation (Bear, 1979):

$$h_{max} = \left[\frac{L^2 I}{4K} + h_0^2 \right]^{0.5} \tag{A.1}$$

where:

h_{max} = maximum hydraulic head,
h_0 = hydraulic head at the southern section of the curtain wall,
I = inflow rate per unit area,
K = hydraulic conductivity of alluvium/fill, and
L = two times the distance between the south curtain wall and north perimeter slurry wall.

Using 235 m (770 ft) for the distance between the south curtain wall and north perimeter slurry wall, 5×10^{-4} cm/s for the hydraulic conductivity of alluvium/fill, 3.99 m (13.08 ft) for the hydraulic head at the south curtain wall (measured from the confining layer), and a total inflow of 829 l/d (219 gpd) over 140,000 m^2 (1,506,000 ft^2) area, h_{max} is calculated to be 4.01 m (13.16 ft). Therefore, the maximum groundwater mound within the area contained by the curtain wall will be 0.02 m (0.08 ft). Actual mounding may be less because of overflow on the east side and the west side curtain walls. Therefore, a uniform water level of approximately 4 m (13.1 ft) should be maintained within the area contained by the curtain wall.

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PART VI

Advanced/emerging solid waste use, disposal and remediation practice

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VI.1
Utilization of waste from food and agriculture

Teodorita Al Seadi and Jens Bo Holm-Nielsen

VI.1.1. Recycling of organic wastes – one of the major tasks of today's waste management policies

The modern agricultural sector generates great amounts of wastes, which represent a tremendous threat to the environment, and human and animal health. The overall policy that controls utilization of agricultural wastes today is part of the general efforts to reduce the pollution and prevent further deterioration of the environment from all types of wastes. One of the main tasks of today's waste management policies is to reduce the stream of organic waste going to landfills and recycle the organic matter and the plant nutrients back to the soil (Al Seadi, 2001).

The intensive agricultural practice and the utilization of mineral fertilizers, pesticides and pharmaceuticals in agriculture have an increasing impact on the environment and have changed the perception of animal manure and other agricultural by-products from valuable resources to a global waste problem.

Agricultural production has an impact on the atmosphere, the groundwater, rivers, and streams as well as on the landscape, in the same way like non-agricultural activities (Bauder and Vogel, 1989–1990). Environmental pollution is mainly caused by emissions and leaching from different agricultural wastes (manure disposal and spreading, slurry storage and spreading, fertilizer lots and spreading, pesticides spreading and disposal, vegetable mass disposals, etc.). Many types of wastes of agricultural origin can be contaminated with crop and animal diseases, chemical and physical contaminants.

Nevertheless, major steps forward have been made to find better ways of utilization of agricultural wastes, currently included in the larger notion of biomass. Biomass-based renewable energy production is today one of the most attractive ways of utilization and recycling of agricultural wastes and by-products, contributing to the reduction of the emissions of greenhouse gases by displacing fossil fuels and preventing pollution caused by traditional waste disposal. The struggle of reducing the global emission of CO_2 from the fossil fuels-based energy production transformed biomass into a very attractive alternative source of renewable energy. In the 15 EU-countries only, the level of biomass conversion to energy was 44.8 Mtoes (million tons of oil equivalents; 1 toe = 1×10^{10} cal) in 1999, and the target for year 2010 is 131 Mtoes (Holm-Nielsen and Al Seadi, 1997). The statistical data from the European Commission show that the primary energy production from biomass increased in EU countries by 29% between 1987 and 1997.

The environmental and waste handling and disposal policies and legislation in most European countries are directly or indirectly encouraging the use of biomass for energy production and the recovery of the energy that results from agricultural waste processing (EC DG ENV, 2001).

Finding sustainable solutions for the utilization of agricultural wastes is one of the greatest challenges of the agricultural sector. This also means that agricultural wastes must no longer be regarded as problems but as valuable resources and utilized in a way that provides maximum safety, minimum environmental impact and as far as possible, recyclable end-products (Al Seadi, 2001). Safe recycling of agricultural wastes is an objective of increased public awareness and the quality control of these types of biomass is therefore essential.

VI.1.2. Utilization of agricultural wastes: the main streams

Agricultural utilization/recycling:

- fodder;
- bedding;
- fertilizer:
  - raw materials,
  - digestate from biogas production,
  - compost;
- other agricultural utilization.

Bioenergy production:

- biogas from anaerobic digestion;
- biofuels;
- incineration.

Industrial non-food utilization:

- biocomposite and vegetable fiber boards;
- starch-based biodegradable plastics and polymers;
- thickeners and lubricants;
- lignocellulosic thermoplastics;
- manufacture industry;
- pharmaceuticals and cosmetics;
- biopesticides;
- structure improvers;
- pulp and paper;
- lactic acid;
- waxes;
- other.

Industrial fodder:

- vegetable fodder pellets;
- alcohols and sugars;

- amino acids and proteins;
- other.

Landfilling:

- Recommended only when alternative options are not suitable. Current environmental regulations in EU limit the landfilling of organic wastes, due to its environmental impact and lack of sustainability (EC, 1999).

VI.1.3. Animal manure – fertilizer or waste

The intensive animal production of the industrialized agriculture, widely practiced during the last 40 years, has created serious problems of agricultural waste disposal. Mechanization and the decreasing labor force have required new animal production systems and use of imported feeding stuffs. The modern stable systems transformed manure consistency from solid to slurry (liquid) and the production of slurry exceeded the capacity of the available land for its optimal use. This situation became common throughout the world, from the large cattle feed lots in North America to intensive pig production throughout Europe (Fig. VI.1.1), America and Asia.

The historical development of agriculture shows what a tremendous impact the use of animal manure had on the supply of nutrients to the soil, increasing the volume and improving the quality of the crops. In the old cropping systems, the nutrients contained in the manure were obtained from the same land that produced fodder for the animals. In this way, the improvement of the soil fertility and a loss of fertility due to crop production mainly took place in the same area (Wadman et al., 1987).

The situation has mainly changed today, when the majority of animal production systems, especially in western and northern Europe and USA are no longer land dependent. Animal feeds are produced away from the place of animal production, more and more often abroad. This phenomena happens together with an unprecedented increase in production in Europe livestock and generally in the whole world, as a consequence of several factors such as increased demand for meat/dairy products on the market originating from increased living standard, increased labor productivity, intensive forage production as a consequence of using pesticides and mineral fertilizer in crops production, use of concentrated forages in animal production, improved veterinary control of diseases, larger export markets, etc. (Wadman et al., 1987).

During all this process, the perception of value of animal manure decreased from a valuable natural fertilizer to a waste product due to two main factors. First, the development of intensive animal production, not land dependent, in many regions of Europe and North America, resulted in high livestock density and an excess of manure in these regions. Secondly, during the same period, mineral fertilizers widely replaced manure in the crop production systems, as a much cheaper alternative. This has made manure no longer an indispensable fertilizer for the crops but an unwanted waste product, as the choice between manure and mineral fertilizers depends on their total costs (Wadman et al., 1987).

It is more likely that the composition of animal manure has generally improved during the last century, as the nutrient content in manure depends on the quality and digestibility

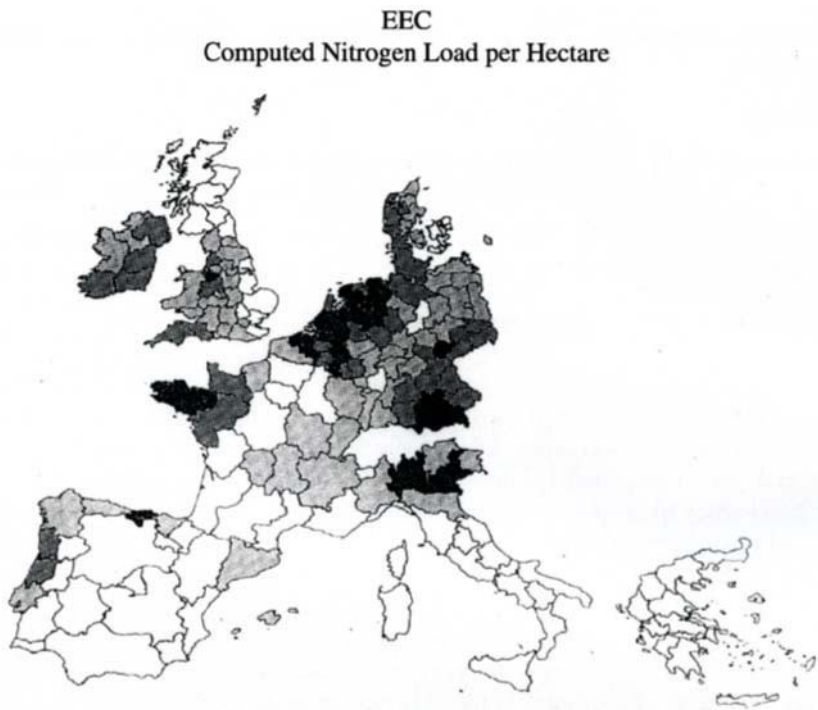


Figure VI.1.1. Manure density (after Danish Energy Agency, 1993).

of the animal feed (Wadman et al., 1987). At the same time, new aspects concerning manure quality appeared, due to the new agricultural practices, such as the use of pesticides, inorganic phosphorous fertilizers or sewage sludge (rich in phosphorous) in fodder production, the use of phosphates in concentrates, as well as due to non-agricultural emissions/pollution. Furthermore, the change of manure consistence from solid to slurry has brought up the necessity of establishing new collection, storage and spreading systems and techniques. The excess of manure production left the farmers with no alternative but the application of high amounts of manure, facing severe environmental problems, or an expensive transfer of the manure in excess to areas in need of organic nutrients. Consequently, regulations and restrictions on manure handling and application were implemented in many countries (storage capacity, amount per hectare, season of application, techniques, etc.), further reducing the value of manure. Consequently, European Community by issuing Council Directive 91/676/EEC (EEC, 1991) also enforced limitations of manure applications in order to protect water resources from pollution caused by nitrates. Industrialized agriculture gradually turned animal manure

from a valuable natural fertilizer into an environmentally problematic waste (Wadman et al., 1987).

VI.1.4. Utilization of animal manure

Modern utilization of animal manure and slurries requires funding and implies social consequences where the environmental effects, both the pollution potential and the energy potential, should be taken into consideration. It also requires regulation of handling, storage, treatment and application as well as improvement of nutrient efficiency. Manure management problems often arise when livestock are added to a farm without increasing the land base.

One of the main problems of using liquid manure as fertilizer is that costs increase with increased distance of transportation. The methods of transport are various and depend on the system of production and the design of the production unit. Normally the liquid manure (slurry) can be transported in vacuum tankers to and from the storage facilities or it can be piped for shorter distances. With conventional transport facilities, animal manure can counterbalance a transportation distance of approximate 15 km, while concentrated manure can counterbalance longer transport distances. Slurry can be handled and treated in many ways, each with its advantages and disadvantages (see Figure VI.1.2). Treating/concentrating manure is one of the common ways of improving its value, by improving the utilization of nutrients, making it more suitable for transportation and redistribution. Treatment of manure transforms it into an attractive fertilizer for all types of farming and contributes to the achievement of a territorial balance of manure concentration (Gasser, 1984). The main issues related to slurry treatment refers to:

- anaerobic digestion combined with concentration;
- mechanical separation/filtration;
- separation and concentration of nutrients/lagoon evaporation;
- decomposing of organic matter;
- precipitation and flocculation;
- accelerated composting and drainage.

VI.1.5. Nitrogen supply from animal manure

The composition of animal slurries varies with species, animals' age, and diet (Wadman et al., 1987), while its concentration is affected by the amount of extraneous added water (Gasser, 1984). The difference between cattle, pig and poultry slurry is the proportion of the three macronutrients: nitrogen (N), phosphorus (P) and potassium (K) (Table VI.1.1.). The table shows a higher proportion of K in relation to N in cattle manure while pig and poultry manures are higher in P.

The use of animal slurry as fertilizer can lead to severe pollution problems for the environment in case of inadequate application practice. The most frequent causes of pollution are surface run-off, losses of ammonia and nitrous oxide to the atmosphere, and

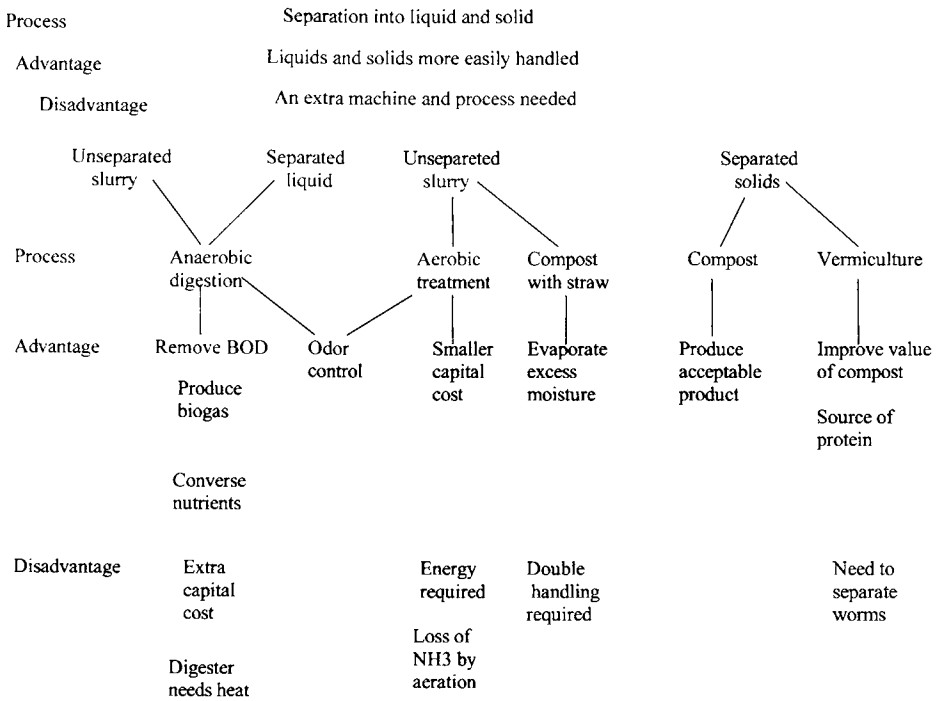


Figure VI.1.2. Treatment of slurry: advantages and disadvantages (after Gasser, 1984).

leaching of nitrate to ground waters (Gasser, 1984). Figures VI.1.3 and VI.1.4, respectively, show the distribution of NH_3 and NH_4^+ in Europe. Figure VI.1.5 shows the N-surplus per hectare in some EU countries and in Table VI.1.2 are given the estimated nitrogen losses from manure.

Table VI.1.1. Typical chemical composition (% dry matter) of faces for the main species of farm animals (after Smith, 1973).

Faces source	Neutral detergent soluble	Nitrogen	Hemi-cellulose	Cellulose	Lignin	Ash
	% dry mater					
Broilers (caged)	69	6.5	16	11	4	22
Lying hens (caged)	65	6.2	17	15	3	28
Pigs (growing and fattening)	60	3.0	20	15	5	17
Beef cattle (fattening)	53	3.0	22	17	8	7
Dairy cattle (lactating)	41	2.6	21	25	13	9
Dairy cattle (all forage feed)	32	2.0	20	28	20	12
Sheep (all forage feed)	45	2.5	15	28	15	13

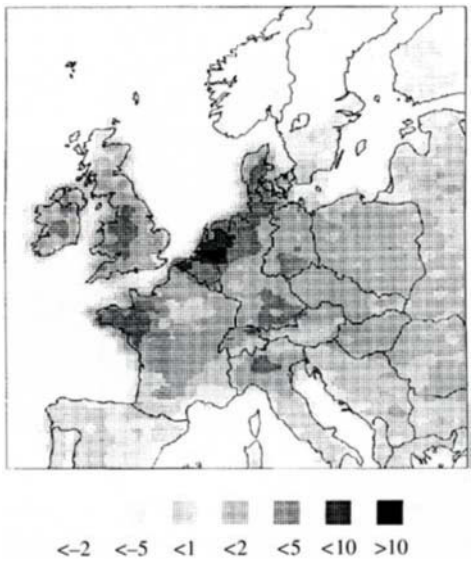


Figure VI.1.3. The calculated distribution of NH_3^- concentrations in air in Europe ($\mu g/m^3$) (after Danish Energy Agency, 1993).

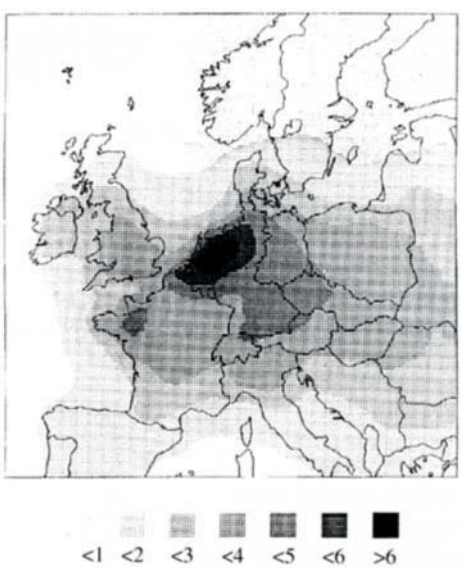


Figure VI.1.4. The calculated distribution of the NH_4^+ concentration in air in Europe ($\mu g/m^3$) (after Danish Energy Agency, 1993).

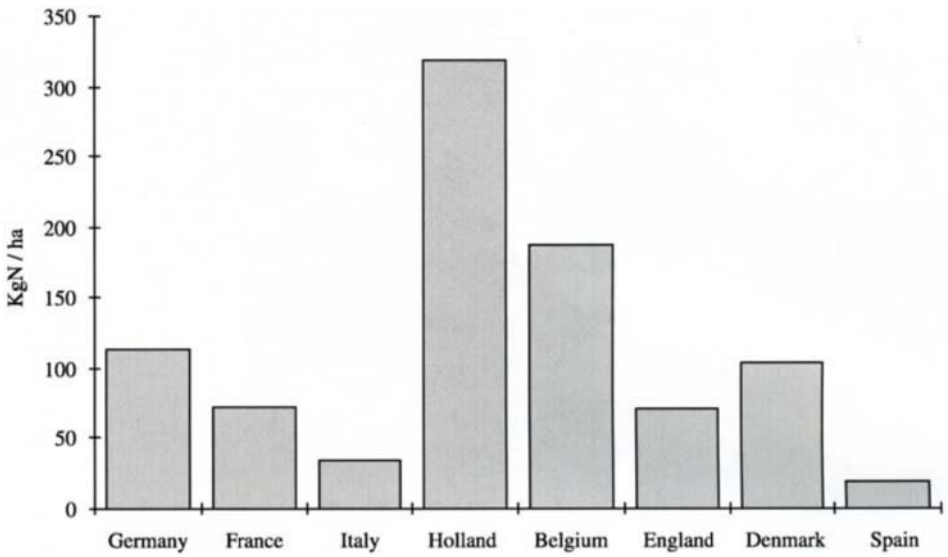


Figure VI.1.5. Nitrogen balance for eight EU countries (N-surplus, in kg/ha) (after Danish Ministry of Environment and Energy, 1994).

The variations in the amounts of nitrogen contained in manure can be large, depending on the digestibility of fodder and the content of proteins. Research work was carried out on the issue of controlling the amount of nitrogen contained in manure by optimized fodder composition. The research results concerning this issue have proven that improved systems of protein evaluation and controlled animal feeding with low protein content have improved the utilization of nitrogen in almost all species of domestic animals (Smith, 1973; Gasser, 1984).

VI.1.5.1. Nitrogen load per hectare and losses of nitrogen

Nitrogen from animal manure may be present in soil as three fractions (Landelout and Lambert, 1980):

Table VI.1.2. Estimated nitrogen losses during storage, treatment and handling of various manure management systems (after Bauder and Vogel, 1989–1990).

System	Nitrogen loss[a] (%)
Liquid pit or silo storage, liquid spreading	30–65
Anaerobic lagoon, irrigation, or liquid spreading	60–80
Bedded confinement, solid spreading	30–40
Open lot, solid spreading, run-off collected and irrigated	50–60

[a]Nitrogen loss values assume that manure is applied to the ground surface and is incorporated within few hours. If not incorporated, an additional loss of 30% on an average can be expected.

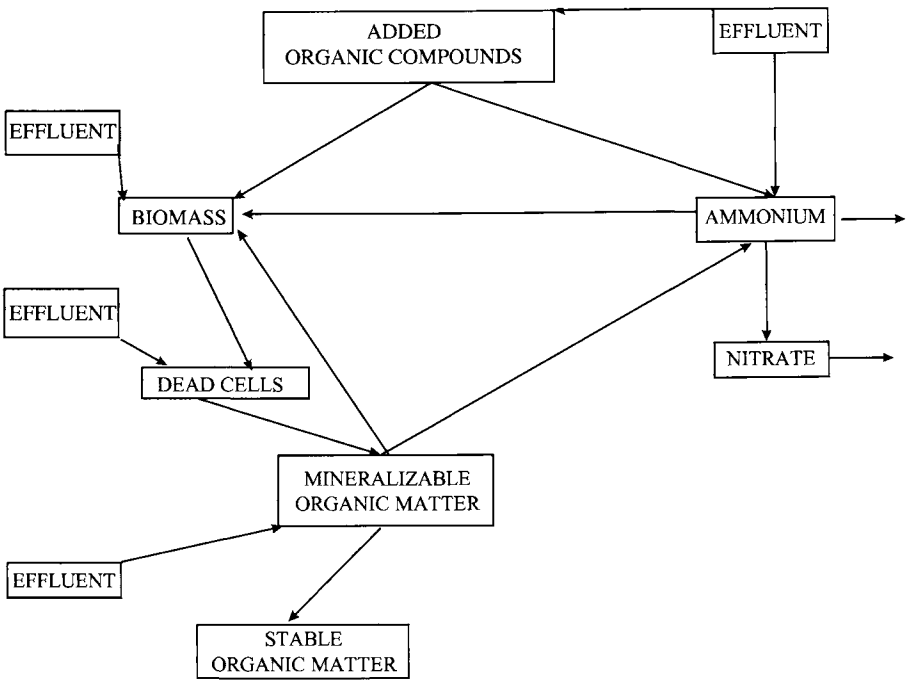


Figure VI.1.6. The simplified fluxes of N in the soil (after Landelout and Lambert, 1980).

- inorganic N (ammonium and some times nitrate) and rapidly mineralizable N from urea and uric acid;
- organic N compounds, easily degradable (with a low ratio of C/N) like proteins and amino acids;
- organic N slowly mineralizable (with high C/N ratio) like lignocellulose.

Manure also contains easily degradable N-free organic compounds like fats, fatty acids, carbohydrates, as well as organic and inorganic phosphorus compounds. Figure VI.1.6 presents a simplified scheme of nitrogen fluxes in the soil.

VI.1.5.1.1. Losses of nitrogen in the fields as ammonia

Animal manure is the main source of ammonia emissions to the atmosphere. The losses of ammonia are particularly large from heavily grazed grassland, surface-spread slurries and uncovered storage capacities. The losses of nitrogen as ammonia depend to a large extent on some factors such as pH, the content of dry matter, temperature, precipitation, wind, type of soil, the rate of covering with vegetation, etc.

The example of the influence of pH on ammonia loss from slurry is relevant. Ordinary slurry is alkaline (pH 7.0–8.0) and contains a large amount of N as NH_3, which is easily evaporable. Lowering the pH of the slurry by adding a strong acid will result in the presence of more N as NH_4^+ that does not evaporate. Table VI.1.3 shows the variation of total ammonia content in slurry at different pH values.

Table VI.1.3. Variation of NH_3 concentration in slurry according to pH values (after Danish Ministry of Environment and Energy, 1994).

pH value	6	7	8
% of NH_3 in $(NH_3 + NH_4^+)_{total}$	0.04	0.4	40

VI.1.5.1.2. Losses by denitrification

Losses of nitrate by denitrification results in the formation of N_2 and N_2O and happens as a natural process in agricultural soils under reducing conditions, as a result of the activity of obligate anaerobic bacteria. Denitrification represents loss of a valuable nutrient for the plants, but in cases of excess manure, denitrification can be considered a beneficial removal of the excess nitrogen, avoiding groundwater pollution with nitrate. The process of denitrification can be prevented by ensuring adequate aeration in the soil, as denitrification occurs under reducing conditions.

VI.1.5.1.3. Losses by leaching of nitrate

Losses by nitrate leaching occur when excess nitrate is present, due to the application of excess slurry to the soil. It can be, e.g. when applying to grassland, when applying slurry during autumn and winter and with increasing intensity of grazed grassland (Landelout and Lambert, 1980). Improved nitrate efficiency can prevent this type of nitrate loss. Table VI.1.4 illustrates the increase in nitrate leaching with the increasing livestock density.

VI.1.6. What controls the recycling of animal manure and organic wastes from food and agriculture

VI.1.6.1. The European framework

The increasing production of wastes of biological origin (biowaste) requires adequate collection, treatment and recovery methods. The general trend of both national and EU

Table VI.1.4. N-leaching related to density of LU/ha (after Danish Ministry of Environment and Energy, 1994).

Nitrogen source	Livestock units (LU/ha)	Average of N leaching (kg N/ha/year)
Crop production	0	68
Animal production	0–1	119
Animal production	1–2	160
Animal production	>2	170

legislation concerning management of agricultural wastes is to strengthen the environmental requirements and quality standards. Numerous EC regulations and guidelines have been issued in this area and more are about to be issued. The selection of regulations listed below (after Braun and Kirchmayr, 2003) have an impact on the practical applications of biological treatment of agricultural wastes, like anaerobic digestion and composting.

VI.1.6.1.1. Council Directive 75/442/EEC of 15 July 1975 on waste

The directive contains definition of wastes, guidelines for waste classification and exclusion of specific wastes (e.g. radioactive materials, animal carcasses, waste waters) as well as necessary measures to ensure safe waste disposal with respect to human health and environmental protection. EU member states are requested to take appropriate steps to encourage waste prevention, reuse and recycling, safe processing of waste, the extraction of raw materials and the energy recovery.

VI.1.6.1.2. The Sewage Sludge Directive 1986/278/EEC

The directive 1986/278/EEC "Protection of Environment and Soil at the Utilization of Sewage Sludge in Agriculture" defines the limit values for heavy metals, organic trace compounds and hygienic requirements for handling and application of sewage sludge on agricultural soils. In addition the Regulation on Organic Farming 2092/91/EWG defines heavy metal limit values for compost derived from source separate collection of municipal biowaste.

VI.1.6.1.3. The Water Framework Directive 2000/60/EC

The water framework directive affects water industry, agriculture, development and construction industry and all businesses that have discharge consents, trade effluent licenses or abstraction licenses. The aim of the directive is to establish a framework for the protection of waters and water environment by setting out a framework for action.

VI.1.6.1.4. Council Directive 1999/31/EC on the Landfill of Waste

The EC directive on the landfill of waste defines the goals of organic waste reduction in landfills, using as base of reference the year 1975. The input of organic waste to landfills should be reduced to 75% by 2006, 50% by 2009 and 35% by 2016.

VI.1.6.1.5. Thematic strategy for soil protection

A thematic strategy on soil protection will be presented by the EC in 2004. The strategy is one of the seven "thematic strategies" foreseen under the EU's 6th Environment Action Program. It will consist of legislation on community information and monitoring system on soil, as well as a set of detailed recommendations for future measures and actions. The monitoring system will build on existing information systems and databases and ensure a harmonized way of establishing the prevailing soil conditions across Europe. By the end of

2004 a directive on compost and other biowaste will be prepared with the aim to control potential soil contamination and encourage the use of certified compost.

VI.1.6.1.6. Directive 2001/77/EC on the Promotion of Electricity Produced from Renewable Energy Sources in the Internal Electricity Market

The document states that the exploitation of renewable energy sources is underused in the community at the moment. For this reason the directive aims to promote an increase in the contribution of renewable energy sources to electricity production in the internal market for electricity and create a basis for a future community framework thereof. Biomass-based electricity and within it biogas is mentioned as one of the important renewable alternatives. To ensure increased penetration of electricity produced from renewable resources, the member states are requested to set appropriate national indicative targets.

VI.1.6.1.7. Working document biological treatment of biowaste

The second draft of the forthcoming regulation "Biological Treatment of Biowaste" was issued. The current version has to be harmonized with the recently published Animal By-product Regulation (EC) No 1774/2002 and a revised third version is expected in 2004. The forthcoming regulation will contain lists of allowable wastes for biotreatment, directives for waste collection, handling and treatment, approval criteria for treatment plants and allowable processing emissions, quality classes for biotreatment of residues and compost, control and analysis of end-products and their application standards. As an example, sanitation of biowaste has to be done at a minimum temperature of 55°C for at least 24 h, at an average hydraulic dwell time in the reactor of at least 20 days. If that is not guaranteed, then a pre-treatment at 70°C for 1 h or a post-treatment of the solid digestate at 70°C for 1 h or composting of the solid digestate is required.

VI.1.6.1.8. Animal By-products Regulation (EC) No 1774/2002

The Regulation (EC) No 1774/2002 of the European Parliament and the Council from October 2002, laying down health rules concerning animal by-products not intended for human consumption, was enforced in all EU member states by 01.05.2003 as a comprehensive attempt to ensure food safety and animal and human health. The regulation is undergoing an amendment process and transitional measures were proposed in several member states.

It is estimated that more than 14.3 million tons (1998) of animal by-products derived from healthy animals, not intended for human consumption, are processed in EU countries every year. These materials are further transformed into a variety of products used in human food, animal feeding, cosmetics, pharmaceuticals, etc. In 1998 16.1 million tons of animal by-products (of which 14.1 million tons derived from healthy animals) were processed into 3 million tons of meat and bone meal and 1.5 million tons of fat (COM(2000)574).

Inappropriate processing standards and the use of rendered products and catering waste are considered to be the reason for major pandemic outbreaks of transmissible spongiform encephalopathy and foot and mouth disease. The regulation brings major changes in

processing procedures by both waste producers and waste managers. Animal by-products are defined as all animals or parts of animals not intended for human consumption. This also includes dead-on-farm animals, animal manure and catering waste. The animal by-products are classified into three categories of risk and new rules for their collection, treatment and disposal are introduced.

VI.1.6.2. National regulations – case study from Denmark

A series of continuously amended and strengthened regulations and legislation concerning production, collection, storage, handling and recycling of animal manure and organic wastes have been introduced in Denmark since 1985, as a result of some serious environmental problems related to intensive animal production and increased production of organic waste from the food processing sector and from the overall society.

Long-term governmental programs and plans for optimal recycling of animal manure and other organic wastes have been implemented in Denmark. The Danish environmental legislation prescribes integrated recycling of suitable organic waste in the farming system and enforces restrictions to secure a safe recycling policy, and to prevent hazards for human and animal health and further pollution and contamination of the environment.

Cleaner technologies, with integrated recycling practices, were developed throughout the years, as well as biomass-based energy systems, due to their feasibility of simultaneously renewable energy, diminishing environmental pollution and obtaining agricultural benefits. The Danish Ministry of Environment and Energy (1992, 1994, 1996, 1999, 2000) introduced and repeatedly strengthened the regulations concerning the handling and application of animal manure, sewage sludge and compost. Some of the statutory orders regulating this area will be further reviewed. The Danish Veterinary Service, under the Ministry of Agriculture and Fisheries, sets standards and runs monitoring programs for sanitary safe utilization of waste products for agricultural purposes (1996).

The agricultural sector has influenced the legislative process. This has directed the regulations towards use of clean technology, elimination of point sources, larger storage capacities, better spreading techniques, change in crop rotation, green fields in winter time, more areas with permanent grassland, etc. The agricultural sector used different policy instruments such as information campaigns like "slurry is gold" aiming to improve the utilization of nitrogen in manure, establishment of more than 600 pesticide groups that seems to contribute to reduction of pesticides up to 25% (1996) compared with the previous national average.

The agriculture sector refused "the polluter pays" principle, and the farmers have received support to build slurry tanks instead and accepted clear political goals of reduction of total nitrogen leaching from the field and reduction of pesticides load per hectare. The national schemes reward farmers producing in an environmentally friendly way. The Danish agro-environmental policy segment has developed (see Table VI.1.5) and is clearly more environmentally integrated and less politically influenced than in the 1980s, with more clearly defined actors and problem issues (Just, 1994).

Table VI.1.5. The Danish agro-environmental policy segment (after Just, 1994).

Time period	Driving forces	Environmental priorities	Most important administrative actor
1960s	State	Open nature conservation	State
1970s	Social movements	Antipollution	Ministry of Environment
1980s	Green movements, scientists, politicians	Agriculture as a polluting activity	Ministry of Environment, Municipalities
1990s	Agro-environmental segment	Integrated environmental protection	Ministry of Environment, Ministry of Agriculture, Municipalities, Counties

VI.1.6.2.1. Manure regulations in Denmark

Since 1985 legislation has regulated Danish agriculture in order to protect the ground- and surface water environment. New law packages were adopted several times during the last decade, and the existing ones were continuously amended and strengthened.

- *Requirement of 6–9 months slurry storage capacity, restricting the seasons for slurry application* (statutory order from the Ministry of the Environment No 1121 of 15/12/1992, on professional livestock, livestock manure, silage, etc.).

According to the law, holdings with commercial livestock keeping and holdings, which store farmyard manure, must have sufficient storage capacity to observe the rules concerning spreading of farmyard manure and utilization of nitrogen from farmyard manure. At least 6 months' storage capacity is required. Sufficient storage capacity corresponds to at least 9 months' supplies, for cattle farms normally at least 7 months when the cattle are pasturing during summer. Consequently, the season for liquid manure application is restricted and the application is not allowed from harvest to February 1st, except for the period from harvest to October 1st in over-wintering grassland crops or on areas with winter rape the following winter. Liquid manure is to be immediately incorporated in soil or no more than 12 h after application.

- *The harmony rules, restricting the amount of manure applied per hectare* (statutory order from the Ministry of the Environment No 906, of 14/10/1996, on professional livestock, livestock manure, silage, etc.).

The harmony rules regulate the maximum input of nitrogen per hectare per year by prescribing the maximum allowed livestock units (LU) loading per hectare and were enforced in 1987 by the Water Environment Action Plan I. The statutory order defines a livestock unit as "a unit of calculation" corresponding to "a maximum of 100 kg of nitrogen in manure, including the quantity deposited by the animals on the field." The prescriptions of the harmony rules are outlined in Table VI.1.6.

- *Minimum coefficients of nitrogen efficiency from animal manure* (statutory order No 587 from 12/07/1999 on utilization of manure as agricultural fertilizer).

The first action plan for sustainable agriculture in 1991 sets up minimum coefficients for the utilization of nutrients from animal manure, in force from the crop year 1994. In 1998, the Water Environment Plan 2 further increased the utilization requirements and

Table VI.1.6. Maximum amounts of nitrogen from manure to be spread per ha per year (converted to kg total N/ha/year) (after Birkmose, 1999).

Type of farm	Until 12/2003	From 12/2003
Cattle farm 1, <70% grass and beets	210	170
Cattle farm 2, >70% grass and beets[a]	230	230
Pig farm	140–170[b]	140
Other animals or mixed	Approx. 200[c]	140
Farms without livestock	140–170[b]	140

[a]The derogation of the EU nitrate directive allows spreading more than 170 kg manure per ha, if larger area is covered with crops with high autumn N intake.
[b]1.7 livestock units per ha – the amount of nitrogen may vary, depending on the relation between sows and pigs for slaughter.
[c]2.0 livestock units per ha.

the coefficients were to be raised in the years to come. In case of pig slurry, for example, the minimum nitrogen utilization coefficient (first year utilization + second year) was 50 + 10% in 1998–1999, 55 + 10% in 1999–2000 and 60 + 10% in 2001–2002. To control the fertilizer use, the farmers must work out compulsory annual fertilizer plans, and submit annual fertilizer accounts to the Danish Plant Directorate. The positive effects of this legal requirement are reflected by the decreasing input of mineral fertilizers. Figure VI.1.7 shows the clear trend of decreasing overall mineral fertilizers' consumption in Denmark, as a consequence of increasing manure nutrient utilization.

VI.1.6.2.2. Organic waste regulation

The Danish waste legislation is characterized by a close interplay between EU regulations, regarding the overall frameworks and principles, and the national waste model, based on a combination of traditional administrative instruments (acts, statutory orders, etc.) and various other instruments such as taxes, charges, subsidies, agreements, etc. The legal framework for waste management in Denmark is given in the Danish Environmental Protection Act (1997) and the subsequent statutory orders and circulars, of which the most important is statutory order on waste No 299 of 30/04/1997 that corresponds with EU Council Directive 75/442/EEC (1975) on waste amended by Council Directive 91/156/EEC (1991) and with the waste management strategy defined and pursued by the European Union (EC DG ENV, 1999). The Danish Government Action plan for waste and recycling emphasizes the importance and the incentives and rules for recycling the plant nutrients between the urban and rural areas.

- *The application of waste products for agricultural purposes is controlled and regulated* (statutory order from the Ministry of Environment and Energy No 49 of 20/01/2000, on application of waste products for agricultural purposes).

Organic wastes can contain organic contaminants, heavy metals and pathogens, which can accumulate in the soils, or create chains of disease transmission between animals, humans and the environment (see Chapter III.1). The legislation outlines the types of organic wastes that can be applied on agricultural soil without restrictions and the types

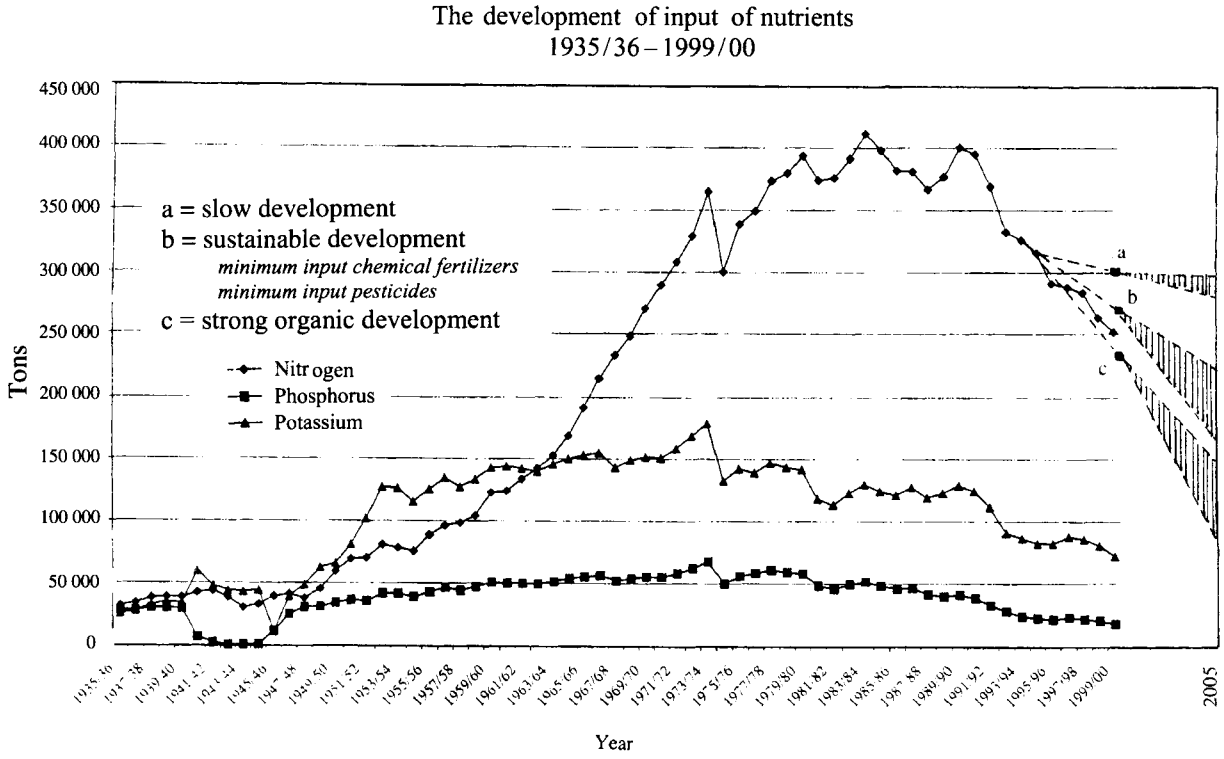


Figure VI.1.7. The evolution of the total consumption of artificial fertilizers in Denmark in the period 1935/1936–1999/2000 (after Danish Ministry of Agriculture and Fisheries, 2001) (a, b and c scenarios by Holm-Nielsen and Al Seadi (2001)).

Table VI.1.7. Controlled sanitation equivalent to 70°C for 1 h, as required by the Statutory Order 49 (after Danish Ministry of Environment and Energy, 2000).

Temperature (°C)	Retention time (MGRT) in a thermophilic digester[a] (h)	MGRT[b] by treatment in a separate tank	
		Before/after thermophilic digestion (h)	Before/after mesophilic digestion[c] (h)
52.0	10	–	–
53.5	8	–	–
55.0	6	5.5	7.5
60.0	–	2.5	3.5
65.0	–	1.0	1.5

[a]Thermophilic digestion is here defined as minimum 52°C, for at least 7 days hydraulic retention time (HRT).
[b]Minimum guaranteed retention time (h).
[c]Mesophilic digestion is here defined as 20–52°C, for at least 14 days hydraulic retention time (HRT).

that require previous treatment, setting up quality standards for the waste products utilized for agricultural purposes. Table VI.1.7 shows an example of requirement of controlled sanitation, for the anaerobic digestion of sewage sludge and other types of organic waste, in order to allow the use of digestate as fertilizer in agriculture.

VI.1.7. Environmental benefits, renewable energy and natural fertilizer from co-digestion of animal manure and organic wastes in Denmark

The agro-environmental legislation outlined earlier motivates the farmers to supply their animal manure and slurries to a centralized biogas plant in order to meet the legal requirements. The Danish livestock counts approximately 2.4 million livestock units, producing approximately 48 million tons of manure per year, of which approximately 1 million tons are supplied to the biogas plants. In Denmark, 20 manure-based centralized co-digestion plants are in operation, processing approximately 1 million tons animal manure and 325,000 tons alternative biomass per year, and producing 50.1 million m^3 biogas (1999 data).

VI.1.7.1. The Co-digestion concept

The first generation of centralized co-digestion plants in Denmark was built in the early 1980s with the only aim of producing renewable energy. The co-digestion concept was continuously developed and improved and represents today an integrated system of renewable energy production, manure and organic waste treatment and nutrient recycling (Fig. VI.1.8), generating intertwined agricultural and environmental benefits (Jepsen, 2002):

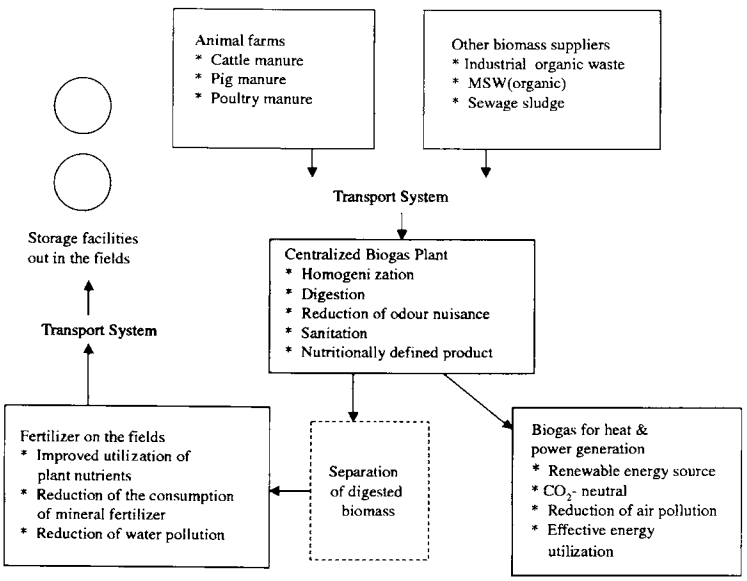


Figure VI.1.8. The main streams of the integrated concept of centralized co-digestion plant (after Hjort-Gregersen, 1999).

- renewable energy production;
- cheap and environmentally sound organic waste recycling;
- less greenhouse gas emission;
- pathogen reduction through sanitation;
- improved fertilization efficiency;
- less nuisance from odors and flies;
- economical advantages for the farmers.

According to the above-described concept, animal manure and slurry are collected from the farmers' pre-storage tanks, transported to the biogas plant, mixed and co-digested with maximum 15–25% digestible organic wastes (also called alternative biomass) from agriculture, food processing industries and municipalities, and submitted to a controlled sanitation process, ensuring effective pathogen reduction.

The digestion process takes place at mesophilic (30–40°C) or thermophilic temperatures (50–55°C), during 12–25 days. A controlled sanitation process takes places as well, where pathogens are effectively reduced, and the contamination cycles are broken. The digested biomass is transferred to the storage tanks, covered with a gas-proof membrane for the recovery of the remaining biogas production (up to 15% of total). Some plants are equipped with installations for fiber separation of the digested biomass, but these technologies are still under development.

The digested biomass is transported back to the farmers, at their storage tanks, placed out in the fields, as a pathogen-free, nutritionally defined fertilizer, to be integrated in the fertilization plan of each farm. The biogas produced is used for combined heat and power generation. The power is sold to the grid and the heat is distributed through the district-heating network to heat consumers. Some of it is used by the biogas plant for process heating.

The legal requirement of 6–9 months slurry storage capacity means a considerable investment for the Danish farmers. The centralized co-digestion plants have built slurry storage capacities for the associated farmers, providing important cost savings from manure storage (Danish Energy Agency, 1995a,b; Holm-Nielsen et al., 1997; Hjort-Gregersen, 1999; Al Seadi, 2000; Al Seadi et al., 2001). Up to 40% investment government grants were given for the establishment of 9 month storage capacity if the farmer supplies the slurry to a biogas plant. The location of the storage tanks is chosen close to the fields where digestate is to be applied and the biogas plant effectuates and supports the cost of biomass transport, providing the slurry suppliers with important cost savings from manure transport.

Danish experience shows that the nitrogen efficiency from digestate application is higher than that from untreated slurry, if the good agricultural practice for digestate application is respected (Holm-Nielsen et al., 1997; Danish Ministry of Agriculture and Fisheries, 1996, 1997). The slurry suppliers also obtain economical benefits in the form of cost savings from chemical fertilizer purchase. The farmers supplying slurry to a centralized biogas plant are also helped to meet the harmony requirements, as they receive back only that amount of digestate they are allowed to spread according to the law. One of the main environmental functions of a centralized plant is the redistribution of manure, and the common practice is that the excess digestate is transferred to arable farms in the area, and the centralized plant supports the cost of transport. The possibility of co-digesting up to 25% alternative biomass offers, to the farmers, opportunities for extra income from the gate fees and from enhanced biogas production. It is also considered a sustainable way of treatment and recycling of the suitable organic wastes.

VI.1.7.2. The place of biogas in the Danish energy strategy

The acknowledgement of the environmental consequences of the intensive animal production, the strengthening of the legislation regarding manure storage as an application, regulations of waste production and treatment increased the interest for biogas plants, which proved to play a new role as providers of manure storage, manure distributors and organic waste treatment facilities. In recognition of this, the Danish Government financed successive RD&D programs and follow-up programs, which proved that the concept offers integrated solutions to a range of environmental problems related to agriculture, waste treatment and energy production. The biogas sector has therefore received growing attention and recognition in Denmark during the last decade. Denmark has an obligation of reducing the emissions of greenhouse gases (CO_2, methane, N_2O and other industry gases) by 21% until year 2012, compared to 1990 as reference year. Biogas shall provide 20 PJ to the national energy production, by year 2030, an 8-fold increase compared with the 1998 level and by this the greatest growth compared with other renewables. In 1999, 2.67 PJ was produced in Denmark from biogas. A significant part of it originates from the large-scale, manure-based co-digestion plants (Table VI.1.8).

The theoretical biogas potential in Denmark is estimated at 34 PJ of which 24 PJ (70%) is represented by animal manure. Energy 21 forecasts 20 PJ by 2030 (Table VI.1.9) that shall mainly emerge from manure-based biogas plants.

Table VI.1.8. Biogas plants and production in Denmark, 1999 (after Danish Energy Agency, 2000).

Type of biogas plant	Amount of plants	Production (PJ)
Wastewater treatment plants	64	0.680
Landfill plants	17	0.550
Industrial waste treatment plants	5	0.150
Manure-based plants		
Centralised, co-digestion	20	1.240
Farm scale plants	25	0.050
Total	132	2.670

VI.1.8. Conclusion

The farming communities represent the main sector and the driving force for a green movement in the rural communities of Europe. The incentives are various: increasing the sustainability of the farm, new income source from selling green electricity to the grid, solving the environmental problems of emissions and odors from manure, better utilizations of farm resources, etc. Further improvement of the utilization of agricultural wastes for industry and renewable energy purposes and for overcoming the existing technical and non-technical barriers must be based on the environmental and economical benefits derived from it and could be directed as:

- Programs to stimulate utilization and recycling of agricultural waste/organic resources;
- Harmonization of animal manure storage, handling and application requirements throughout the EU. Focus on environmental problems of industrialized animal production, such as large-scale production, with no or little land area to recycle manure and organic wastes through crop production.

Table VI.1.9. Potential, actual production and targets for biogas in Denmark (after Danish Energy Agency, 2000).

Energy source	Potential (PJ)	Production 1999 (PJ)	Target prod. 2112 (PJ)	Target prod. 2030 (PJ)
Animal manure	24.0	0.50	3.00	13.0
Sewage sludge	3.0	0.79	1.15	1.5
Organic waste from industries	2.0	0.81	1.50	2.0
Household waste (organic)	2.5	0.01	0.70	2.2
Green waste (parks and gardens)	1.5	0.00	0.25	1.2
Landfill gas	1.0	0.55	0.40	0.1
Total	34.0	2.67	7.00	20.0

- An overall strategy of mandatory harmony between animal stocking rate and farmland area, or demands for maximum limits of nitrogen and phosphate fertilization, following EU environmental strategies, exemplified in the nitrate directive (EEC, 1991).
- Improvement of the present biomass for industry and energy technologies:
  - reduced costs of advanced technologies,
  - developing suitable scale systems,
  - RD&D programs.
- Programs for active promotion and dissemination of well-established technologies and knowledge transfer.
- An overall policy to stimulate fuel and electricity production from renewable sources

The utilization of agricultural wastes for industry and energy purposes will depend to a large extent on availability. Availability and implementation is dependent on agricultural, environmental and energy policies (Nordberg, 1999). The growing awareness of the pollution problems, associated with inadequate management of animal manure and organic wastes, emphasizes the need for appropriate solutions to deal with the problem. A strengthening of the overall policy on environmental protection in relation to the organic agricultural wastes as well as the animal manure handling and utilization, with well-defined enforcement measures, will stimulate the implementation of the appropriate utilization and recycling strategies.

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VI.2

Success stories of composting in the European Union. Leading experiences and developing situations: ways to success

Enzo Favoino

VI.2.1. The development of composting strategies and schemes for source separation of biowaste in European countries: a matter of quality

Since the late eighties, composting has been experiencing a huge growth across Europe. Even before that time, actually composting had been adopted as a disposal route for Municipal Solid Waste, (MSW) through the attempt to sort the putrescible fraction mechanically; such strategy proved to be unsuccessful mainly due to the following reasons:

- the increasing presence of contaminants inside municipal waste;
- the lack of suitable refining technologies that could effectively clean up the end product in order to let it be accepted by end users;
- the consequent lack of confidence among farmers and other potential users;
- the increasing awareness, among scientific bodies and institutions, of the importance to keep soils unpolluted – with specific reference to potentially toxic elements such as heavy metals.

As a consequence, the recent and effective growth of composting programs started in parallel to the growth of schemes for source segregation of biowaste that were increasingly adopted as the proper answer to the need to have quality products suitable for a profitable use in farmlands and other cropping conditions (forestry, nursery, gardening, pot cultivation, etc.) (Amlinger, 2000; Barth, 2000; EC DG ENV, 2000).

Figure VI.2.1 mirrors the influence of source segregation on the quality of composted products (taken from a data base including some 400 samples). At a glance, what stems out is the sharp decrease of heavy metals in those composting schemes where source segregation is in place, as compared to compost produced through mechanical sorting of mixed waste. Also sludge often negatively affects the concentration of certain heavy metals, namely copper and zinc, though provisions for "Pollution Prevention Programs" included in the proposed revision of the EC Sludge Directive (EC DG ENV.E3/LM, 2000) could have a positive impact in the future on that side. Still, whenever we come to sludge-derived products, we will have to tackle the problem of organic pollutants also. Amazingly, in most composted products stemming from manure and slurries we can detect relatively high concentrations of zinc and copper, as they get often included in the diet

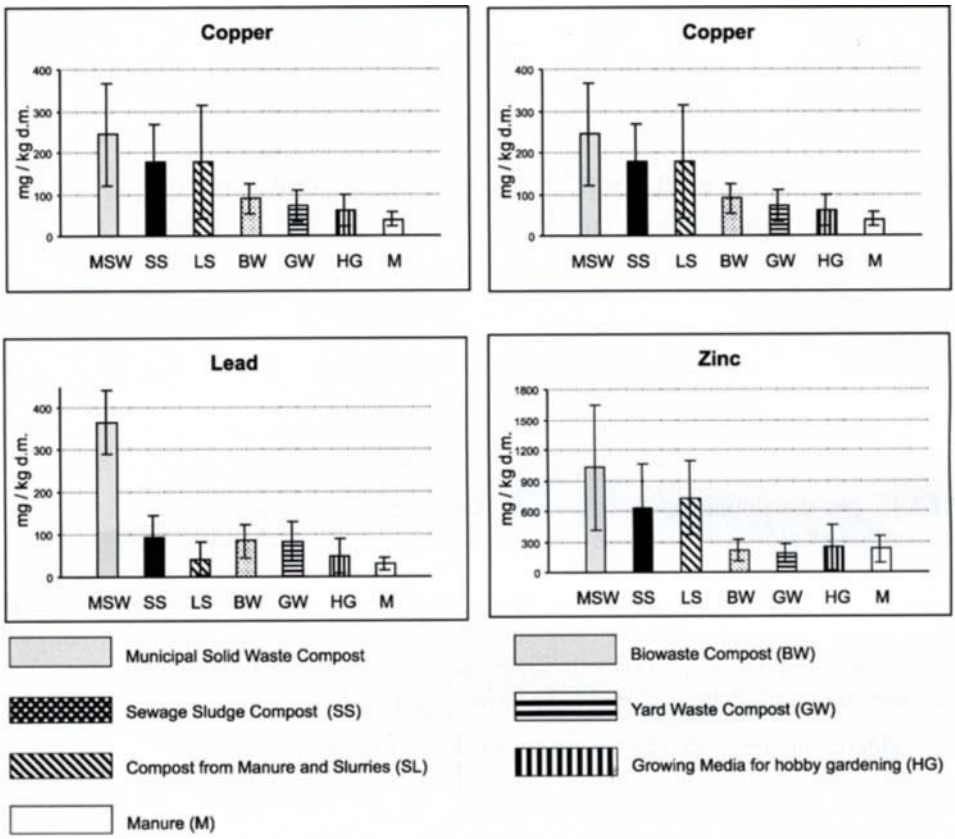


Figure VI.2.1. Concentration of some heavy metals in composts stemming from different waste materials, also in comparison with other soil improvers.

of animals. What matters here is that *the concentration of heavy metals in compost stemming from source-segregated biowaste and yard waste does not significantly differ from that of traditional soil improvers and of manure itself* – above all if we consider that this latter has not undergone yet the mineralization of organic matter, which would make the concentration seem higher.

With reference to activities in the field of source separation and composting of biowaste, European countries can be grouped into 4 categories (Fig. VI.2.2). In *Austria*, Belgium (*Flanders* in particular), *Germany*, *Switzerland*, *Luxembourg* and the *Netherlands* strategies and policies are already fully implemented nationwide. The contribution of these countries – and Germany in particular – to the overall recovery of biowaste in the EU is fundamental and was around 80% in 1999. Anaerobic digestion plays a minor role for the time being, partly due to the higher specific investment cost and to the need for integrated waste and wastewater management schemes that actually still happens fairly seldom.

In the second category we find *Denmark*, *Sweden*, *Italy*, Spain (*Catalonia*) and *Norway*. In these countries the policies are fully outlined but schemes of the needed composting capacity and of the marketing framework are still under an ongoing development.

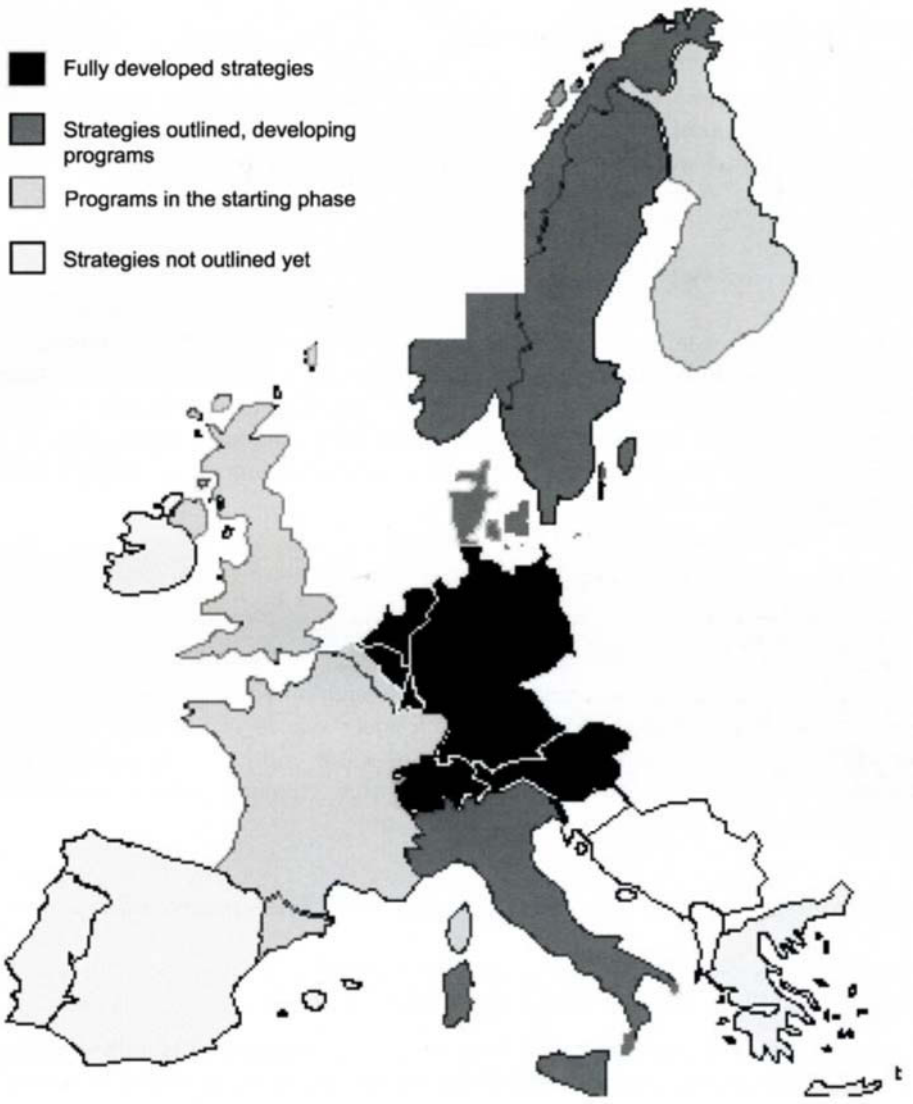


Figure VI.2.2. Development of source separation and composting in Europe (adapted from Barth, 2000).

Finland, *France*, the *United Kingdom* and *Walloon* (Belgium) belong to the third category, where programs are at the starting point though policies have been sometimes fully laid out.

To the fourth category belongs countries where no effort on composting of source-separated organic waste can be detected just yet; these include most regions in *Spain*, besides *Greece*, *Ireland* and *Portugal*. In these countries composting from mixed urban waste is still being practiced and sometimes plays an important role (e.g. many local strategies in Spain and Portugal).

VI.2.2. The driving forces for composting

There is a diffused awareness among technicians and decision-makers that composting will still play the most important role in forthcoming European Strategies for Waste Management. This chapter briefly describes what are the most important driving forces at EU level for that.

VI.2.2.1. Directive 99/31/EC on Landfills

The Directive on Landfills (EC, 1999) basically provides for the landfilled biowaste to be sharply reduced within the next years. This is aimed at effectively reducing the production of biogas at landfilling sites (one of the highest contributions to the global warming potential from waste management) and to improve the conditions at which landfills are operated (e.g. lower chemical strength of leachates, less settlements in the shape of the site after the landfill gets shut down).

Biowaste to be landfilled should be reduced by:

- 25% (with reference to 1995) within 5 years,
- 50% within 8 years,
- 65% within 15 years.

Though this could be accomplished also through thermal treatment, biological treatment and composting are likely to play a major role in this respect. In the end, composting is the most *natural* way to manage biowaste, and its cost is generally lower than that of incineration – above all once this latter has to comply with the provisions of the recent Directive on Incineration (EC, 2000).

VI.2.2.2. Proposed directive on biological treatment of biodegradable waste

The EC recently took the initiative to propose a Directive on Biological Treatment of Biodegradable Waste (EC DG ENV.A2/LM, 2001), in order to:

- Ensure a balanced approach to the commitments on reduction of landfilled biowaste outlined in Directive 1999/31/EC (EC, 1999), i.e. set the need to have recycling of organic matter as a better option than its thermal recovery (once we consider that energetic exploitation of putrescible waste is made most difficult for the high moisture it carries along).
- Fix some recycling targets for biowaste, so as to ensure an even development of composting across Europe.
- Define common limit values and conditions for use and marketing of composted products across Europe.
- Further develop the production of high-quality composted soil improvers to be used in organic farming and as a tool to fight desertification processes in Southern European Member States.
- Cover also those processes, usually worded as mechanical–biological treatment (former MSW composting) that are at present experiencing a wide development above

all to treat residual waste, in order to define their role in integrated waste management strategies and conditions of use (e.g. in land reclamation) or landfilling of their end products.

One of the most important provisions included in the current proposed draft is that source separation of biowaste should be developed, besides in rural areas and small municipalities, also in big cities (with possible exceptions only in inner cities). Such a provision could be disputed, as in general, it is argued that purity of sorted food waste tends inevitably to get much lower in highly populated areas. Actually, on the contrary, *the quality of collected biowaste seems to be much more dependent on the system adopted for collection than on the size of towns*, and many situations are reported where schemes prove to be successful also in big towns and inner cities (EC DG ENV, 2000). Coming to Italian schemes, for instance, the Working Group on Composting and Integrated Waste Management of Scuola Agraria in Monza, Italy, represented by the author of this chapter, has plotted the numbers about purity of separated biowaste (percentage of compostable materials) reported in various sorting analysis performed across Italy (Fig. VI.2.3). What turns out is that no relation can actually be detected between the size of the population covered and the purity. This means that other factors are affecting the purity more than the population covered by the scheme, and namely the *type* of the scheme put in place; doorstep schemes generally perform much better than schemes run through containers on the road. Similar outcomes are reported in Catalonia (Spain), where similarly both types of scheme are currently run (Favoino and Giró, 2001).

Statistical treatment of numbers yields a very low relationship ($R^2 = 0.0174$), and this is in itself a demonstration of a low dependence of purity on the size of towns running the scheme for source separation. Even at a first glance, it is easy to get aware of the presence

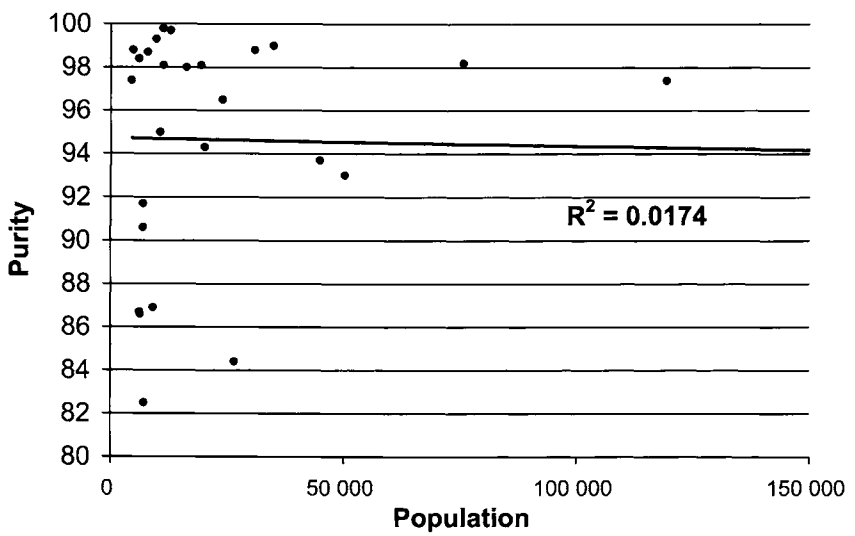


Figure VI.2.3. Purity of collected food waste vs. population covered.

of cases of high purity in medium to big towns, besides low purity, sometimes, in a certain number of tiny villages.

VI.2.3. Keys to success: quality assurance systems and marketing conditions in Central European Member States

The wide development of strategies aimed at recycling of biowaste through composting in the Central European Member States is largely based upon steady marketing conditions. This, in turn, ensures outlets for the end product, thus providing further justification for the strategy (EC DG ENV, 2000).

Quality assurance systems (QAS) for composted products have already long been playing a central role in the composting framework in Central Europe (Amlinger, 1998). As a matter of fact, a QAS links the quality of the end product to all the elements of the process management; a comprehensive quality management of the composting plant gets thus possible.

As Table VI.2.1 clearly shows, QAS play a central role in those countries with a well-developed composting system like Austria, Germany, Denmark, the Netherlands and Belgium. These countries have established an extensive quality management system for the composting plants that in 1998 already covered around 400 composting plants (Table VI.2.2).

Quality criteria for compost differ in each Member State as to requirements and limit values. Quality classes based directly on heavy metal limits exist only in Austria (class I and II such as the types "A" fresh and "B" matured compost) and in the Netherlands (Table VI.2.3). The Dutch requirements for the class "very good compost" are so high that they can only be reached very seldom; therefore the Dutch Compost Plant Association is now proposing different limit values. The Belgian QAS, distinguishes only on the basis of raw materials.

What turns often out is that when diversified compost qualities based on heavy metals are available only the best one gets effectively marketed. As a matter of fact, in such a situation customers are led to believe that the lower quality is not reliable. This means that larger quantities of compost still profitable for many applications will fail to be used in most cases (Barth, 2000).

Quality classes based on the raw material (as in Belgium), or on the features of the product, affecting the suitable application (as in Germany) are on the contrary effective tools to meet the requirements of the compost market.

Countries shown in the Table VI.2.3 have different priorities in their quality criteria and efforts for quality control.

Organic pollutants are highly focused upon in Denmark; the *hygienic aspects* for the moment are the main concern in Germany, and *odor emissions* create problems in Belgium.

An important point is that the development of steady and reliable markets for composted products require a *standardized quality of the product* and a *proper quality assessment*, in order to both develop confidence among customers and users and to ensure proper, "aware" management conditions at composting facilities (that in turn makes the acceptability of plants among local dwellers grow).

Table VI.2.1. Status of compost quality efforts in various EU Member States (modified from Barth, 2000).

Country	Status of quality assurance/certification of compost
Austria	Fully established QAS
Belgium	Fully established QAS in Flanders, the Walloon and the Brussels region will probably follow the Flanders example
Denmark	Just started with QAS for compost (criteria, standardized product definition, analyzing methods)
France	Proposal for quality criteria, research program for a quality management system
Germany	Fully established QAS
Italy	Proposal by the Composting Association (CIC – Consorzio Italiano Compostatori) for QAS, to be implemented
Luxembourg	Some plants according to German QAS
Netherlands	Fully established QAS and certification systems
Spain	Proposal for "Bill on the Quality of Compost" in Catalonia
Sweden	Recently started with QAS for compost
UK	Proposal of quality standard by the Composting Association (TCA – The Composting Association)
Finland	No official efforts until now
Greece	No official efforts until now
Ireland	No official efforts until now
Portugal	No official efforts until now

Table VI.2.2. Status of QAS at composting plants in Central European Member States (as per 1998).

Country	Plants with quality assurance[a]	Plants with quality sign or certificate
Austria	ca. 18	2
Belgium (FL)	ca. 21	5
Germany	ca. 340	ca. 300
Netherlands	22	2

[a]This figure includes plants that have applied for a quality sign or a certificate but the process is not yet finished.

Table VI.2.3. Classification of compost quality in Europe.

Country	Type of compost/quality class
Austria	Quality Class I and II, Type A (mulch) and B (matured) compost
Belgium (Flanders)	Yard and vegetable, fruit and garden VFG compost
Germany	Fresh and matured compost, mulch and potting soil compost
Netherlands	Compost and very good compost

Testing of composts through the application of a QAS proves thus to be a crucial point in the overall development of composting strategies as:

- The quality assurance is a good tool for *sales promotion, for public relations* and a good argument for the building up of confidence in compost.
- The quality label allows the establishment of a branded "quality-tested compost" and a positive compost image.
- *Regular* testing during compost production guarantee a *quality-assured product.*
- *Standardized* analyses carried out in accordance with specified methods enable a nation-wide objective assessment of the compost quality.
- The results of the assessment are a most important basis for the *product declaration* and the *recommendations on suitable application* (that obviously shows to be a powerful marketing tool).

The overall result is a compost of defined quality, which is therefore marketable and saleable on a large scale.

Of course, compost with a quality label or a quality certificate will not be simply sold as such, and further marketing activities are needed. The application of a QAS, however, is a fundamental step for compost plants because products with tested quality always attract more interest on the market. To compete with peat, soil and bark industries in the market of soil improvers and potting mixes, compost plants need to undertake additional and common efforts in their marketing activities.

The successful development of QAS in the Central European Member States has led also other countries to put efforts on such an issue. More and more often, proposals for the introduction of a QAS are being raised across Europe (see Table VI.2.1); governmental bodies often play a major role in fostering the development of the system, as for instance in Sweden. Other times proposals have been developed directly by the associations of compost plant managers – as lately happened in the UK and Italy.

VI.2.3.1. Marketing conditions and trends

Compost marketing shows various trends in Europe. Significant differences on the market situation can be identified. Generally speaking, it turns out that *even in the countries with*

most diffused schemes and the highest compost production, compost is effectively marketed; an effective marketing framework and proper marketing strategies have been fundamental to overcome the initial worries about a lack of enough demand for the product.

In all countries hobby gardening, horticulture and landscaping are a successful market; in general they constitute the main marketing basis for composted products and shows proper conditions for its development.

Green compost (where only yard and wooden waste gets processed) is an organic fertilizer and soil conditioner well accepted by the markets all over Europe. It can be produced in a good quality without much technical equipment.

Market for compost from *biowaste* (including food waste) shows two contrary developments: by means of the decreasing or low tipping fees, some of the composting plants try to minimize their treatment and marketing costs – e.g. producing "fresh" compost, with a low maturity for field applications, which results mostly in delivering the compost free of charge to farmers without additional marketing efforts. On the other hand a lot of composting plants start to add value to their compost products and produce mixtures or special products according to customers' needs and requirements of the market. They either co-operate with producers of growing media or build up a mixing, bagging and marketing activity by themselves.

The quality assurance organizations support these tendencies through the organization of research projects for compost application and for new blends of composted products with other materials.

Table VI.2.4 reports on the market shares in the various Member States in Central Europe; in order to allow a comparison, also data from Italy have been included. It turns out that applications linked to gardening, pot cultivation and landscaping play a major role and the application in agriculture does not cover the main market share – though potentially its size is, of course, the biggest one. The high percentage in Germany is mainly due to the trends on the production of fresh compost already described; in Austria, on the contrary, the diffused presence of rural composting sites ("Bäuerliche Kompostierung") boosts the interest of farmers for a direct application of compost on farmlands.

Coming to Mediterranean countries, there is a strong evidence that the use of compost in farmlands could play on the contrary a major role in the future. There is a also great awareness, among composting plant managers and research centers, that in future the use of compost in field crops has to be developed, besides that for potting mixes, in order to back up the growth of compost production.

It has to be underlined that specific weather and cropping conditions determine – in general – a huge request for organic matter in Mediterranean agriculture. Warm and dry climates and the intensive, humus-consuming crops (e.g. horticulture, fruit growing) make soils hungry for organic matter; decades of chemical fertilization as a complete substitute for organic fertilization have worsened the overall situation. Also in Northern flatlands, many soils are currently reported at less than 1.5% organic matter. Moreover, the recent Dakar Conference has shown that many Mediterranean countries are threatened by the process of desertification.

This picture leads, on the whole, to a favorable situation to promote the use of composted materials (Oriol, 2002; Tittarelli, 2002). Many farmers' associations are now addressing compost as a suitable tool to restore fertility and allow the development of

Table VI.2.4. Market shares of compost sales and market size.

	Market shares in selected EU countries (in %), 1998/99						
	Austria (1998)	Flanders (1999)	Germany (1998)	Denmark (1998)	Italy (1999)	Netherlands (1998)	Market size
Landscaping	30	24	25	19	30	30	Large
Landfill – restoration	5	5	–	13	–	–	Small
Agriculture + special cultures	35[a]	5	43	10	20	40	Very big
Horticulture	5	6	5	3	–	–	Medium
Earth works	5	33	10	–	50	–	Medium
Hobby gardening	20	20	14	48	–	20	Large
Export	–	4	–	–	–	–	Very small
Miscellaneous	–	11[b]	3	7	–	10	–

[a]60% of the Austrian VFG and green waste is on-farm composted.
[b]Decontamination.

those crops that best fit the Mediterranean climate (e.g. horticulture, fruit-trees, etc.) in place of animal husbandry that cannot be competitive to the Central European Member States.

A major challenge is still represented by the *need to find suitable equipment for mechanical spreading*, as old machinery fits the features (moisture content, consistence, grain size) of either manure or chemical fertilizers. Recent trials (e.g. Bisaglia and Centemero, 1998) indicate that such a need has been successfully addressed finding suitable solutions.

From a "strategic" viewpoint, there is a great awareness – by some central institutions – of the importance to restore organic fertility in the soil. For instance, ANPA, the Italian National Environmental Protection Agency, is committed *to promote a National Plan for Organic Matter to the Soil*, in which the overall needs, calculated by fertility restoration programs, have to be supplied by organic fertilizers, among which composted products are forecast to play a key role.

In such respect, more and more often local institutions outline programs and funding to promote the use of compost as an organic amendment; most often, main provisions of such programs are:

- funding farmers with a certain sum per unit area where compost gets land applied,
- the preference for composted products in tenders for public green areas (gardens, parks),
- funding farmers to replace old machinery when the new equipment is mechanically suitable to spread compost as an organic fertilizer.

Supporting the strategy on the agronomic side has to be foreseen in future as one of the key elements in a general strategy that targets full recovery of the role of organic matter from waste materials in agriculture. The size of the potential request is big enough to justify the effort; Table VI.2.5 shows that even at complete development of schemes for

Table VI.2.5. Percentages of arable land area potentially interested by compost application in the EU countries[a].

EU Member State	Inhabitants 1995 (10^3)	Arable land area (ALA)	Food and green waste compost		Arable land needed for compost application	
		Total (10^3 ha)	Potential production (10^3 t)		Total (10^3 ha)	% ALA
			f.m.	d.m.		
Austria	8040	1500	321	161	16.1	1.07
Belgium	10,131	700	405	203	20.3	2.90
Denmark	5216	2500	208	104	10.3	0.41
Finland	5099	2500	204	102	10.2	0.41
France	58,027	18,000	2321	1160	116.1	0.65
Germany	81,553	12,000	3262	1631	163.1	1.36
Greece	10,063	3000	402	201	20.1	0.67
Italy	57,248	10,000	2290	1144	114.5	1.15
Ireland	3577	1000	143	72	7.1	0.71
Luxembourg	407	60	16	8	0.8	1.35
Netherlands	15,423	900	616	308	30.8	3.43
Portugal	9912	3000	396	198	19.8	0.66
Spain	39,170	16,000	1566	783	78.3	0.49
UK	58,276	7000	2331	1165	116.5	1.66
Sweden	8816	3000	352	176	17.6	0.58
EU	370,958	81,200	14,833	7416	741.6	0.91

[a]Calculation: (i) collection of organic waste: 100 kg/in. year; (ii) process yield: 40%; (iii) dry matter 50%; (iv) application rate: 10 t/ha d.m.

source separation of biowaste (100% of the population involved) the potential request is by far bigger than the potential production.

VI.2.4. Countries in the starting phase: the development of programs for source separation of household organic waste in Mediterranean countries

As a consequence of a growing number of provisions in national or local legislation, and/or mandatory programs, a growing number of districts in Southern Member States have lately adopted those strategies already well developed in Central and Northern Europe, aiming at source segregation of the organic fraction of municipal waste. During last years, the development has been particularly noticeable in Northern Italy and Catalonia (Spain) (Favoino, 2000; Giró, 2000; Cortellini and Favoino, 2001).

VI.2.4.1. Italy

In Italy schemes were first developed during the early nineties; Milan Metropolitan Area widely adopted composting and recycling since 1994–1995 as a fundamental tool to seek for solutions to their disposal crisis (Consorzio Provinciale della Brianza Milanese, 1997; Provincia di Milano, 1998a,b). Some 600 municipalities across Italy had already been reported to run source-separation programs for food waste early in 1997–1999 (Provincia di Lecco, 1997; Lazzari, 1998; Azienda Municipale di Igiene Ambientale di Torino, 1999; Favoino, 2000).

For the time being, the development of recycling programs mainly refers to Northern Italy, though many programs are starting in central and southern regions. Among these, noteworthy is the situation in some districts in Abruzzo, where two municipalities were reported in 1999 at more than 50% recycling; thanks above all to door-to-door schemes for sorting food waste.

Table VI.2.6 refers to the 1999 update; numbers are now likely to be at more than 1000 municipalities across Italy (the overall number of Italian municipalities being somewhat more than 8000). During last spring and summer, many more towns – even among those with medium to high population – have started separation of food waste in Southern Italy, e.g. Matera (some 60,000 people) and Battipaglia (60,000).

The main cause for such a growth in source separation of food and green waste has to be found in recent developments of the environmental policy. Decree 22/97, the National Waste Management Law of February 1997, sets a recycling goal at 35% to be met by 2003. Source separation of the organic waste is not compulsory, and it is just depicted as a "priority". Still, food waste source separation is a need in order to reach the medium-term recycling target set by the Decree at 35%. In effect, intensive collection of dry recyclables (paper, glass, plastic, etc.) does not allow local authorities – in general – to meet such a goal (it has to be noted that home composting and demolition debris are not included into the total figure of recycling rate). Thus, most regions and provinces are including source separation of food waste in their waste management plans (Bigliardi, 1998; Lazzari, 1998; Favoino, 2000).

Source separation of food waste has already allowed some provinces, Milan Province included (some 190 municipalities, $>3{,}500{,}000$ inhabitants), to meet the 2003 recycling

Table VI.2.6. Municipalities and inhabitants involved in source separation programs for food waste in Italy (update: January 1999).

Region	Municipalities	Inhabitants
Abruzzo	11	76,511
Campania	8	93,865
Emilia-Romagna	36	218,682
Liguria	2	4900
Lombardia	329	3,027,950
Marche	2	6000
Piemonte	41	109,184
Toscana	12	113,724
Veneto	109	887,151
Trentino-Alto Adige	26	46,012
Total	576	4,583,979

goal (35%), with many single municipalities overcoming 60%; two provinces (Lecco and Bergamo) have already exceeded the 45% recycling rate on aggregate. The use of specific tools and systems for door-to-door source separation of food waste has proven to be effective with relevance to quantity and quality of food waste collected, and very cost-competitive.

The collection of yard waste is even more developed, above all in such regions as Lombardia, Veneto and Piemonte (some 4000 municipalities, 17,500,000 inhabitants) where it has been made compulsory since 1994. Many other regions, above all in Northern Italy, such as Emilia Romagna and Tuscany are also recording a wide extension of programs to collect yard waste, even though they have no compulsory action in such respect.

VI.2.4.2. Spain

Biological treatment on the whole is experiencing a fast growth in Spain, as well. As far as schemes for source segregation are considered, Catalonia is undoubtedly gaining the leading position in Spain (Giró, 2000). Actually source segregation of "bassura orgánica" (organic waste) has been developed also in other areas, both rural and urban. Among these latter, an outstanding scheme – if referred to the population covered – has already long been run in Cordoba (some 300,000 inhabitants).

In Catalonia, as per July 2000, 63 municipalities were reported to source separate biowaste, for an overall population of some 430,000 inhabitants (see also Table VI.2.7); an update in November was reporting 72 municipalities and 640,000 inhabitants. The Catalan development takes its steps from a Regional Law (Law 6/93) that outlines compulsory programs for the source segregation of organic waste in all municipalities with a population over 5000 inhabitants. This mandate affects 158 municipalities with a population of 5.3 million inhabitants, or nearly 90% of Catalan population. The remaining

Table VI.2.7. Source separation of biowaste in Catalonia: development of programs.

Schemes	Compulsory municipalities >5000 inhabitants		Voluntary municipalities <5000 inhabitants		Total municipalities	
	Municipalities	Inhabitants	Municipalities	Inhabitants	Municipalities	Inhabitants
Overall	158	5,304,724	786	785,316	944	6,090,040
Schemes by July 2000	49	393,000	14	40,000	63	433,000
Schemes by November 2000	57	557,000	16	44,000	73	601,000

municipalities, those with populations under 5000 inhabitants, are not required to comply, although they may participate – and many are doing so – on a voluntary basis.

Though deadlines for the full development of programs defined in 1993 had to be postponed, the strategy has steadily grown up and will continue to be fully developed. The Metropolitan Waste Management Plan sets a target for 350,000 t biowaste (including big producers) to be source separated by year 2006 (that means covering all the population inside the metropolitan area).

Underpinned by the success of Catalan schemes, lately a similar regulatory approach has been adopted by the Spanish National Law on Waste Management 10/98 and by the PNRU (National Plan for the Management of Municipal Waste) 2000–2006, which specifies that all municipalities with a population above 5000 inhabitants (within 2001) and those with a population above 1000 inhabitants (within 2006) have to run schemes for the source separation of municipal wastes. Though no further explanation is provided for what materials should be tackled by schemes to be included in "source separation", it seems generally agreed that – also under the spur of what is happening in Catalonia – the strategy will also cover source segregation of organic waste. For instance, it must be noted that a National Composting Program has been defined accordingly. In this program targets and deadlines for recycling of organic matter by means of composting, and anaerobic digestion, have been defined.

This led many regions to include provisions for the development of programs for the source segregation of organic waste in their local plans. Let us quote:

- Comunitat Valenciana ("Pla Integral de Residus de la Comunitat Valenciana").
- The Autonomous Waste Management Plan of the Autonomous Community of Madrid, with provisions for separate collection of biowaste to be established as a general rule in a second phase, as from 2003.
- Comunidad Autónoma de Aragón has included in its "Plan de Ordenación de la Gestión de Residuos Sólidos Urbanos" the implementation of the separate collection of biowaste.
- Comunidad Autónoma de Castilla – La Mancha has also established in its *Plan de Gestión de Residuos Urbanos de Castilla – La Mancha* the implementation of the separate collection of biowaste.

- Comunitat Autònoma de les Illes Balears, by means of the "Pla Director Sectorial per a la Gestió dels Residus Urbans a Mallorca", and, in a near future, with the elaboration of the "Pla Director Sectorial per a la Gestió dels Residus a les Illes Balears" and the Law on Wastes for the Balearic Islands, has also fixed the implementation of separate collection of biowaste.

VI.2.4.3. The composting capacity in Italy

Italy faced a significant development of source-separated waste composting capacity in the last 10 years, also as a consequence of the implementation of the new regulation on waste and the development of source separation.

According to the preliminary results of a survey led by ANPA (the National Environmental Protection Agency) the number of plants increased from 10 in 1993 to 114 in 1999 (135 if also sites with a capacity of less than 1000 t/year are considered). In the same time frame, the overall quantity of raw materials treated (source-separated organic waste) increased from 0.25 to 1.34 million tons (Table VI.2.8). Actually, the overall potential capacity of plants was even higher, topping some 2,020,000 t in 1999.

In 1999, 24% source-separated waste treated in composting plant was food waste, 38% yard waste, 28% sludge, 10% other organic waste materials; 44 additional plants were not yet in operation, or under construction or planned, with an overall capacity of 0.63 million tons/year, so that the overall treatment capacity is expected to increase in the short term from 2 million tons in 1999 to 2.6 million tons.

The Italian composting capacity is mainly concentrated in Northern and Central regions; however, more recently, many efforts have been made in Southern regions, in order to fill the gap starting or increasing the composting capacity. This refers above all to Campania, and Puglia; in this latter region for instance, recently a tender has been issued by the Governmental Task Force on Waste Management, aimed at building 8 large-sized new composting plants. In many cases, public initiatives have been followed or even anticipated by private action that finds a growing place for profitable operational conditions, as fees for landfilling are getting increasingly higher.

As a consequence of the overall composting capacity, the production of high-quality compost in Italy, in 1999, has been estimated at 600,000–650,000 t.

Table VI.2.8. Trend of the composting capacity for source-separated organic waste in Italy (after ANPA, 1999).

Year	Number of composting plants	Treatment of source separated waste (1000 t/year)
1993	10	250
1997	85	899
1999	114[a]	1340

[a]135 if decentralized facilities for yard waste with a capacity below 1000 t/year are also considered.

Also the biological treatment of residual waste is under development as Decree 22/97 asks for the waste to be pre-treated before being landfilled by July 1, 2001. In the past, many mixed MSW composting plants aimed at producing compost for field crops. Some 30 plants under operation have been recently reported (ANPA, 1999). In 1997 the overall capacity for mixed MSW or residual waste reached some 1,650,000 t/year. Referring to 1995, some reported 65 mixed MSW composting plants (with an overall capacity of some 3,000,000 t/year), only 23 of which are in operation (some 850,000 t/year), 16 are shut down and 25 are under construction or are undergoing upgradation (Merzagora and Ferrari, 1996). Many of those plants have been shut down in the past years; accordingly, many others have not been fully completed. Such shortcomings were due to:

- poor environmental conditions (lack of odor-treatment systems);
- poor process management (with production of immature compost) or, most of times;
- the unsuitability of the targeted end use, as farmers seldom have trusted mixed MSW compost to be used in farmland applications, with a few exceptions due to the need for organic amendments to restore fertility in the deep far Southern regions.

The strategy has thus undergone a sharp change; more and more often old composting plants get fully or partially converted to quality composting of source-separated organic waste and/or used for biological treatment of residual waste. Moreover, new ones have been recently opened. In particular, Milan biological treatment plant has probably to be considered as the biggest one across the world, as its capacity is 2000 t/day of residual waste.

Nowadays, biological treatment for residual waste targets different possible aims:

- stabilization prior to landfilling, in order to comply with provisions of both the National Waste Management Act and of Directive 99/31/EC on Landfilling (EC, 1999);
- drying up of residual waste before thermal valorization, along the lines of the *Dry stabilization* method increasingly developed in Central European Member States;
- use of organic soil improvers ("Gray compost" or stabilized organic fraction (SOF)) for land reclamation. It has to be mentioned that the huge needs of organic matter in Mediterranean weather and cropping conditions, leads to the need of saving quality compost only for application in cropping and gardening.

Some regions and provinces have already issued guidelines and/or technical regulations to allow the use of MSW compost for land reclamation (Favoino, 1998); their principles have been taken over by a draft national regulation expected to be issued in the future. Such regulations rely upon the hypothesis of one-off applications with high loads in order to promote biological activities in surface soil layers on exploited mines, slopes to be consolidated, anti-noise barriers, etc. As for technical requirements of such applications, regulations address above all the need to check both:

- heavy metals load and
- nitrogen load.

Loads have to be calculated in order to stay within maximum concentration of potential toxic elements (PTEs) in the soil and to prevent massive release of nitrogen to the groundwater.

VI.4.3.1. Technical features of composting sites: a balanced approach to environmental standards

A fast evolution is taking place in Italy as to *environmental standards* of composting plants, with specific reference (but not only) to odor management. Actually, people are getting increasingly sensitive to the need of ensuring proper conditions for waste management, and nearby dwellers have often been raising complaints against the way "low-tech" sites were performing as to nuisance.

Most operators and institutions are now aware that in order to ensure a steady growth of composting activities, proper standards have to be outlined both for building and running composting sites. This refers not only to "wealthy" Northern regions, where composting is often cost-competitive, even at highest environmental standards, to landfilling; but also to many situations in Southern Italy, where public funding programs to build composting sites enable local institutions to have relatively low operating costs (as they do not have to take into account depreciation of capital costs) even with the utmost care for proper and safe management of exhaust air.

Thus far, no technical guidance has been issued in National Regulations about process management, except in the Decree 5/2/98 on "Simplified Permitting Procedures"; according to the Decree, composting sites treating fermentable feedstock such as sludge and food waste have to be fitted with enclosed processing systems for first steps and technologies for exhaust air treatment, regardless of their size/capacity and distance from dwellings. These provisions have been regarded by experts as too "tough" for many composting sites where odors would not constitute a problem due to:

- low capacities,
- specific processing systems (e.g. piles with cover layers) and
- distances from dwellings.

Moreover, no standard has been issued in the Decree on dimensioning and assessment of effectiveness of odor treatment; this leads to situations where composting plants install biofilters poorly dimensioned that will be too far from being effective.

To date, "regular" permitting procedures (the ones most used) do not undergo any provision for technical features of composting sites. A further Decree is on draft, anyway, and it sets some basic principles as:

- retention of first process steps for fermentable feedstock in enclosed buildings or containers, till a certain fermentation level (to be assessed through the "oxygen uptake" test);
- simplified provisions both for yard waste and for sites processing also food waste at low throughputs (less than 3000 or 6000 t/year); this is also deemed to promote composting in rural and hilly areas (e.g. the Alpine regions), where generally composting is done at less facilities along the lines of the Austrian "Bäuerliche Kompostierung".

Meanwhile, many regions have issued regulations of their own that cover, in a more or less detailed way, environmental standards to be met at composting sites. Table VI.2.9 reports on some of the most significant situations both at national and local level.

One of the most debated topics is the way to assess performances of systems for treatment of odors. In past years, many times institutions were asking for analytical

Table VI.2.9. National and local provisions for environmental standards.

Regional or national regulations	Guidance for:				
	Mandatory enclosure of early process steps for fermentable feedstock (e.g. food waste, sludge)	Dimensioning of systems for odor treatment	Test methods to assess performances of systems for odor treatment	Management of wastewaters	Simplified provisions for yard waste composting
Lombardia	Yes, till a certain residual fermentability	Yes	Yes, including olfactometry	Yes	Yes
Veneto	Yes, till a certain retention time and residual fermentability	Yes	No	Yes	Yes
Piemonte	Yes, till a certain retention time	Yes	No	No	Yes
Emilia Romagna	No	Yes	Yes, only analytical measurements	No	Not needed (see 1st column)
National Decree 5/2/98 ("simplified permitting procedures")	Yes, but only the principle has been outlined, with no retention time	No	No	No	Yes

measurements, including the assessment of volatile organic compounds (VOCs) with limits set at 5–10 mg/N m^3; this was mirroring provisions for much more hazardous facilities, such as incinerators, where a low concentration of VOCs in emissions witnesses good combusting conditions. Actually, as in most composting sites biofilters have been installed as a very effective means to reduce odors; one must consider that biofiltration beds contribute themselves to VOC emission, stemming for example from degradation of wood. This is why many technicians have been harshly disputing the *real* effectiveness of VOC provisions. Lately, the attention of institutions has been attracted to *olfactometric measurements*, according to the internationally adopted methods (CEN/TC 264, 2002); this method is proving to be very effective in describing the real odor potential at composting sites. Olfactometry has already been adopted by Region Lombardia as the reference test method to assess performances of treatment systems for exhaust air.

VI.2.4.4. The composting capacity in Spain

The capacity of biological treatment in Spain, actually, is to date mostly covered by composting of unsorted waste (production of gray compost). Composting facilities in different regions are listed in Table VI.2.10.

The overall composting capacity is reported at some 3 million tons of waste, mostly covered by plants for unsorted waste.

It is anticipated that – along the lines of what already happened in other countries – in the future such facilities will be assigned a different aim (namely biological treatment of residual waste), or will be upgraded into composting plants for source-separated organic waste.

As a consequence of the development of source-separate collection, Catalonia is the region with the larger capacity for composting of source-separated organic waste.

A specific feature of the Spanish situation is that a large capacity for anaerobic digestion is being developed, as mechanisms for public funding of capital investments – mostly through EU financial provisions – tend to make it cost-competitive. Just on the basis of projects already underway, the overall Spanish capacity for anaerobic digestion will be likely at some 2 million tons in the medium term; anyway, as most facilities are meant to treat mixed MSW, the actual capacity of digesters will cover only a minor flux of total input waste being delivered at the plant (underflow materials stemming from primary screening). To date, 8 digesters are under construction.

VI.2.5. The possibility to optimize the schemes and to cut cost down

One of the major concerns of waste managers across Europe is the common opinion that source-separation system aiming at reaching high recycling rates, are bound to suffer from the lack of cost-competitiveness as compared to the traditional mixed collection of MSW. Operators think that in particular, sorting food waste leads to higher costs for the overall collection scheme.

Table VI.2.10. Composting plants in Spain (update: late 2000).

Region	Source-separated waste			Mixed municipal waste			Total
	Operating	Under construction or planned	Total	Operating	Under construction or planned	Total	
Andalucia	2	0	2	8	1	8	10
Aragon	0	8	8	0	0	0	8
Asturias	0	0	0	0	0	0	0
Iles baleares	0	1	1	1	1	2	3
Islas canarias	0	3	3	2	0	2	5
Cantabria	0	0	0	0	0	0	0
Castilla-La Mancha	0	0	0	3	1	4	4
Castilla y Leon	0	0	0	2	2	4	4
Catalonia	9	8	17	0	0	0	17
Comunitat Valenciana	0	10	10	8	3	11	21
Estremadura	0	0	0	0	2	2	2
Galicia	0	5	5	0	0	0	5
Madrid	1	0	1	2	2	4	5
Murcia	0	0	0	1	0	1	1
Navarra	1	1	2	0	0	0	2
Euskadi	1	0	1	0	0	0	1
La Rioja	0	0	0	0	0	0	0
Ceuta	0	0	0	0	0	0	0
Melilla	0	0	0	0	0	0	0
TOTAL Spain	11	39	50	26	12	38	88

It is therefore useful to make a cost-assessment on main systems for source separation currently in operation. Cost analyses carried out so far across Europe have traditionally focused on costs *per kilogram* (or *per ton*) *for a single waste material collected.*

However, there is evidence that this biases the true picture, because *the higher amount of waste is collected, the lower are the costs of the collection service per kilogram.* This distortion obscures some important outcomes of integrated source separation and waste management:

- the reduction of total waste delivered as a consequence of effective waste reduction policies;
- the much lower delivery of industrial waste to the MSW collection route where large-volume road containers get substituted by low-volume bins and bags to be placed at the doorstep;
- the contribution of home composting programs to the overall reduction of organic waste collected.

Furthermore, the evaluation of the cost for a single waste flow, *does not allow for advantages on collection costs for other materials*, flowing from "operational integration". In effect, the collection of food waste – above all when it shows high captures – allows important changes in the collection scheme, by reducing, for instance, frequencies of collection for residual waste (often termed colloquially as "restwaste").

Moreover, it has to be stressed that the cost of the system (collection plus transport) is not paid for by the municipality according to the amount of the waste collected, but considering the general operational scheme (the number and frequency of collection rounds, the number of workers, vehicles, pick-up points, etc). It is therefore incorrect to express the cost of this service per unit mass, rather it should be expressed as cost per person. This is why we have focused in the many surveys we have led on cost optimization, on costs per person (Favoino, 2002).

In order to get an unbiased assessment, we have reported costs of different collection systems run in homogeneous areas, with even weather conditions, dwelling types, social features, etc.

For instance, data from district "Venezia 4", close to Venice (Fig. VI.2.4), clearly show that source segregation of food waste with doorstep schemes *can be run with no substantial increase in overall cost, and sometimes costs are even lower than with traditional collection (no segregation of food waste) or with food waste segregation by means of road containers.*

To understand the unexpected outcomes of the survey, we must underline that if source separation of food waste is *added* to that of commingled municipal waste, with no modification in the previous scheme for MSW collection, total costs are bound to rise; this actually happens with the collection of food waste by means of road containers. But this is not the case when food collection is *integrated* into the overall collection scheme: namely, when doorstep schemes are implemented, notwithstanding the much higher number of pick-up points.

The trick is that *intensive doorstep schemes for food waste – when made comfortable for households – yield high captures.* This cuts in turn the percentage of food waste in the residual waste, which can then be collected less frequently. Furthermore, *food waste on its own needs no compaction* – letting operators use cheaper collection vehicles; however, this only holds true in those schemes where the delivery of yard waste along with food

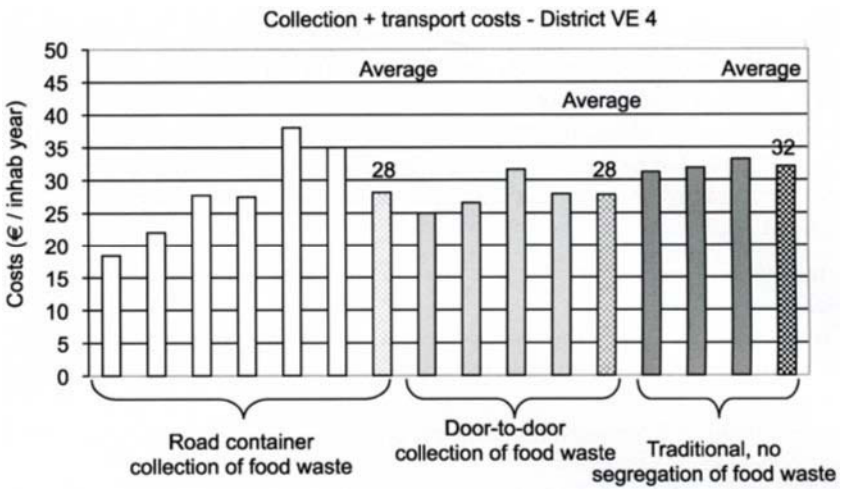


Figure VI.2.4. Cost comparison of different systems for source separation of biowaste in the Province of Verona and in the District "VE 4".

waste (that would be particularly high in areas with detached houses and private gardens) is prevented by means of low-volume buckets (10–20 l). In such situations yard waste gets collected at Civic Amenity Sites (*Recyclinghöfe, Piattaforme ecologiche*) or at the doorstep, but with much lower frequencies.

Table VI.2.11 recaps on most important tools and systems to integrate collection schemes once source separation of food waste gets implemented.

VI.2.6. Conclusions

According to the numbers shown, it is clear that the main mistake made when planning sorting schemes, is the *added* feature of the scheme. That means, a new collection scheme is run *in addition to* the previous mixed MSW collection, and cannot therefore yield savings to fund a new scheme. It is vital – on the contrary – that the new separate collection is *integrated* into the established waste management system, e.g. changing frequencies and volumes to collect residual waste, provide the collection of food waste yields high captures through a *comfortable* scheme. Furthermore, "integration" has to take into account the features of the area where the scheme has to be put in place; above all considering the need to find specifically suited systems for food and yard waste, where a large amount of yard waste is to be expected (low-density areas).

We have to remember that collection frequencies of residual waste can be cut only where a high capture of food waste reduces the fermentability of residual waste. From this standpoint, the use of comfortable tools such as door-to-door schemes and watertight, biodegradable bags has proven to be very effective (Favoino, 1999). This is why an "intensive" collection, run through doorstep schemes, notwithstanding a much higher number of pick-up points, has shown to be less expensive than collection of food waste

Table VI.2.11. Main tools to optimize collection schemes for food waste.

Tool	Details	Applies where...
Reduction of the frequency of collection for residual waste	Effective systems to collect biowaste – allowing people feel comfortable-make its percentage in the "Dry MSW" fall down to 20% and less	...frequent collection rounds for mixed waste are adopted (warmer climates)
Use of bulk lorries instead of compactors	Bulk density of food waste on its own is much higher (0.7–0.8 kg/dm^3) than when biowaste is composed of both food and yard waste	...food waste collection is being managed in order to keep it separated from the collection of yard waste
Lowering the number of washing rounds	The use of "personal bins" and watertight devices allow the requirement for households to take care of bins on their own	...a "door-to-door" program is suitable (private space available)

through road containers, due to the integration of the system and much lower collection costs for residual waste.

Moreover, *door-to-door collection of food waste allows municipalities to perform much higher recycling rates* (up to 60% and more in municipalities with around 10,000 inhabitants, 50% in Monza, which has 120,000 inhabitants) and a much better quality of collected food waste.

A further tool to optimize the scheme is the use of suitable vehicles to collect food waste, due to its high bulk density when yard waste is kept away from the collection scheme. One of main lessons to be learned from these astonishing outcomes is that *the more flexible and varied the fleet of collection trucks, the better it is.* This goes against some tendencies that we have unfortunately recorded across Europe, where huge expenditures have lately been done to buy *only* packer trucks for side-loading road containers. We have to be well aware that *this is fighting against optimized schemes for high-yielding collection of food waste*; the lack of flexibility does not allow optimization at all.

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Permanent Electronic *Biowaste Conference* in the form of a Quarterly Newsletter, links and hints with special information packages. The Austrian Society for Environment and Technology. Website: http://www.biowaste.at; http://www.oegut.at/biowaste/recent.html

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VI.3
Thermal waste treatment – a necessary element for sustainable waste management

Paul H. Brunner, Leo Morf and Helmut Rechberger

VI.3.1. Introduction

This chapter focuses on the role of thermal waste treatment within waste management as a whole. First, it is shown that the amount and composition of wastes are changing due to the changing pattern of consumption. Second, the goals of waste management are introduced, and means to reach these goals are discussed. It is concluded that even if many waste materials are recycled, there are plenty of wastes that have to be disposed of. Third, the most common thermal waste treatment processes (including co-firing) are presented.

Priority is given to understand that municipal solid waste (MSW) incineration is an important process for environmental protection and resource recovery. The goals of incineration are discussed, and detailed examples are given to show how these goals can be reached. Also, deficiencies and routes for further improvement of incineration technology are pointed out.

The chapter is brought to a close by an example of how MSW incinerators are actually used to routinely analyze the composition of MSW in a cost-effective and continuous way.

VI.3.2. Materials consumption, goals of waste management and incineration

VI.3.2.1. Phenomena of modern anthropogenic metabolism

In order to optimize waste management, the so-called "Metabolism of the Anthroposphere" has to be understood: input and output of man-made systems are related to each other, waste generation is a function of production and consumption processes. Hence, it is essential to look first at the most important phenomena of today's metabolism (Brunner and Rechberger, 2001).

1. Since prehistoric times, the turnover of materials has increased dramatically. This is not only due to population increase, but also mainly due to the enormous technological and economic advancements in the last few centuries. Today, modern man consumes in his household more than 80 t per capita and year (Baccini and Brunner, 1991). If the material flows in the hinterland and the so-called rucksacks are included, this amount is easily doubled (Schmidt-Bleek, 2000). The mining and consumption of many individual substances such as lead has grown even more (Fig. VI.3.1): since the first industrial use

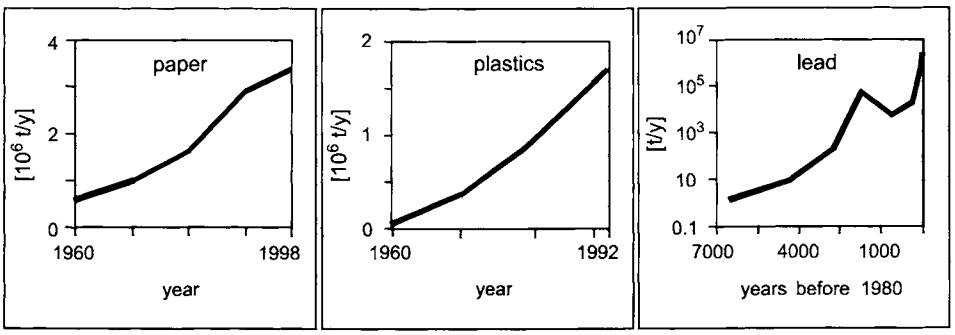


Figure VI.3.1. The rates of material consumption are high and growing. All these materials have to be recycled or disposed off by waste management. Figures for paper and plastics are from Austria, figures for lead are global production figures according to Settle and Patterson (1980).

of lead, there has been a 10 million-fold increase in the utilization of this mineral. This is the case for other substances too. The main material turnover is the water used for the transportation of dirt (toilet, personal hygiene, laundering and dish washing). Second comes air for the oxidation of fuel for heating/cooling and transportation. Third are construction materials and fuel. The large input implies a large and unprecedented output of sewage, off gas and solid wastes.

There are no indications yet that material growth will come to an end. Both per capita consumption rate as well as population rate increase, and thus for most regions on the globe, the material turnover is increasing. Figure VI.3.1 clearly illustrates the growth: in the past 30–40 years, the production of paper has grown by a factor of five; plastic consumption has risen by more than an order of magnitude. Due to the high increase in consumption, the mass of wastes generated is also large and growing. For goods with long residence times, huge amounts of wastes will arrive in the future. Hence, the main challenge for waste management is to come: future amounts and compositions of wastes are much different than today's wastes and they cannot be avoided by prevention because they already exist today in the stocks (see below). Prevention strategies can only be successful if they take into account, production and consumption. They have to be directed towards a reduction of the material input into the anthroposphere, as well as the prolongation of the residence (= utilization) time.

2. Due to the large consumption rate, some anthropogenic flows are surpassing natural flows of erosion and weathering. This means that concentrations in certain environmental compartments become dominated by man-made impacts. Nature will have to adapt to these new anthropogenic conditions. If changes induced by man are too fast, environmental problems can arise. It may be hypothesized that the limits to growth are not at the supply side of the system: resources are still abundant for long time periods. But at the backend of the material flow system, new limits become visible: the anthropogenic metabolism seems to be limited by the availability of final sinks for material disposal. A first example was given by halogenated hydrocarbons (chlorinated and fluorinated hydrocarbons (CFCs)) that diminished the stratospheric ozone layer. While the production of CFCs is not bound to any resource limitations at this moment, the efficient collection and disposal of these chemicals is a problem not solved yet, and thus they have been

banned from being produced. A next and still controversial example is carbon: while the resources of coal will still last for a couple of centuries, the products of the utilization of coal, namely CO_2, contribute to the greenhouse effect. Experts predict global warming to an unacceptable level if the consumption of coal continues to grow at the present growth rates. Other examples are nutrients: in countries such as the Netherlands, the main problem is not how to get the resource nitrogen, but how to get rid of it. Groundwater concentrations are high and rising due to high imports of nutrients for agricultural purposes not paralleled by corresponding exports.

3. The input of materials into most urban regions is larger than the output, resulting in an increase of stock within the anthroposphere, in particular in cities. Figure VI.3.2 demonstrates this for plastic materials in Austria. There are two stocks of plastics: first, the materials stored in "consumption", e.g. in products with long residence times such as construction materials, floor linings, car parts, etc. and second, the stock in landfills. Of the two stocks, landfill is more important. The stocks can serve as future resources, but is also a future threat to the environment.

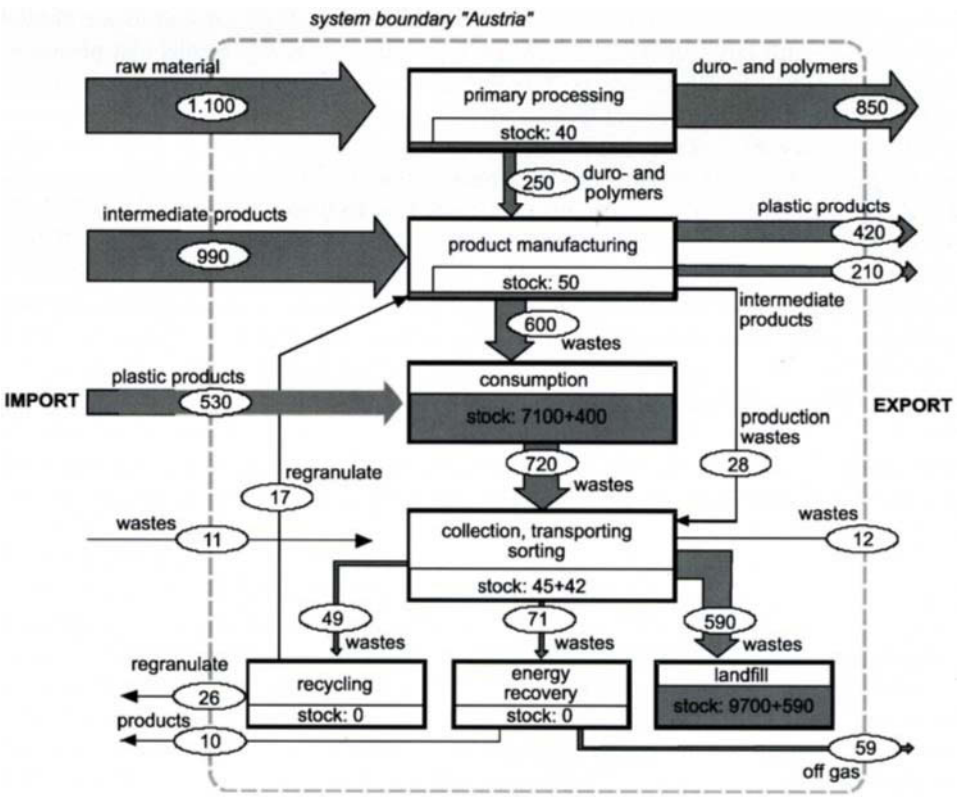


Figure VI.3.2. Inputs of materials into regions are generally larger than outputs, resulting in huge stocks of materials that have to be managed in the future. The figure on flows of plastic materials in Austria [in kt/y for 1994] shows that the growth rates of the stocks of plastic are high, and that large amounts of valuable resources (energy!) are disposed off in landfills (Fehringer and Brunner, 1997).

4. The flow of materials through the anthroposphere is mainly linear; there are hardly any cycles yet. The task to recycle materials at a considerable amount within an urban region is very challenging. It is doubtful if a significant fraction can be recycled within the next 25 years. In any case, it would mean a completely new management of materials within this time span.

5. In advanced societies, and due to pollution prevention measures, the emissions from consumption are larger than the emissions from production. This implies new priorities in environmental management. The new focus must be on non-point, consumer-oriented sources. Since the number of consumers is more than the producers, it is more difficult to reduce emission flows from consumer sources. For producers, it is "easier" to add pollution abatement equipment to their facilities than to design and introduce new low-emission consumer products. For example, in earlier days the process of galvanization was a major source for heavy metals in the environment. Today it is the use of corrosion-resistant consumer goods such as zinc-coated surfaces that are most important as emission sources.

The significance of these phenomena of modern metabolism for waste management is the following: as the amount of consumer waste increases, industrial wastes become comparatively less important. Even if some of the most dangerous substances are phased out, there are still large stocks of hazardous materials, e.g. heavy metals and persistent organic chemicals, in use as well as "hibernating" (out of use but not collected by waste management yet). They represent legacies of past products containing high concentrations of harmful materials, and they have to be safely treated by waste management. As a result of the past and present production and consumption pattern, today's and tomorrow's wastes are composed of an uncontrollable number and kind of substances. This is especially the case for many combustible wastes (Table VI.3.1, Figs. VI.3.3 and VI.3.4). They have to be treated with care. Due to the content of hazardous materials, some wastes are not at all suited for recycling. The only way to dispose them is thermal processing that destroys organic substances and controls heavy metals (see below).

VI.3.1.2. Goals of sustainable waste management

Although there are many definitions of sustainable materials management, some common concepts are found across the literature (Enquete-Kommission, 1994; SUSTAIN, 1994).

Table VI.3.1. Composition of combustible wastes in Austria.

Concentration (mg/kg d.m.)	N	Cl	Cd	Hg	Pb	Zn
Minimum	200	10	0.01	0.001	<1	1
Maximum	670,000	480,000	500	10	4,000	16,000
Average of all waste	9,100	4,300	5.7	0.8	230	520
MSW	7,000	8,700	10	2	800	1,100

There is a large variety in the content of metals and non-metals; while some wastes are well suited to be used in thermal processes with little APC such as cement kilns, others can only be treated in incinerators with the most advanced control equipment.

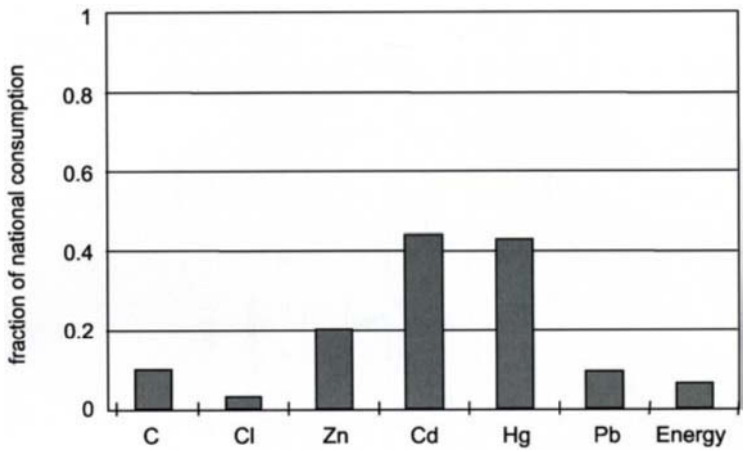


Figure VI.3.3. Relative flow of materials and energy in combustible wastes in Austria: while the contribution of all wastes to the national energy balance of Austria is small (< 10%), more than 40% of the national import of cadmium and mercury is found in combustible wastes. Thus, priority in thermal treatment has to be put first on safe material handling, and only second on maximum energy recovery.

- *Conservation of renewable resources*: The present use of renewable substances should not reduce the capital stock of future generations.
- *Sustainable emissions*: Material flows from the anthroposphere[1] to the environment should neither exceed local and global assimilation capacity nor surpass the range of natural material flows.
- *Change in stocks of materials*: Material flows should be managed in a way to prevent the depletion of useful and the accumulation of harmful materials in the environment.

In the context of the above principles, the main tasks of waste management are twofold: first, waste treatment acts as one of the main interfaces between the anthroposphere and the environment, ensuring that material flows across this boundary have an acceptable impact on the environment. Second, waste management is a key element in conserving material and energy by recycling. The two goals, "protection of men and the environment" and "conservation of resources", have been introduced in the legislation on waste management of many countries. In addition, based on the precautionary principle, which is also a major principle of sustainable development, some nations such as Austria, Germany and Switzerland are aiming at landfills, which do not require after-care measures. This strategy calls for extensive waste pretreatment before landfilling.

Environmental protection and resource conservation are goals not only for waste management, but also for all activities of a sustainable economy. It is thus important to compare the costs to accomplish these goals by means of waste management with other measures such as pollution prevention and air or water pollution control in the production and consumption sector. In this respect, it is important to note that the ratio of consumption emissions versus production emissions is constantly rising. Also, some of the new and

[1] The *anthroposphere* is the sphere where human activities take place, comprising all man-made sources, sinks, processes, flows and stocks of goods and substances.

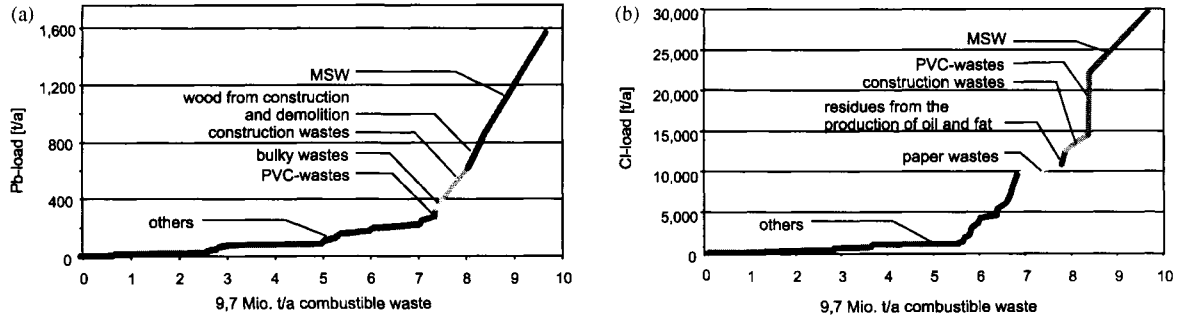


Figure VI.3.4. Load of materials (a: lead, b: chlorine) in combustible wastes in Austria: MSW is the most important carrier of many hazardous material.

growing consumption emissions, such as the loss of metals from surface coatings during a life cycle, take place outside the range of the classical measures of waste management and pollution control.

As stated above, the first objective of waste management is the protection of man and the environment. In the past, this meant to prevent hygienic risks by organizing the proper collection and disposal of wastes. Today, these risks have been minimized in advanced countries. Keeping the goals of sustainable materials management in mind, the new challenge stems from the large amounts of materials that are being consumed by modern societies. Waste management must be able to handle this large amount, recycle or dispose it in a manner that observes environmental quality standards. In particular, waste management must find for all non-recyclable materials *appropriate final sinks*, such as landfills, soils or sediments. Since the material flows have increased tremendously in the past century, this task cannot be fulfilled by uncontrolled dispersal of materials in water, air or soil.

The main challenge for waste management does not arise from the *bulk properties* of the waste itself, such as MSW, construction wastes or sewage sludge. The real assets and hazards are the very *substances* contained in these wastes. This is demonstrated by the following examples. (1) Due to the fact that MSW contains the *substances* carbon and hydrogen, it is well suited for incineration and energy recovery. However, due to the small amounts of substances such as mercury and cadmium, incinerators utilizing MSW must be equipped with highly efficient air pollution control (APC) devices. (2) It is the content of nutrients and humic substances, which makes sewage sludge attractive for land application. On the other hand, there are severe restrictions for the application of sewage sludge in agriculture because of small amounts of organic and inorganic trace substances in sludge such as heavy metals, PCBs and dioxins. (3) The reuse of certain plastic materials is challenged by the presence of traces of hazardous substances used as stabilizers. (4) The potential of waste biomass to be turned into useful compost is again limited by an array of refractory and harmful trace substances.

These examples show that *substances* contained in waste materials are important to consider when decisions in waste management are taken. In order to reach the goals of wastes and material management, the fate of the important matrix and trace substances contained in wastes has to be known. Substances have to be actively managed and directed to appropriate anthropogenic or natural "conveyor belts", such as recycling goods or water and air. The power of a waste treatment process to concentrate or dilute substances must be taken into account. In every case, it must be considered that ultimately, a final sink has to be found for all substances contained in all goods. Decisions regarding the management of wastes have to be based on sufficient information about the fate of materials in waste treatment processes. Up to now, such comprehensive sets of information are abundantly available for MSW incineration, and lacking for many other waste treatments.

The means to reach the goals of waste management are prevention, recycling and disposal. It is important to note that prevention and recycling *per se* are not goals, but they can be efficient instruments to fulfill the goals. In general, a decision about the choice of any of the three means should be based on the goals to be fulfilled and the costs of the measures to reach the specified goals. Thus, the three means are competing with each other for overall efficiency in environmental protection and resource recovery. From science and technology, as well as economy point of view, an *a priori* preference for prevention,

recycling or disposal is hard to justify. It is noteworthy that under certain boundary conditions, recycling of a material may be a less favorable scenario when compared to the linear disposal option.

In general, waste management in view of the sustainable materials management means to choose one of the following options or combinations thereof:

1. recycling of material and energy with acceptable emissions, including treatment and disposal of the recycling good after x cycles (e.g. plastic materials, cellulose);
2. dilution of waste materials by water, soil and air to environmentally acceptable levels (e.g. biochemical or thermal degradation of biomass resulting in dilution of CO_2 and chlorides in air and surface water);
3. treatment and storage in a final sink, namely in a storage with a very long residence time and small long-term emissions below environmental standards (e.g. storage of MSW filter ash in underground salt mines or immobilized MSW bottom ash in mono fills).

In summary, there are large amounts of potentially hazardous substances in waste materials, many of which will be encountered in ordinary MSW. There is a high uncertainty about the distribution of the substance concentrations in wastes. Therefore, it is important that waste treatment processes are able to cope with a very wide array of substances and in a sufficiently broad concentration range, including peak loads. Safe, goal-oriented treatment processes are required, which will direct both the organic and the inorganic substances to the appropriate recycling processes and sinks. For many organic substances, this means complete transformation by thermal processes to CO_2, water and other mineralized end products. For inorganic substances, either recycling as a mineral or immobilization and disposal in a final storage landfills is required.

VI.3.3. Thermal processes used for waste treatment

Thermal processes for waste treatment can be divided into the actual combustion process and the following steps necessary for air and water pollution control. The choice for the combustion technology is mainly determined by the physical (particle size distribution, density, aggregate state, water content, etc.) and chemical (elemental composition, calorific value, ash content, etc.) characteristics of the waste. MSW as an example for a heterogeneous feed is often incinerated in the so-called mass-burn facilities (Fig. VI.3.5).

Waste is stored in a fully contained waste bunker for time periods up to 1 week. Combustion air is taken from the bunker thus preventing odor outside the facility. An automatic or man-controlled crane mixes incoming wastes to increase homogeneity (especially with regard to calorific value), and lifts the waste via a feeding hopper in a water-cooled gravity chute, which serves as an air seal between the bunker and furnace. Usually a hydraulic or mechanical ram system expels the waste from the chute onto the furnace grate where the actual combustion process takes place. The grate consists of moving and fixed elements (rows) that guarantee controlled transportation, mixing of the waste and equal distribution across the grate. Several grate designs exist (reciprocating grate, drum grate, traveling grate, etc.). Part of the combustion air is injected as primary combustion air from underneath through the grate (underfire air). This provides cooling for the grate material to prevent heat damage and excessive oxidation. In addition, the waste is

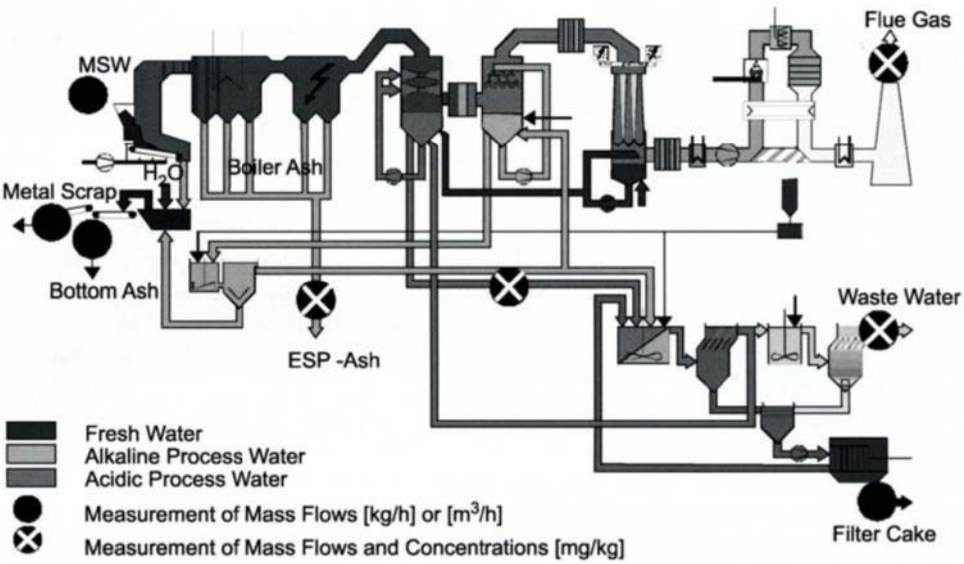


Figure VI.3.5. Modern MSW incinerator with state-of-the-art APC device. The incinerator shown treats 34 t/h of MSW resulting in 9.2 t/h bottom ash, 1.1 t/h scrap metals, 0.97 t/h filter-ash, 14 t/y wastewater, 0.055 t/h filter cake, 230 t/h flue gas. Indicated are measuring points for routine measurements of waste composition according to the method described in Chapter VI.3.3: iron is determined in metal scrap, mercury in acid scrubber discharge, chlorine in treated wastewater, carbon in cleaned flue gas and lead, cadmium, copper and zinc in ESP ash.

well mixed with air, a requirement for complete mineralization of all organic carbon. Secondary combustion air (overfire air) is injected into the combustion chamber above the grate to guarantee maximum oxidation of all organic compounds (carbon and tar particles, hydrocarbon vapors, etc.) and low CO concentrations in the flue gas. At the end of the grate, the mineralized bottom ash is discharged into a water basin, where it is cooled and removed to the bottom ash bunker. The water basin acts as a seal for the furnace.

The flue gas after the combustion chamber contains high amounts of particulates (3–5 g/m^3), acids such as SO_2 (sulfur dioxide), HCl (hydrochloric acid), HF (hydrofluoric acid), and NO_x (nitrogen oxides), which require extensive flue gas treatment. Particulates are either removed in electrostatic precipitators (ESP) or bag house filters (also referred to as fabric filters). ESPs use electric forces to charge and move particulate matter in a flowing gas stream to a collecting surface. They are more robust towards temperature changes, have lower pressure drops and are easy to maintain. Bag house filters (particulate removal by filtration on fiber surfaces) achieve high removal efficiencies for fine particles (<5 μm, $>99.9\%$). Additionally, they can be employed in combination with pollutant-adsorbing substances (e.g. activated carbon to remove mercury and dioxins; $CaCO_3$ (limestone), CaO (lime), $Ca(OH)_2$ (hydrate lime) or a mixture of it to remove acids) that are injected into the flue gas up-stream (spray dryer absorber) and collected in the filter device. Acids can be very efficiently and separately removed by a two-stage wet scrubber system. HCl and HF are physically absorbed in the first acid scrubber stage at pH $\approx$ 1. The low pH prevents absorption of SO_2. The scrubber liquid is water, and no neutralization agent has to be used. Also, mercury-chlorides are removed from the flue gas at this stage.

During the second stage, SO_2 is chemically absorbed using either $CaCO_3$, $Ca(OH)_2$ or NaOH (sodium hydroxide) for neutralization at pH $\approx$ 7. The final product of the sulfur removal is gypsum, which is washed, dewatered and either (if sufficiently clean) recycled in the gypsum industry or landfilled together with the other filter residues. Part of the scrubber water is continuously purified by an on-site physical–chemical wastewater treatment process. Neutralization sludge is precipitated and dewatered in a filter press. Chloride is discharged with the treated wastewater. Provided the receiving water for the incinerator is sufficiently large (a matter of appropriate site location), this is the most advantageous solution because the oceans are appropriate sinks for chloride. In case no adequate receiving water is available, HCl can be purified and concentrated to over 30% for recycling. Alternatively, the acid can be neutralized with NaOH, and sodium chloride brine can be recycled.

NO_x is reduced to N_2 and H_2O by injecting NH_3 (ammonia). The reaction requires high temperatures (900–1000°C). A ceramic catalyst (based on TiO_2 and V_2O_5) reduces the temperature need to 200–300°C and enhances the efficiency of the reaction from 70–80 up to 90%. With proper design, the catalyst can also be utilized to oxidize polychlorinated dibenzo-dioxins and furans (PCDD/Fs). Sometimes activated carbon filters are employed as a final stage to adsorb organic compounds (e.g. PCDD/F), metallic mercury (Hg^0) and other trace pollutants passing the previous APC stages.

State-of-the-art combustion and APC systems destroy organic and remove inorganic pollutants with high efficiency. Various full-scale plants demonstrate the reliability of these technologies; they operate at emissions way below the stringent emission limits enacted, e.g. by the European Union (EC, 2000). Figure VI.3.6 exemplifies the development of MSW incineration emissions over the past 70 years.

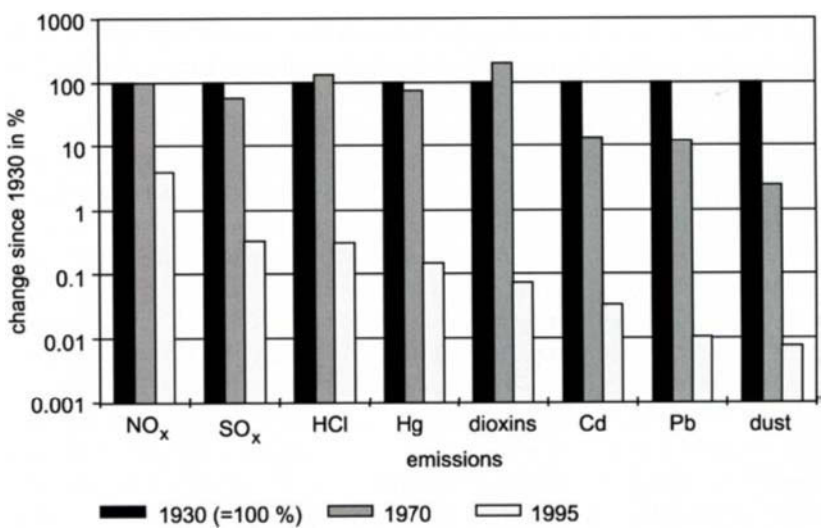


Figure VI.3.6. Reductions of MSW incineration emissions from 1930 to 1995 as a result of improved APC technology. Modern APC technology can decrease emissions to levels that are orders of magnitude lower than emission limits set by advanced environmental protection legislation. Values given are for single, state-of-the-art MSW incinerators in 1930, 1970 and 1995.

Emissions have been reduced by one (e.g. NO_x) to four (e.g. particulates, Pb) orders of magnitude. Note that particulate removal by ESP alone (standard filter technology until 1980) is not sufficient for MSW incineration. Today, state-of-the-art MSW incinerators are of no relevance anymore on a national emission inventory level. Figure VI.3.7 and Table VI.3.2 show this for SO_2 and PCDD/PCDFs for Germany and Austria. Similar results are obtained when heavy metals and other air pollutants such as NO_x and dust are discussed.

State-of-the-art APC systems of the 1990s comprised several processes such as ESP, multi-stage scrubber, $DeNO_x$ catalyst for the reduction of nitrogen oxides (Thomé-Kozmiensky, 1993). In order to reduce capital and operation costs, engineers have developed more compact APC systems with few treatment steps only. Adsorbing and absorbing substances are injected into and removed from the flue gas stream in two consecutive processes. The result of such an APC system is a mixture of fly ash, reaction and injection products. Drawbacks are higher quantities of filter residues and residues less suited for landfilling due to high fractions of mobile salts, and mixed and diluted pollutants in one stream of residues only. The latter point is in conflict with recovery goals, e.g. for metals recycling from fly ash.

Another field of research and development is how to produce: (1) bottom ash and filter residues that have improved landfill properties with regard to composition and emissions; and (2) residues that can be utilized as secondary resources. This can be achieved by either after-treatment of bottom and/or fly ashes in thermal and/or chemical processes or designing new technologies that are not necessarily based on the grate furnace technology. Bottom ashes can also be further treated by mechanical processes (sieving, screening) and magnetic separation of iron scrap. Adequate thermal after-treatment of bottom ash results in three products: (1) a silicate product that can be utilized for construction purposes; (2) a metal melt containing mainly iron, copper and other lithophilic metals (metals of low vapor pressure); and (3) a concentrate of atmophilic metals. The latter two fractions can be recycled in the metal industry. In a few European countries (Germany, Denmark,

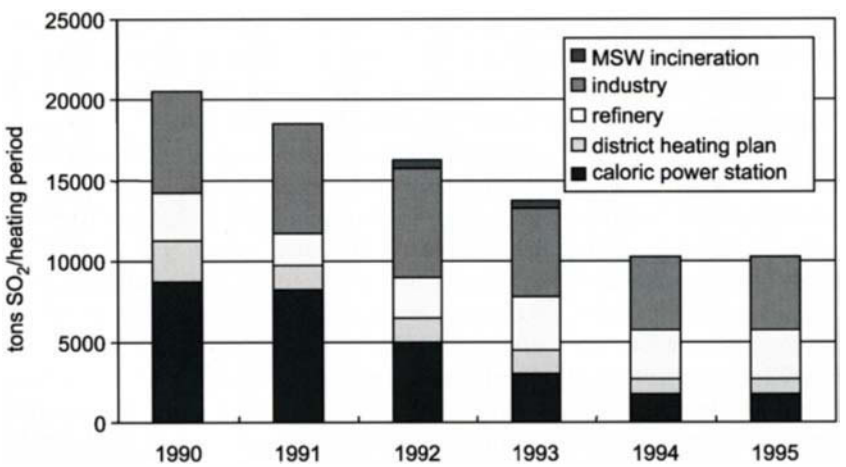


Figure VI.3.7. Contribution of MSW incineration to SO_2 emissions in Austria (König et al, 1997).

Table VI.3.2. Contribution of state-of-the-art MSW incineration to national emissions of dioxins and furans.

Country	Total emissions of PCDD/PCDF (g TEQ/a)	Contribution of MSW incineration[a] to PCDD/PCDF	
		g TEQ/a	%
Germany[b]	800–1200	5.5	0.5–0.7
Austria[c]	50–320	5.53	0.2–1.1

Modern incineration is a minor source of PCDD/F.
[a]Assuming all MSW is incinerated.
[b]Wintermeyer and Rotard (1994).
[c]Orthofer and Vesely (1990).

the Netherlands), some of the bottom ash is upgraded (crushing, sieving, curing through wet storage) and used as aggregate substitutes for road construction. However, the resource recovery effect is modest. Baccini and Bader (1996) investigated the potential of bottom ash to replace gravel in Switzerland. They found that even if 90% of MSW (360 kg/capita year) are incinerated, bottom ash could only substitute 2% of the 4.6 t of gravel utilized per capita. On the other hand, significant quantities of copper, chromium and other lithophilic metals are directed into buildings and roads by the utilization of bottom ash for construction.

Fly ash can be vitrified to produce an immobilized product for landfilling, or metals can be chemically and thermally extracted for recovery. Immobilization can also be achieved by solidification/stabilization when additives such as cement are used to physically and/or chemically immobilize hazardous substances in ashes.

Some new incineration concepts combine pyrolysis and high temperature processes with conventional APC as described above. Goals of these technologies are to produce residues with better qualities with respect to disposal and recycling than mass-burn systems. None of these new technologies have experienced a breakthrough. Up to now, they could not prove yet that they are able to reach the same or higher goals than traditional MSW incineration at lower costs and at the same reliability.

Homogeneous wastes of changing characteristics as well as wastes of high physical and chemical heterogeneity, e.g. sludges, slurries, pastes, liquids in barrels, contaminated soils and hazardous wastes from chemical and other industry branches are often treated in rotary kilns. This technology is mechanically and thermally robust, can handle gaseous (injection), liquid and solid wastes, as well as batch feeding. More homogenous wastes that are generated at a more or less constant level such as sewage sludge, shredded wastes like plastics, wood waste and bark are usually incinerated in fluidized bed furnaces. Wastes are injected into a fluidized bed of an inert material (mostly silica sand). Fluidization is achieved through forcing combustion air through a bed of sand and waste. The particles become suspended in the rising air stream and take on the behavior of a turbulent liquid. This reactor is characterized by excellent mixing conditions, which results in a fast heat exchange and mass transfer (no temperature peaks and therefore no

production of thermal NO_x at operation temperatures between 800 and 900°C). The heated sand buffers variations in the calorific value, allowing the treatment of wastes with low and varying energy content. Limestone to bind SO_2 and other surface-active substances to remove pollutants can be injected into the bed or the flue gas stream. Rotary kilns as well as fluidized bed boilers can be equipped with standard APC devices.

Wastes contaminated by organic substances such as waste oil and spent solvents can be utilized as an alternative fuel in cement rotary kilns. High combustion temperatures (2000°C) guarantee destruction of organic compounds. If equipped with adequate APC, industrial boilers are in general a good option to utilize the energy content of combustible wastes and to conserve fossil fuels. On the other hand, wastes with metal contents similar to MSW such as mixed plastic fractions, combustible fractions from MSW and demolition debris, etc. require advanced APC systems, which industrial boilers often are not equipped with. Also, products (e.g. concrete, bricks, asphalt) should not be used as sink for heavy metals. If toxic metals are directed towards such products, the goals of waste management and sustainable materials management are not fulfilled. Metals are valuable resources that should be recovered rather than diluted and dissipated via products.

Today, incineration combined with advanced APC represents a reliable, robust, and compared to other available options, environmentally sound technology to dispose combustible and hazardous wastes. Further development should be focused on producing more residues that can be recovered in an environmentally sound manner, and to use thermal processes to turn waste management into an integrated part of a sustainable materials management.

VI.3.4. Goals of thermal waste treatment

The following goals for thermal waste treatment have been derived as a direct consequence of the objectives of waste management, the mass and composition of combustible wastes and the technological capability of thermal processes combined with APC. They are listed in the order of their historical importance.

VI.3.4.1. Volume reduction

Volume reduction of wastes was one of the first goals in solid waste management together with disinfection and energy recovery. Big cities experienced problems in waste disposal in their immediate surroundings because landfill space became scarce, and farmers did not accept MSW anymore as a "soil conditioner". Landfills were filled up and opening new landfills was difficult as a result of diminishing space, the NIMBY syndrome ("not in my backyard") and finding sites providing the geological and hydrological conditions for a state-of-the-art landfill. Waste combustion was, and still is, regarded as an excellent solution to this problem.

Incineration transfers 1 t of MSW into 700 kg of cleaned flue gas, 230–270 kg of bottom ash, ca. 30 kg of scrap iron (usually recovered in the steel industry), 20–30 kg of filter ash and possibly 1–2 kg of sludge from wastewater treatment depending on the APC technology (Fig. VI.3.8).

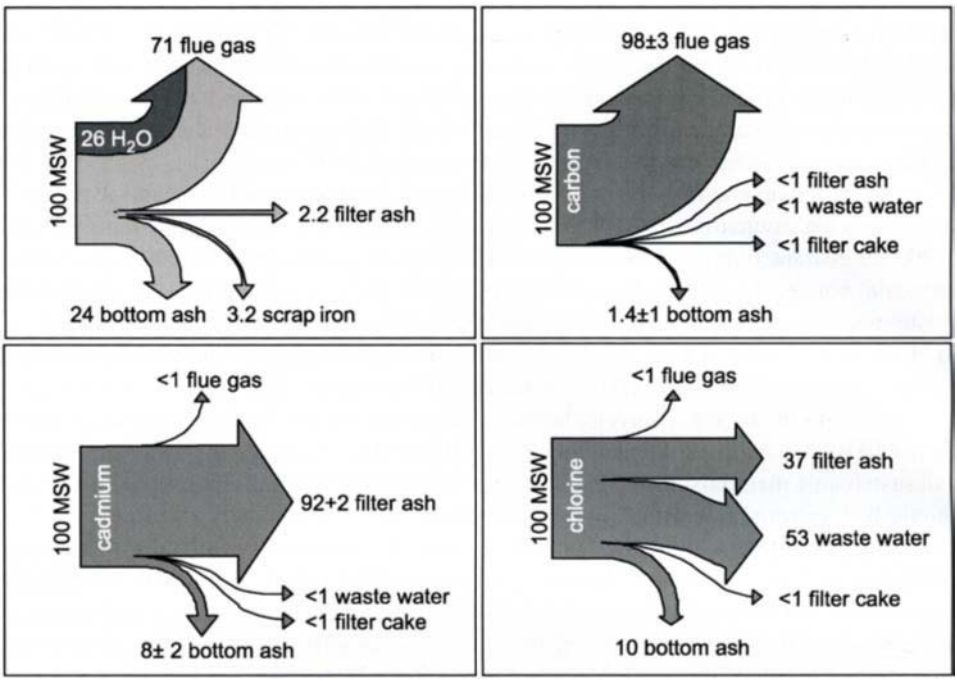


Figure VI.3.8. Mass and element partitioning by MSW incineration. The values for mass and element flows vary due to the technology applied for combustion and APC, and due to waste composition.

The specific volume of MSW in a landfill is between 1 and 2 m^3/t depending on waste compaction, composition and disposal time (Rhyner et al., 1995). Bottom and fly ash have a specific volume of ca. 0.6–0.7 m^3/t. This results in a total volume reduction of some 80–90%. Bottom ash landfills do not need a gas collection and treatment system like MSW landfills. The leachate collection system is similar to a state-of-the-art MSW landfill; since ash leachates do not contain large amounts of organic carbon and nitrogen as in the case of MSW, leachate treatment systems can be much simpler than in the case of MSW landfills. Replacement of MSW landfilling by incineration and bottom ash landfilling prolongs the lifetime of a landfill by a factor of 10. Filter residues and sludge that contain higher concentrations of heavy metals than bottom ashes have to be disposed off in safe landfills that are not in contact with the hydrosphere and that are capable of retaining hazardous substances for very long time periods. Separated and specially equipped compartments, the so-called mono-fills, or underground disposal facilities such as empty mines and salt domes serve this purpose. In principle, there are technologies available that turn bottom ashes into a substitute for gravel (see Section VI.3.2). A combination of mechanical and thermal processes can achieve this. Also, when concentrated and refined, metals in fly ash can be utilized as a resource. At the moment such technologies are not yet economic but they could contribute to a volume reduction beyond 95%, achieving maximum conservation of landfill space.

VI.3.4.2. Disinfection

Nowadays, in affluent countries, the main reason for waste management is no longer to protect human health. Due to efficient collection and sound waste treatment practice, it has become rare that diseases are spread by waste materials or by inappropriate waste management. The situation is completely different in developing countries: it has been stated that for a given amount of money, the improvement of waste management practice could save more lives and contribute more to the general health than any other single measure. One of the reasons is that waste materials can pollute surface and groundwater and thus pose a threat to the health of large populations that depend on rivers and wells for drinking water. Other reasons are infections from food grown on waste contaminated land or from food contaminated during processing and transport.

At the end of the nineteenth century, a few European cities were disposing off their municipal wastes by spreading them on agricultural fields. Due to rising hygienic problems, they started to incinerate wastes. Even simple thermal treatment resulted in a sterile waste that was hygienically safe for landfilling. Rodents and birds could not feed from ash landfills, and thus the spreading of diseases by improper waste management was brought to a close. Today's modern incinerators operate at 850–950°C and produce sterile bottom ash, filter residues, wastewater and off gas.

Recently, the potential of thermal waste treatment to destroy harmful microorganisms has been "rediscovered". Hygienic crises such as bovine spongiform encephalopathy (BSE; mad cow decease) resulted in large masses of materials that were used as a feedstock in the past and suddenly turned into waste because of new legal requirements to stop the spreading of BSE. Since these materials were infectious, they could not be landfilled, composted or recycled. The only way to dispose them was incineration. At present, MSW incinerators, hazardous waste incinerators and cement kilns are successfully treating infectious wastes. For future accidents and catastrophes, it appears essential to have thermal treatment plants that can handle large amounts of contagious wastes in a safe way.

VI.3.4.3. Energy recovery

Already at the end of the nineteenth century, energy was recovered from waste, e.g. in Oldham, England; Hamburg, Germany; and Brussels, Belgium. The motivation at this time was the production of steam in a waste heat boiler for internal power use and electricity production.

Nowadays, the motivation for energy recovery from waste is:

- conservation of non-renewable energy resources;
- reduction of greenhouse gas emissions (decrease of CO_2 emissions by burning renewable carbon in waste instead of fossil fuels);
- cost reduction of waste incineration by the production and sale of electricity and heat.

Depending on the criteria such as the energy market and the location of the waste incinerator plant (proximity of clients to buy steam/heat), incinerators are designed to produce electricity, heat (steam and/or hot water) or a combination of both. The following criteria are essential for a commercial production of steam for industrial applications and

heat for district heating: (a) constant energy demand (summer and winter) and (b) short distances to the consumer(s) with an existing distribution network. The key property for energy generation is the heating value of the waste. The heating value historically has risen during the last 50 years. Nowadays, in industrialized countries, MSW has a heating value (approximately 10 MJ/kg) close to that of brown coal, thus making MSW an interesting energy source. Economic drawbacks of energy from waste are high investment costs for flue gas cleaning systems, operation costs due to auxiliary material consumption, disposal costs for residues and corrosion problems.

The overall energy recovery potential of all combustible wastes of a central European country (e.g. Switzerland, Austria or Germany) is estimated to be about 5–10% of the average national energy consumption. The potential of certain hazardous materials in the same combustible wastes is much larger (Fig. VI.3.3): about 40–50% of the total amount of cadmium and mercury used in Austria is contained in combustible wastes. Thus, the primary focus in thermal waste treatment should be on material management, and only secondly on energy recovery. Aspects of human and environmental protection are more important!

VI.3.4.4. Environmental protection

For long time periods, MSW incinerators polluted the environment severely and with long-lasting effects. The main contaminants until the 1950s were dust, heavy metals and organic products of incomplete combustion in the flue gas. Hence, the first regulation concerned dust removal. Due to the increasing content of polyvinyl chloride in MSW, off gases of MSW incinerators become increasingly acidic. Wet scrubbers were introduced to control acids. A major breakthrough in APC policy was the regulation of volatile metals in the flue gas: to reach the new emission limits of 0.1 mg Hg/N m^3, advanced APC technologies had to be developed. It became necessary to remove small particles below 1 μm, acids such as HCl, HF, SO_2 and NO_x and reduce the emissions of PCDD and PCDF by activated carbon or other means. Today's technology for APC allows meeting emission values that are one to three orders of magnitude below existing advanced emission regulation limits. Figure VI.3.6 displays the tremendous progress and reduction in emissions from MSW incineration that was achieved during the last 70 years. Table VI.3.2 and Figure VI.3.7 show that if MSW incinerators are equipped with state-of-the-art APC devices, emissions are much smaller than pollutant flows from other sources. Thus, priority of APC strategy has to be given to these other sources. Table VI.3.3 serves as an example of such sources: if MSW is combusted in a stove of a private home, the emissions are about three orders of magnitude larger than that in an MSW incinerator with appropriate APC. Since it has become popular to replace traditional oil or gas-based furnaces by wood furnaces, it is important to make sure that burning wastes in such home furnaces without APC device does not take place.

A second issue for environmental protection is climate change and greenhouse gas emissions. Hackl and Mauschitz (2000), have shown that the contribution of MSW incineration to the reduction of greenhouse gas emissions can be substantial. Schachermayer et al. (1999) have calculated that half of the reduction goal set by the Austrian Federal Government can be reached if Austria changes from present day waste management to an incineration scenario where all combustible wastes are incinerated in

Table VI.3.3. Emissions from burning waste in household furnaces and in state-of-the-art MSW incinerators.

Emissions	Dust (g/t)	HCl (g/t)	SO_2 (g/t)	NO_x (g/t)	CO (g/t)	Hg (g/t)	Dioxins (mg TEQ/t)
Household	30,000	5,300	1,000	2,000	60,000	1	3,200
MSW incineration	40	40	150	400	200	0.3	3

Even if only a small percentage of MSW is disposed off in inappropriate combustion devices, this can result in comparatively large emission flows to the environment.

MSW incinerators, cement kilns and industrial boilers, and no untreated wastes are landfilled anymore.

Residues of incineration such as bottom ash, filter ashes, scrubber water and filter cakes are a third environmental topic. They have neither the same composition as the earth's crust, which would qualify them as a building material, nor are they sufficiently highly concentrated to qualify as an ore. Hence, these materials have to be further treated (see below) and/or purified (wastewater).

VI.3.4.5. Complete mineralization

MSW contains many hazardous organic substances. Separation and input control will not be able to reduce much of these compounds. When composted or landfilled, these substances may enter the environment. The objective of incineration is to completely transform organic carbon to CO_2. Due to the physical and chemical heterogeneity of MSW and other wastes and the changing waste composition, it is in general more difficult to oxidize wastes than conventional fuels such as coal, oil or gas. Hence, the mineralization rate (defined as the percentage of carbon that is converted to CO_2) of MSW incineration is lower than that of other thermal processes.

There are two reasons why a mineralization rate of 99.9% is desirable: first, bottom ash will contain less organic carbon, hence landfilling of the ash will result in a leachate with low dissolved carbon content. Low organic carbon in the bottom ash means also not enough carbonic acid resulting from biochemical degradation of organic carbon to mobilize metals in the bottom ash. Second, a high mineralization rate means less organic compounds and products of incomplete combustion in the off gas and the fly ash particles, yielding less dioxins too. Hence, also from the points of view of air pollution and filter residue disposal, a high mineralization rate is favorable.

VI.3.4.6. Immobilization

In Section VI.3.2, it was shown that a large amount of hazardous materials and heavy metals is introduced into the anthroposphere. Waste management serves the purpose of a filter between the anthroposphere and the environment. Waste incineration may release only such substances into water, air and soil that are environmentally compatible. Since the flow of substances through the stack is very low (except for carbon, see Figure VI.3.8),

most substances will remain in the solid residues. The solids may be partially recycled (see below) or have to be landfilled. In order to stay in the landfill, they must be immobilized before disposal. Bottom ash as an alkaline material that was soaked in water for some time, contains much less mobile substances than the dry filter residues that contain large amounts of readily soluble chlorides. Filter cake on the other hand is less soluble because it has been precipitated from wastewater. For any residue, pretreatment is necessary before landfilling. The goal of this treatment is the immobilization of heavy metals. It has to be taken into account that redox conditions, pH and other chemophysical parameters can change considerably in long time periods (centuries to millennia).

VI.3.4.7. Concentration

It has been described that certain elements can be significantly enriched in certain products of incineration (Brunner and Mönch, 1986). Figure VI.3.8 shows that 92% of cadmium can be concentrated in the filter ash during MSW incineration. Atmophilic metals are to a large extent transferred to the flue gas and thus collected in the filter residues such as ESP ash or filter cake. Since these residues amount to only a few percent of the total waste incinerated, atmophilic metals become highly enriched in the residues.

Chlorine is also mainly transferred to the flue gas and is washed out in the first scrubber stage. Carbon is completely transferred to the flue gas. More than 80% of the iron is found in the product of magnetic separation of the bottom ash, making scrap iron recycling a profitable business for MSW incinerators.

The concentration effect of volatile metals in the filter residues has two benefits: first, bottom ash gets comparatively "cleaner", making it a product better suited for reuse as a construction material. Second, filter ash becomes more like an ore, enabling recycling of metals. More recently, the incineration process as a whole has been investigated in view of concentrating certain elements in certain products. It is likely that the next generation of incinerators perform better in view of controlled concentrating and diluting of elements.

VI.3.4.8. Materials recycling

Figure VI.3.9 displays the total flow of cadmium through a modern economy: about 25% of the cadmium imported is eventually found in MSW. If all wastes are incinerated in state-of-the-art incinerators, more than 80% of the cadmium entering the incinerator will be concentrated in the filter ash. By a second thermal treatment, this filter ash can be further upgraded, yielding a metal concentrate well suited for recycling. Hence, 20% of the national import can be substituted by the incineration of MSW.

At present, this scheme of cadmium recycling is not economically beneficial if done in a decentralized and small-scale way. For the future, it seems feasible to collect and store filter residues for several decades and then centrally process these materials for metal recovery. Due to the better economy of scale and the high concentration, it may become more economic to produce metals by this recycling scenario than by traditional mining. Hence, in the future, thermal treatment may contribute to energy supply and materials recycling too.

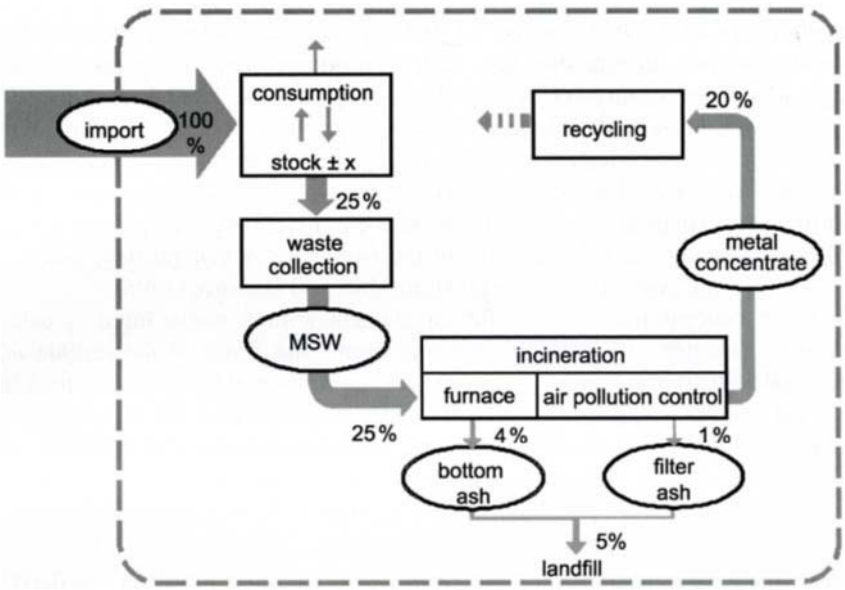


Figure VI.3.9. Materials recycling by incineration: since about 25% of the imported cadmium is finally found in combustible wastes, and by incineration more than 80% of this cadmium is transferred to filter residues, the recycling of cadmium and other atmophilic metals by thermal processes seems feasible.

VI.3.5. The municipal incinerator as a monitoring tool

Information about waste composition is crucial for planning and decision making in waste management. Efficient methods are needed to assess the effect of legislative, logistic and technical measures on the waste stream. Routine determination of waste composition and trends is essential to assess the effect of such measures. Various approaches to characterize wastes have been described previously. It has been proposed to determine elemental waste composition by investigating the material flux through an MSW incinerator plant (Brunner and Ernst, 1986). If all residues of the incineration are analyzed and the total input and output mass flows are determined over a certain period of time, the composition of the input to the plant can be calculated. This allows determining the flux of selected elements through an MSW incinerator, calculate the chemical composition of the waste input and assess the partitioning of selected elements in the SWI. The method has been successfully applied before (Agenend and Trondt, 1990; Reimann, 1989; Schachermayer et al., 1993; Vehlow, 1993; Belevi, 1995). More recently, the method was further developed to routinely monitor the waste composition by the analysis of a single incineration residue only (Morf and Brunner, 1998).

The new method consists of three parts. First, a general model is established to calculate the chemical composition of the waste input by the analysis of a single incineration residue. Second, a sampling model is developed and optimized to minimize sampling costs (samples, sample frequency and size). In the third part, parameters such as transfer coefficients (the partitioning of the elements from the waste input into the different residues) and variance of transfer coefficients are identified. They are already needed as

base assumptions in the first and second part, and are successively improved. Transfer coefficients and their uncertainties have to be determined in a well-designed measuring campaign where the overall SWI has to be balanced during a defined time period. For this purpose, all residues are analyzed, and mass flows of all relevant input and output flows are measured. The flux of selected elements through incineration and the corresponding transfer coefficients are calculated. Also in the third step, specific residues are selected for monitoring waste composition, e.g. flue gas for determination of cadmium, filter ash for cadmium, wastewater for chloride, etc. In the following, a general description of the method is presented. More details are given in Morf and Brunner (1998).

The mean concentration $\bar{C}_{k,\text{waste}}$ for an element k in a waste input is calculated according to Equation (VI.3.1) from the measured mass flows of the residue $\dot{m}_p$ and the measured waste input flow $\dot{m}_{waste}$, the mean concentration of the element k measured in the selected residue $\bar{C}_{k,p}$ and the mean transfer coefficient of k for the corresponding residue $\bar{\varepsilon}_{k,p}$ (which is determined in an earlier measuring campaign; third part).

$$\bar{C}_{k,\text{waste}} = \frac{\dot{m}_p}{\dot{m}_{\text{waste}}} \frac{\bar{C}_{k,p}}{\bar{\varepsilon}_{k,p}} = P \frac{\bar{C}_{k,p}}{\bar{\varepsilon}_{k,p}} \tag{VI.3.1}$$

To calculate the uncertainty of the mean concentration, $\text{Var}(\bar{C}_{k,\text{waste}})$, the law of propagation of error is applied on Equation (VI.3.1). The result may be simplified if the covariance terms prove to be small compared to the variance terms. This has to be checked individually. If it can be assumed that the variance of routinely measured waste and residue mass flows and any covariance terms are negligible in a first order approximation, the propagation of error applied on Equation (VI.3.1) yields Equation (VI.3.2):

$$\text{Var}[\bar{C}_{k,\text{waste}}] = \left(\frac{P}{\bar{\varepsilon}_{k,p}}\right)^2 \text{Var}(\bar{C}_{k,p}) + \left(\frac{P\bar{C}_{k,p}}{\bar{\varepsilon}_{k,p}^2}\right)^2 \text{Var}(\bar{\varepsilon}_{k,p}) \tag{VI.3.2}$$

where P is the ratio of the measured residue versus the measured waste mass flow, $\text{Var}(\bar{C}_{k,p})$ the variance of the calculated mean concentration of element k in the selected residue p and $\text{Var}(\bar{\varepsilon}_{k,p})$ the variance of the mean transfer coefficient of element k from the waste into the residue p.

The approximate 95% confidence interval for the mean concentration μ in the time period considered is given by Equation (VI.3.3).

$$\left[\bar{C}_{k,\text{waste}} - 2\sqrt{\text{Var}(\bar{C}_{k,\text{waste}})} < \mu < \bar{C}_{k,\text{waste}} + 2\sqrt{\text{Var}(\bar{C}_{k,\text{waste}})}\right] \tag{VI.3.3}$$

The mean transfer coefficient for the element k into the residue p, $(\bar{\varepsilon}_{k,p})$ and the variance $\text{Var}(\bar{\varepsilon}_{k,p})$ are to be determined experimentally by an earlier substance flow analysis (third part).

The method was first applied in the MSW incinerator Spittelau, Vienna, Austria in 1999, and is routinely applied to determine waste composition since then. The capacity of the incinerator is 34 t/h of MSW. Figure VI.3.5 shows the incinerator with waste heat boiler, flue gas cleaning and wastewater treatment system as well as the measuring points for monitoring selected elements (C, Cl, Fe, Hg, Cu, Cd, Pb and Zn).

First results of MSW concentrations are shown in Figures VI.3.10 and VI.3.11: monthly mean values of Cl and Hg vary up to a factor two (Fig. VI.3.10). Daily flows of the two

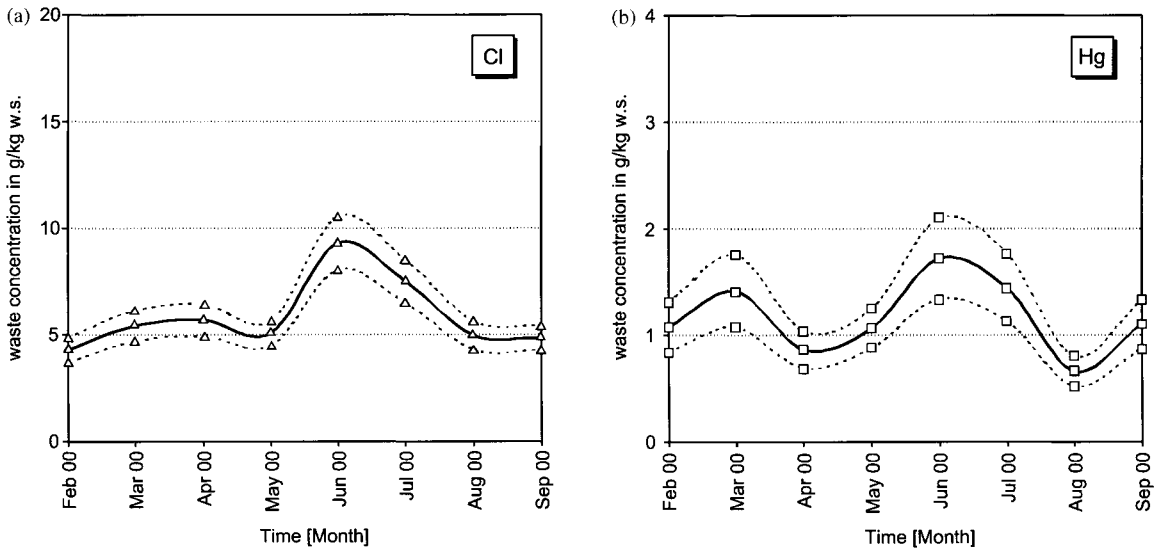


Figure VI.3.10. Time trends for monthly mean MSW concentrations of (a) chlorine and (b) mercury as determined for the Vienna MSW incinerator Spittelau, Austria between February 1 and September 30, 2000; given are means and lower and upper limits for an approximate 95% confidence interval (w.s. = wet substance) (Morf et al, 2001).

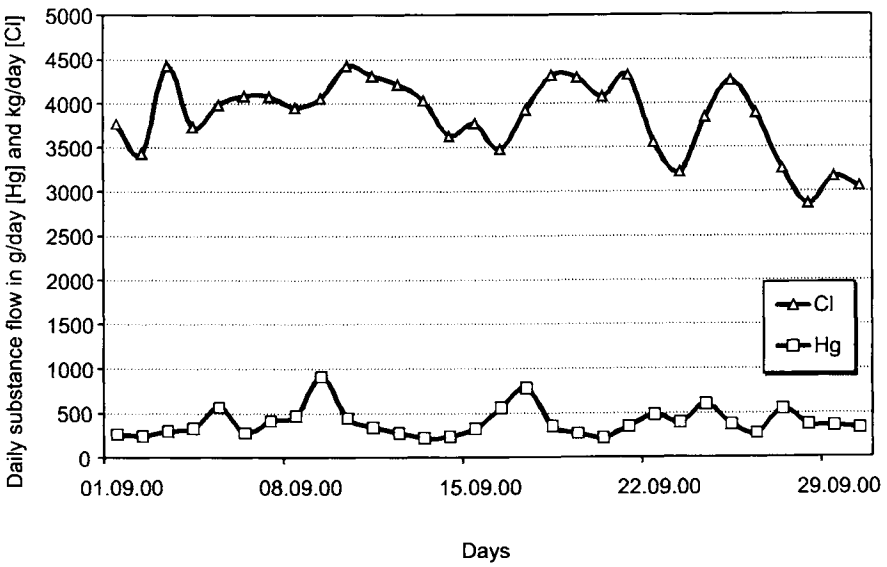


Figure VI.3.11. Time trends for daily flows of Cl [kg/day] and Hg [g/day] through the MSW incinerator Spittelau, Austria between September 1 and September 30, 2000 (Morf et al, 2001).

selected elements, Cl and Hg, vary quite substantially (up to a factor of four) within a period of a few days (Fig. VI.3.11). Both concentrations (Cl and Hg) were analyzed continuously together with the corresponding mass flows of wastewater and acid scrubber discharge, respectively. Daily substance flows in the waste input were calculated using previously measured transfer coefficients.

The proposed method to routinely monitor waste composition by analyzing single incineration residues has significant advantages regarding data quality and costs compared to the normally applied direct waste analysis. When dealing with wastes, it is of high importance to consider uncertainty and assess aspects of quality control. The use of an appropriate mathematical tool to handle substance flow analysis including error propagation is helpful.

If waste composition is measured in the same way on several MSW incinerators throughout a large region or a country, this would allow comparing the waste composition in a more cost-effective and objective way than present practice of direct waste analysis. Future MSW incinerators should be designed for and supplied with hardware and software to apply the proposed method for waste analysis. The additional costs will be small, and the return on investment large when compared to the costs and accuracy of conventional waste analysis.

VI.3.6. Conclusion

The amount of waste produced is a function of materials consumed. In the past century, material turnover in all sectors (industry, trade, agriculture, private households) has increased tremendously; there are no strong signs yet that this trend will change in the near

future. Hence, the amount of wastes will further increase. Recycling can divert an important fraction of the total waste stream back to consumption. But due to energetic and economic reasons, the total recycling of wastes is not feasible. Thus, means to dispose large amounts of wastes in a safe and goal-oriented way are necessary. Goals of waste management comprise protection of man and the environment, the conservation of resources such as energy, materials and land and after-care-free landfills (precautionary principle). Since wastes are important carriers of hazardous as well as valuable materials, waste management plays a major role in environmental protection and resource conservation.

In service-oriented economies, non-hazardous wastes are larger carriers of hazardous substances than hazardous wastes. Hence, if risks from hazardous substances are to be minimized, the environmentally safe management of non-hazardous wastes, in particular MSWs, is crucial. State-of-the-art thermal treatment is a feasible way to process many hazardous and non-hazardous wastes. There are different thermal processes available to treat waste materials; each has its specific advantages and disadvantages. Investigations into mass balances of modern thermal processes show that incinerator emissions can be much smaller than the most advanced standards. If state-of-the-art APC technology is applied, flows of heavy metals and organic substances from incinerators are of no significance when compared to other emission sources. The new question is what to do with the resulting incineration and filter residues. Results from material flow analysis point to the large potential for future reuse. If long-term scenarios are investigated, it seems feasible that certain materials such as atmophilic metals can be efficiently recycled by thermal processes. It is necessary to develop new strategies in waste management such as combining energy recovery with materials recovery. If introduced on a large scale, such reuse strategies could successfully compete with present waste management trends, which are often based on dilution strategies.

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VI.4

Municipal landfills. A case study: remediation and reclamation at Nanji Island

Christopher G. Uchrin and Seok Soon Park

VI.4.1. Introduction and background

The Nanji Landfill, located on Nanji Island in the Seoul Metropolitan Area, South Korea (Fig. VI.4.1), is considered to be one of the largest landfills in the world. The landfill comprises a surface area of nearly two million (1,760,000) square meters (Nanji Island comprises three million square meters) and reaches an elevation of 75 m. Landfilling operations commenced in 1978 and ceased in 1992. At least at the beginning of landfilling very few limitations existed regarding materials that could be dumped. It appears that landfilling initially started on Nanji Island as a flood protection measure. The nature of the municipal solid waste at that time was predominately in the form of coal ash and fill collected from construction sites. The industrial boom, which South Korea experienced in the 1980s profoundly, changed the nature of the solid waste as well as increasing its volume (Fig. VI.4.2). In 1990, solid waste per capita had reached 2.2 kg/day that represented the highest in the world (Park et al., 1994). In addition, there are indications that during this time, industrial wastes were often mixed with the municipal solid waste and landfilled, as there were no other alternatives at that time. Records were not kept.

The landfill, at present, poses an immediate chronic environmental threat to the local populace although immediate acute risk is minimal. The landfill is covered with soil so that airborne transport is minimal. The landfilling operations started, however, without a leachate control system, which is standard practice today. Hence, it is not unique among older landfills. Koo and Yoon (1994) showed that leachate generated in the landfill from infiltrating precipitation percolates through the underlying sand layer and contaminates the underlying groundwater.

Hydrogeological data around Nanji Island is limited (Koo and Yoon, 1994). In similar cases, however, mounding of the groundwater table in landfills can affect changes in the natural groundwater flow patterns. Thus, percolating leachate may not only be affecting underlying groundwaters but may also be affecting the quality of the local surface waters, especially if these are fed by the groundwater. As a result, in 1993 the Seoul City's water intake was moved to a site far enough upstream of the head of tide on the Han River to eliminate the threats caused by the leachate and the contaminated tributary near Nanji Island.

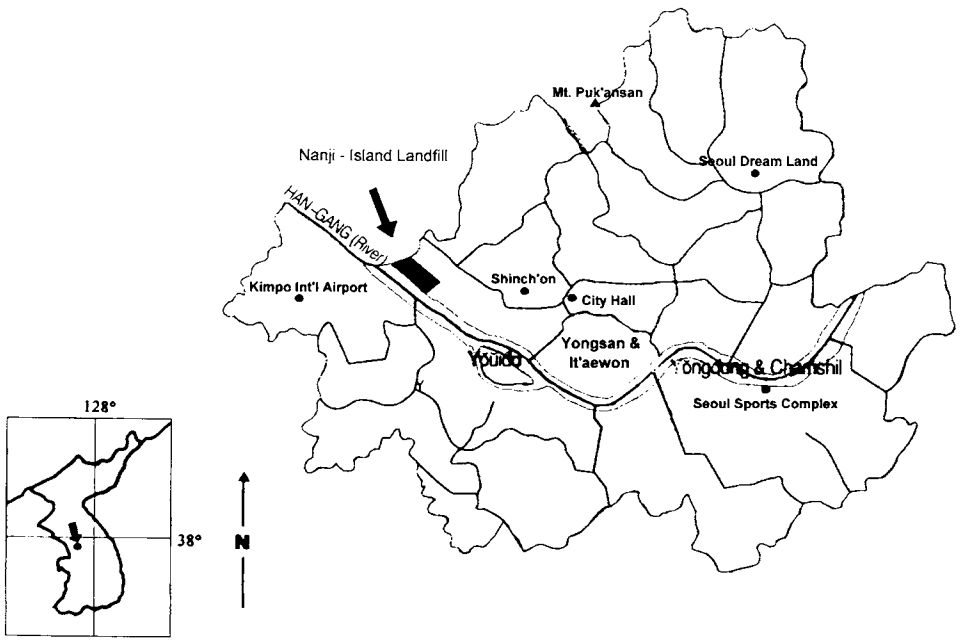


Figure VI.4.1. Location of Nanji Island Landfill in the City of Seoul.

Attention has recently been focused on Nanji Island from concerns other than purely environmental. An estimated 15 million people live within the Seoul Metropolitan Area. Available land in this area has become extremely scarce and, thus, valuable. The landfill is in close proximity (10 km) to downtown Seoul. Nanji Island is being considered as an

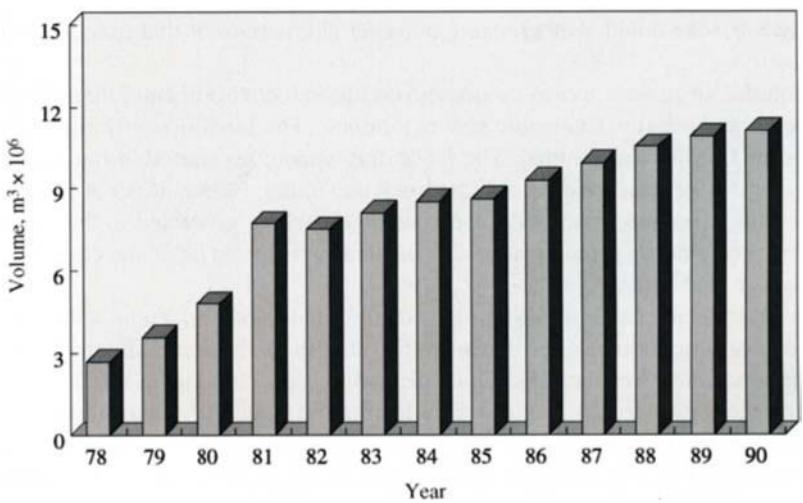


Figure VI.4.2. Solid waste volume generated versus time.

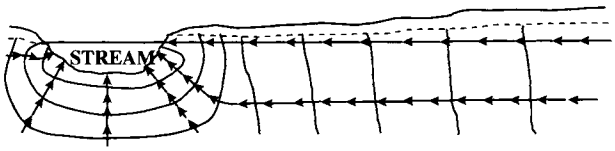
extremely valuable piece of real estate. The presence of the landfill represents a serious impediment to development. A rather singular problem is posed: can a serious environmental condition be mitigated in such a fashion that the cost be offset by potential resource recovery? This case study will discuss some of the issues, which must and are being considered.

VI.4.2. Environmental problem definition

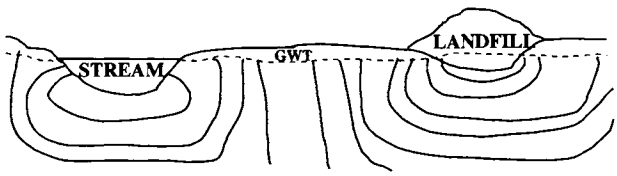
If left as is, even if no further solid waste is input to Nanji Island, the landfill will still represent an environmental threat to the local populace. Covering and vegetating will and has seemingly closed off one of the sources of environmental risk, namely blowing of solids offsite and transport by birds. However, the anaerobic decomposition endemic to sanitary landfills produces methane and other gases, which can not only contribute to air pollution but also ignite and burn (Vesilind and Rimer, 1981). In fact, the Nanji Landfill was burning in 1993 when the authors inspected it during a field investigation. Finally, hazardous industrial wastes, which may be present in the landfill, may be ignitable (Michaels et al., 1986) or reactive, generating toxic gases (Handy et al., 1986). Numerous complaints of headaches, vomiting and respiratory ailments have been registered by nearby residents (Daewoo Engineering, Inc., 1992). It is well known that infiltration percolating through landfills can generate leachate, which can contaminate underlying groundwater (Khanbilvardi et al., 1987). Another, not so obvious potential problem, is that of groundwater mounding which can cause localized reversals of flow direction. This phenomenon is illustrated in Figure VI.4.3. This figure also shows that the hydraulic gradients in the vicinity of landfills can be increased by mounding, thus increasing the groundwater flow rate. If the natural direction of the groundwater is toward the stream, some of the contamination would be expected to reach the stream. Since the Nanji Landfill does not have a leachate collection system, one would expect leachate to contaminate both the groundwater and the Han River. Recently, several groundwater wells adjacent to the landfill were closed due to leachate contamination. These wells had been used for drinking water and farm irrigation since before the landfill. Koo and Yoon (1994) investigated groundwater contamination by inorganic compounds around the Nanji Landfill. Kaur et al. (1996) tested the toxicity of the Nanji Landfill leachate using the Japanese Medaka Embryo Larval Assay. Water samples from surface waters proximate to the landfill did not exhibit toxicity, even at 100%. The leachate, however, was found to exhibit extreme toxicity. At least at present, it thus appears that the leachate entering the surface waters is being sufficiently diluted. This could, however, change.

VI.4.3. Site remediation/reclamation

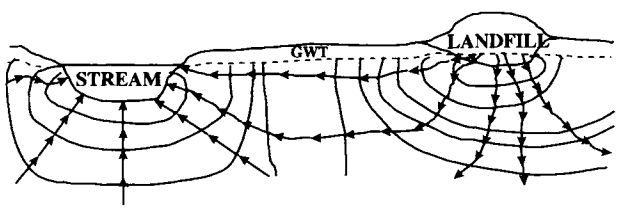
One of the challenges facing potential remediation of the landfill site is its heterogeneous nature. A study conducted by Daewoo Engineering, Inc. (1992) reported results of test borings drilled at the apex of the landfill and some of these results are presented in Figures VI.4.4–VI.4.6. Figure VI.4.4 displays percent combustible and non-combustible matter versus depth. The upper 15 m shows approximately 45–55% of each while deeper



Equipotential lines and flow streamlines before landfill



Equipotential lines after mounding due to landfill



Equipotential lines and flow streamlines after mounding

Figure VI.4.3. Groundwater table mounding resulting from landfill.

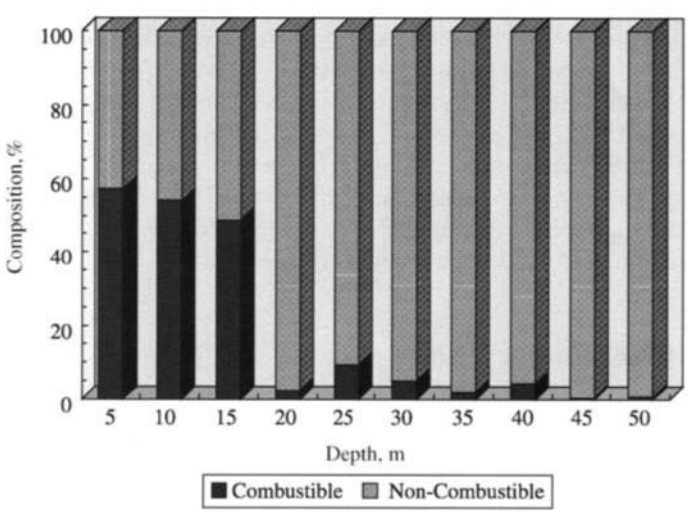


Figure VI.4.4. Combustible and non-combustible matter versus depth.

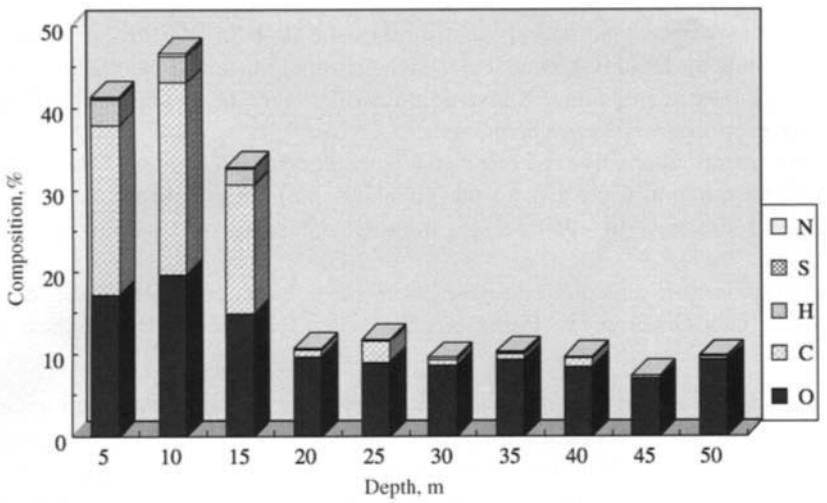


Figure VI.4.5. Composition of Nanji Landfill versus depth.

the amount of combustible matter falls off dramatically to less than 10%. Figure VI.4.5 shows that much of the deeper inorganic matter is ash. Finally, a partial elemental analysis displayed in Figure VI.4.6 shows that the combustible matter is primarily carbon, hydrogen and oxygen (as expected). These figures underscore the dramatic change in the nature of the landfilled materials over time.

Several alternatives are available to address the Nanji Island Landfill Site. These range from no action to remediation and reclamation of the land. The remediation/reclamation alternative is extremely challenging, however, it is thought that the potential real estate

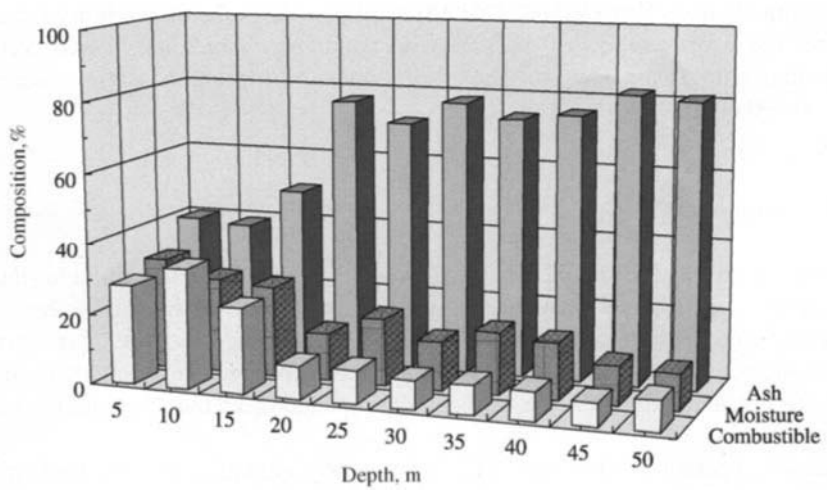


Figure VI.4.6. Elemental composition of Nanji Landfill versus depth.

value of the reclaimed land would greatly offset the cost. In addition, it must also be remembered that the landfill is located in a large metropolitan area. Potential human health risk resulting from remediation/reclamation activities must be considered and, in some cases, may even severely limit operations.

The no action alternative is most likely unacceptable. Although the landfill at present offers minimal acute risk to the populace, no such conclusions can be drawn regarding chronic risk. In addition, gas venting and subsurface burning present real potential risk.

Four options for remediation/reclamation have been considered by the Seoul Metropolitan City Government (Daewoo Engineering, Inc., 1992). Each of these will be described.

1. *Landfill mining.* In this option, the landfill materials will be excavated and screened to separate inorganic and organic materials. Organic materials will be composted and inorganic materials will be transported to and landfilled at another site. This type of remediation has been successfully performed at several sites in the United States. The cost estimate for this option is approximately US $860,000,000.
2. *Solidification/resource recovery.* This option involves excavating the landfill solids and then mixing the solids with cement. Blocks are then formed which can be used for building materials. The cost estimate for this option is approximately US $7,700,000,000. It is important to note that the resultant blocks may be sold, thus recovering some of the cost.
3. *Bioremediation.* This option involves enhancement of the natural microbial degradation processes occurring in a sanitary landfill. This involves the introduction of nutrients and an electron acceptor to enhance anaerobic microbial activity. The by-product methane gas can be vented and taken to minimize the potential of slope failure. Another drawback is that the landfill material is highly heterogeneous. The cost estimate for this option is approximately US $61,000,000,000.
4. *Excavation and movement to a new site.* An alternative site is currently being used several miles from Nanji Island. This alternative involves the excavation of the Nanji Island Site with transport of the solids overland (by either truck, closed conveyor, railroad or ship) to the new site. The cost estimate for this option is approximately US $7,700,000,000.

VI.4.4. Summary

The Nanji Island Landfill situation is representative of environmental problems that face many rapidly industrializing nations today. Initially, landfilling operations had started without any consideration of environmental concerns. During the 10 years of operation, however, the volume increased and nature of the material changed in dramatic fashion. To further exacerbate the situation, the city spatially expanded such that the landfill is near the center of town.

Landfilling operations were initiated as a flood protection measure. The land on which the landfill is situated has a potentially high real estate value. The projected value of the land could help offset the cost of remediation/reclamation. A number of technologies are

being considered. This site, pending successful remediation/reclamation, could be transformed from an unfortunate environmental disaster to a success story of great proportions.

Acknowledgements

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VI.5

Recycling of plastic waste, rubber waste and end-of-life cars in Germany

Peter Dreher, Martin Faulstich, Gabriele Weber-Blaschke, Burkhard Berninger and Uwe Keilhammer

VI.5.1. Introduction

Among different types of consumer waste in Germany, plastic waste, rubber waste and end-of-life cars are closely intertwined. Processing techniques applied to these types of consumer waste are identical in many cases. In this chapter, similarities are outlined and one section is devoted to each type of consumer waste as follows:

- Plastic waste (Section VI.5.2)
- Rubber waste (Section VI.5.3)
- End-of-life cars (Section VI.5.4)

It should be added that as a member state of the EU, Germany is bound by the Community law on waste. Therefore, the EC Packaging Directive (1994) and Directive on end-of-life vehicles (2000) have been adequately implemented into German national law to comply with the relevant EC regulations.

VI.5.2. Plastic waste

VI.5.2.1. Legal framework and organization

At present, regulations for plastic waste recycling only apply to private households. Regulations are limited to packaging waste with the ordinance on packaging waste being the legal provision. Recycling of packaging, remnants from production or defective production units is partially organized by producers themselves.

The packaging waste ordinance of 28 August 1998 obliges every store to take back packaging waste unless industry provides for a collection and recycling network. Furthermore, the packaging waste ordinance requires 80% of the packaging to be collected and another 80% thereof to be recycled. The distributor of packaging has to collect 100% of the packaging at the place of distribution. Thus 65% of the packaging waste has to be recycled, beginning 1 July 2001 (VerpackV, 1998).

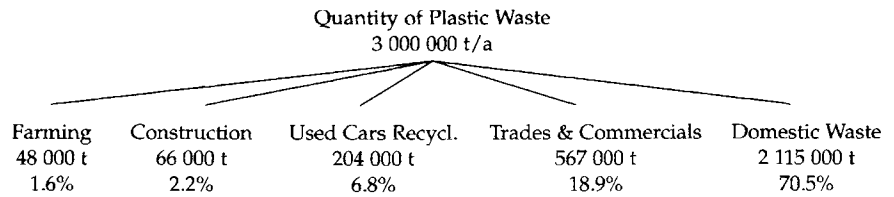


Figure VI.5.1. Origin and quantities of plastic waste (after DKR, 1995).

The German industry responded to these provisions by establishing a collection and recycling network. The Duales System Deutschland (DSD) organizes collection. The DSD entrusted the Deutsche Gesellschaft für Kunststoffrecycling (German Association for Plastic Recycling, DKR) with the recycling of packaging waste. DKR is an incorporated limited liability company, owned by the DSD (49.6%), a consortium of banks (25.2%) and the Association of Plastics Manufacturing Industry (25.2%) called "Beteiligungs- und Kunststoffverwertungsgesellschaft mbH" (DKR, 1995).

VI.5.2.2. Quantities of plastic waste

Annual volumes and percentile of plastic waste from different sources generated in 1995 in Germany are shown in Figure VI.5.1. The recovery of plastic waste according to the data of DSD and DKR (1995) are given in Figure VI.5.2.

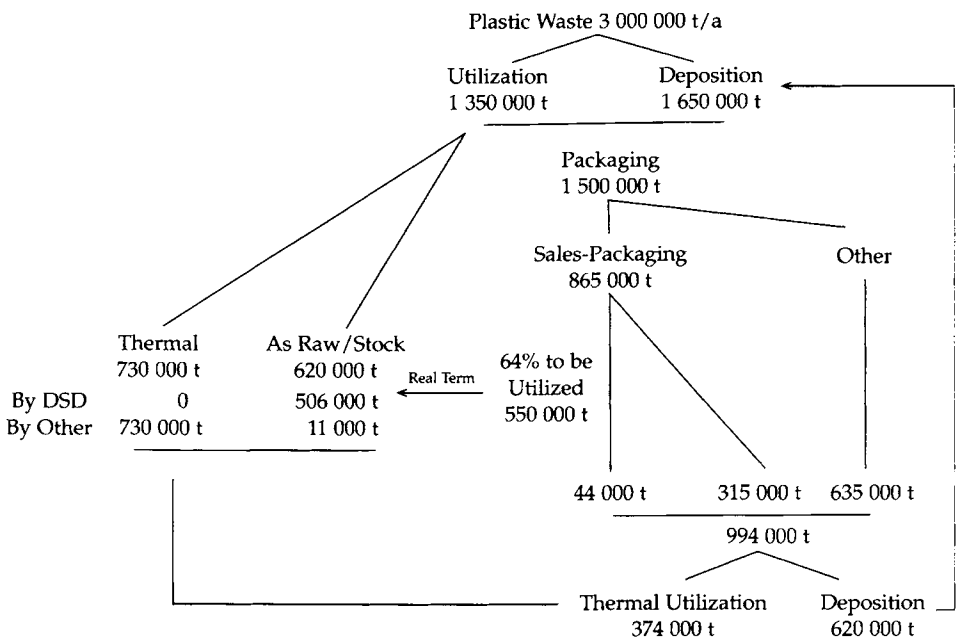


Figure VI.5.2. Recovery of plastic waste (after DKR, 1995).

Table VI.5.1. Distribution of main plastics in urban waste (after DKR, 1995).

Type of plastic	Polyolefins (PE/PP)	Polystyrene (PS)	PVC	Other
wt.%	65	20	5	10

VI.5.2.2.1. Urban waste

In 1995, out of 36 million tons (Mt) of urban waste, a total of 1.5 Mt were plastic packages that had to be taken back by trade and industry (Statistisches Bundesamt, 1996). Packaging from commercial enterprises, returnable packaging, secondary packaging and packaging for transportation purposes amounted to 635,000 t leaving 865,000 t real packaging waste to the DSD. According to the ordinance, 64% or 550,000 t had to be treated (Gesellschaft für Verpackungsmarktforschung, 1994).

Of the urban waste, 90% is composed of thermoplastics, which can easily be recycled (Table VI.5.1).

The plastic packaging waste is divided into four major categories (Fig. VI.5.3).

The fractions from sheets size A4 according to DIN (German industry standard) and bottles smaller than 5 l are made mainly of one type of plastic – either polyethylene (PE) or polypropylene. Compared to granulate from other fractions, the quality of this polyolefine granulate is the highest.

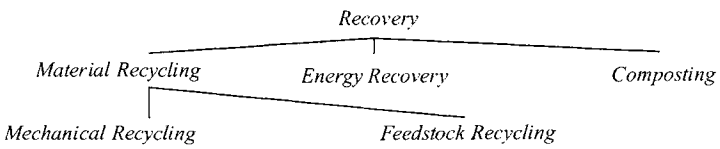
VI.5.2.2.2. Non-urban waste

The category of plastic packaging also comprises:

- commercial/industrial waste such as sheets, monobatches;
- bulky waste such as refrigerators, foams from pads or mattresses, plastic coated nog plates from the furniture industry;
- automobile parts such as molded parts, foams, shredder light fraction;
- building and construction waste such as PVC floors, tubes, roof-boarding;
- agricultural plastic sheets.

VI.5.2.3. Recovery

According to DIN and CEN standards, recovery is conceptualized as follows:



Composting of plastic waste is less important in Germany. Therefore, the emphasis will be on energy recovery, mechanical recycling and feedstock recycling.

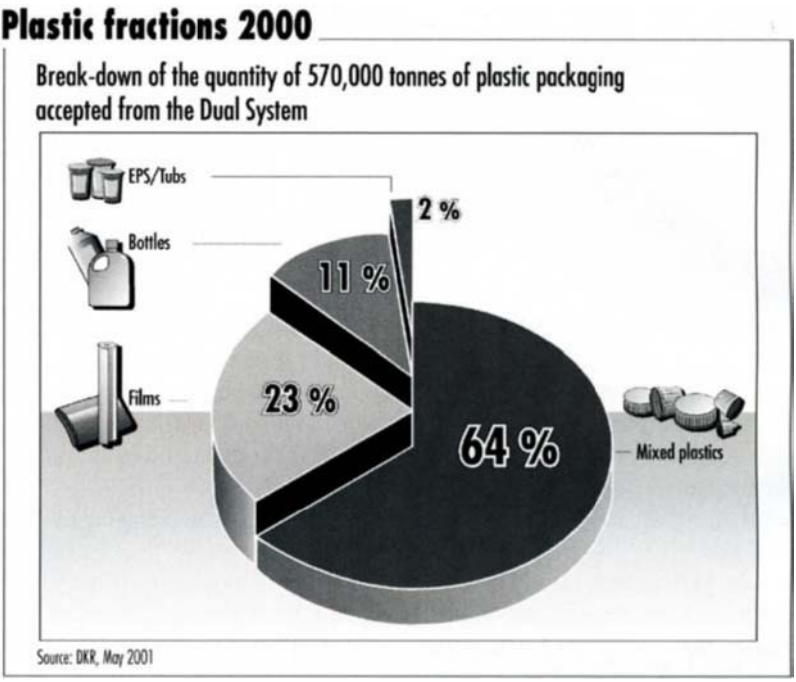


Figure VI.5.3. Distribution of plastic packaging waste according to packaging type (after DKR, 2002a).

From the three types of plastics

- thermoplasts,
- duroplasts,
- elastomeres,

only thermoplasts can be melted. Duroplasts and elastomeres are mainly disposed off by incineration or pyrolysis.

A survey of plastics recovery is shown in Table VI.5.2.

Energy recovery of plastic packaging is limited to combined heat and power stations. Combustion at waste incineration plants is forbidden according to the packaging waste ordinance. Packaging waste that cannot be submitted to mechanical recycling is usually treated by means of feedstock recycling. Packaging waste that cannot be submitted to feedstock recycling due to lack of profitability or certain regulations (e.g. plastic containers, which carried chemicals have to be treated as hazardous waste) will be treated in combined heat and power stations.

VI.5.2.3.1. Recovery pathways for plastic waste

The recycling of plastic packaging waste has increased 10-fold in the last decade (Table VI.5.3).

Table VI.5.2. Recovery – priority setting and application according to purity grade.

Recycling type	Objective	Legal provision (DSD, packaging waste only)	Application to	Permitted degree of contamination
Mechanical	Reuse material by melting and molding	65% of material recycling	Pure grade plastics	Low
			Mixed plastics	Medium
Feedstock	Depolymerize to chemical units for next synthesis	35% of material recycling	Mayor part of mixed plastics	Medium
Energy recovery	Make use of energy stored; substitute traditional fuels	>75% of energy recovery	All types, preferably if alternate recovery is too costly	High

The scheme for utilization of plastic packaging waste in Germany is shown in Figures VI.5.4 and VI.5.5.

VI.5.2.3.1.1. DSD plastic waste

In the packaging waste ordinance, a ratio of 65% mechanical recycling to 35% feedstock recycling was set to ensure a reasonable amount of feedstock recycling. However, in 1995, the ratio had rather been 81% mechanical to 19% feedstock including recycling in foreign countries. Ratio formulas are, therefore in the long run, supposed to be replaced by product

Table VI.5.3. Development of packaging waste recycling (after DSD, 1996, 2002; DKR, 2002a,b).

Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
(a) Quantity of packaging forwarded for recycling according to DSD (1996, 2002)											
Forwarded for recycling (in 1000 t)	20	30	40	281	461	506	532	545	548	555	548
(b) Quantity of plastic packaging accepted from DS sorting plants and forwarded for recycling according to DKR (2002a,b)											
Accepted from DSD (in 1000 t)								567	600	610	570
Forwarded for recycling (in 1000 t)								615	634	629	602

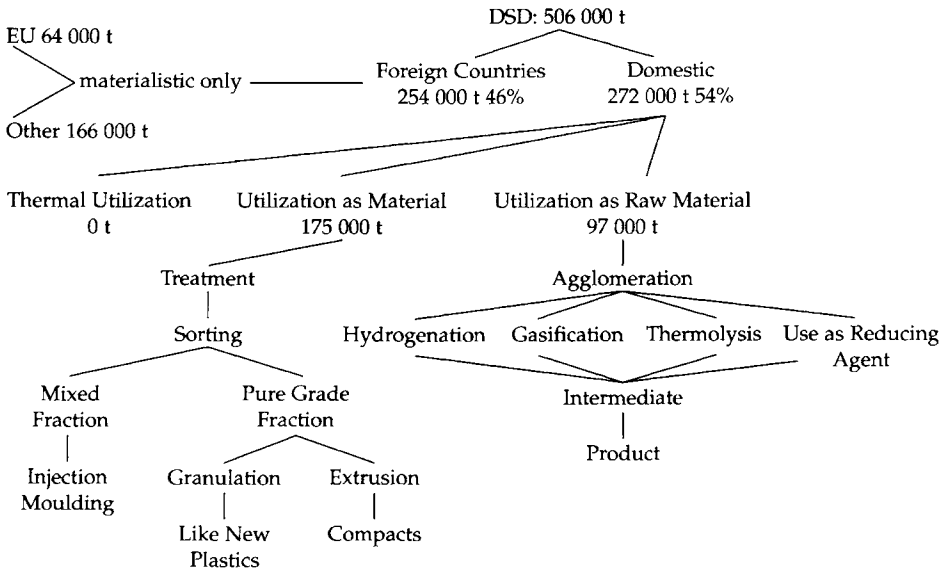


Figure VI.5.4. Flow chart for plastic packaging waste in 1995.

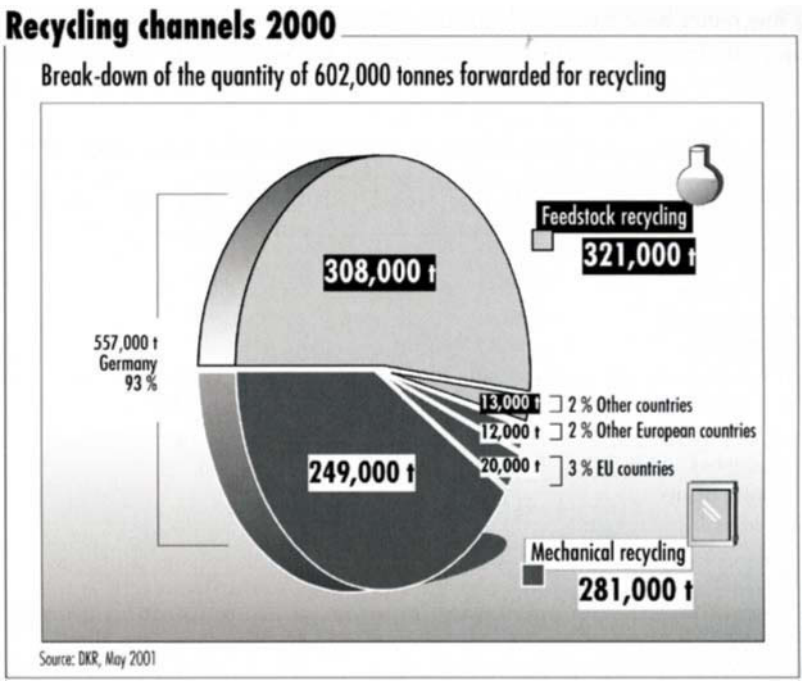


Figure VI.5.5. Destination of DSD packaging waste for recycling (plastics) (after DKR, 2002b).

specifications. If plastic waste complies with certain specifications, it follows either the pathway of mechanical recycling or feedstock recycling depending on plastic waste quality. Thus both recycling pathways are connected via a flexible switch. For instance, if there is no market for secondary plastics from mechanical recycling any more, plastic waste may also be disposed off by feedstock recycling. Recycling companies would no longer be subject to market conditions because they deliver directly to DKR. For DKR, this would mean more security in recycling (Lindner, 1996).

VI.5.2.3.1.2. Other plastic waste

Plastic waste from commercial enterprises. Plastic waste from commercial enterprises is usually pure grade, for instance, large containers or monobatches. Large containers and other commercial packaging are collected and recycled by specialized providers, e.g. "Gesellschaft zur Rückführung industrieller oder gewerblicher Kunststoffverpackungen RIGK mbH"/Wiesbaden (a company collecting industrial and commercial packaging waste), Interseroh AG/Köln, "Vereinigung für Wertstoffrecycling Vfw GmbH"/Köln or "Folienverwertungsgesellschaft mbH"/Düsseldorf (a company specialized on sheets).

Moreover, a significant amount of plastic waste (1993: 382,000 t) from companies is collected as urban waste (1993: 24,203,000 t total urban waste, of which 1.6% were plastics) (Statistisches Bundesamt, 1997).

Plastic waste from bulky waste. These are foams from pads or mattresses or coated nog plates. Pure grade collection could easily be achieved by introducing special collection days. Currently, plastics from bulky waste cannot be subject to treatment other than disposal or energy recovery, for profitability reasons. Refrigerators also belong to bulky waste. Their coolants are removed before refrigerators are submitted to energy recovery. Deposition is deemed to contribute to ozone layer damaging from degassing of non-CFC-free insulating foams. Refrigerators that are collected today have been produced long before the Montreal Treaty and contain up to 13% CFC 11.

Plastic waste from used car recycling. End-of-life cars and linen goods are shredded together. The light fraction is mainly deposited. A minor portion is treated at garbage incineration plants or gasification plants. Recycling of plastics from the light fraction is not profitable yet and is only carried out to a minor extent. About 20% of polypropylene shock absorbers are recycled for the manufacturing of new shock absorbers. Small quantities of varnish do not spoil the recycling process (VW) (Schäper, 1993). Another example is duroplast granulate substituting for other fillers.

Plastic waste from electronic scrap. The metal conductors and the plastic insulation are separated. Since insulation is contaminated with about 1% metals it cannot be recycled for the same application (Masshöfer, 1989) but e.g. anti-noise sheets instead, thereby recovering 90% of the plastic. Usually, the casing is made of pure grade plastic thus rendering mechanical recycling possible in principle.

Plastic waste from buildings and construction. The plastic waste from demolition amounted to an estimated 2.4 Mt in 1989 (Kohler, 1991). The demolition of more recent constructions, in the following decades, will result in the dramatic increase of the plastic waste from this source, reflecting fast growth of plastic use for construction purposes. Most of the plastics will be deposited. In case rubble is sorted, the plastics fraction will either be left for treatment or submitted to energy recovery. Due to an initiative by the working group on PVC (Arbeitsgemeinschaft PVC Bodenbelag-Recycling), PVC floors

and roofing have been collected separately since 1990 (Hofmann, 1993). The Society for Plastics Recycling (Entwicklungsgesellschaft zur Wiederverwertung von Kunststoffen) supported a recycling concept for PE from demolition waste. It is used for the manufacturing of non-compression-proof tubes with up to 30% secondary PE (Anonymous, 1993a).

VI.5.2.4. Treatment

The treatment of plastic waste comprises fragmentation, sizing, sorting, washing and drying, agglomeration and granulation. The more intense the treatment, the cleaner and purer the granulate will be matching the characteristics of new material. The latter is important since granulate from plastic recycling has to compete with new material on the market (see Section VI.5.2.12).

VI.5.2.4.1. Sorting

Sorting aims at gaining the maximum purity grades possible. It especially serves purification of mixed plastic waste. The usually applied techniques are as follows.

VI.5.2.4.1.1. Separation by float-sink processing
Plastic fragments will be stirred into a pool. According to its specific density, PE and polypropylene will float and can be decanted; PVC and polystyrene PS will sink to the bottom and will be removed using a scraper.

VI.5.2.4.1.2. Separation by hydrocyclone
In the hydrocyclone method, the washed and fragmented plastics will again be separated according to their densities. The separation is induced by centrifugation and takes place in a vortex. For instance, DSD-plastics will be separated to 99% purity. Fractions are:

- polyolefins (PE, PP)
- polystyrene and
- PVC

The separation capacity of Thyssen-Henschel-plant/Hamburg is 1 t/h.

VI.5.2.4.1.3. Separation by centrifuge
This technique is suitable even for filthy plastic waste. Plastic waste is ground, washed and stirred giving it an aqueous suspension, which is separated by three consecutive centrifuges. If DSD-plastics are supplied, the following fractions will be gained:

- polyolefins (PE, PP),
- polystyrene,
- PVC,
- metals,
- paper,
- other plastics.

The plastics suspension will be pumped into the centrifuge. The plastic particles will hit a ring of water that moistens the cylinder of the centrifuge moving with it. Lighter plastics such as PE or polypropylene will float on the surface of the water ring and are extracted by a worm conveyer. In contrast, PVC and polystyrene, which have a higher density, will sink through the water ring to the funnel-shaped cylinder of the centrifuge to the extraction site. KHD Humboldt Wedag AG/Köln has developed this process. It is called "Censor" and separates up to 99.9% purity.

With regard to DSD-plastics, sorting serves two purposes:

- separation of non-plastics;
- fractionation into
  - sheets,
  - hollows,
  - mixed fraction.

Further treatment in plastics recycling requires a constant plastics quality. This requirement is met by sorting. For instance, sheets should be sized at least DIN-A4 or the purity grade should be 92% for further processing (DSD, 1996), at the minimum.

VI.5.2.4.2. Agglomeration

Agglomeration helps to maintain quality standards of recycled plastics such as bulk density, particle size, ash content, chloride loading or residual moisture. A frequent prerequisite for further processing is the conversion of mixed plastics into a semi-finished product. This conversion can be achieved by agglomeration, e.g. in a circular die (Fig. VI.5.6). Agglomeration is a multistep process as shown in Table VI.5.4.

Plastic waste is collected by the DSD as a mixed fraction for commercial reasons (DSD, 1996). In order to recycle plastics from the mixed fraction, certain quality standards must be met. This can be achieved through agglomeration as shown in Table VI.5.5.

VI.5.2.5. Feedstock recycling

In feedstock recycling, plastics are depolymerized. The monomers gained will be used for synthesis of new products in the petrochemical industry. Feedstock recycling is a means to recover even plastics that could not be traded otherwise.

Feedstock recycling is applied to contaminated and heterogeneous plastics waste. Most of the plastics entering this process originate from the urban waste and shredding light fraction with PE, polystyrene, polypropylene and polyvinyl chloride as the main constituents. For feedstock recycling, plastics have to comply with certain minimum quality standards, which do not apply to plastics from the above-mentioned sources. Therefore, feedstock recycling is preceded by extraction of contaminants, i.e. dehalogenation and degrading extrusion to separate halogens and heavy metals contained in additives.

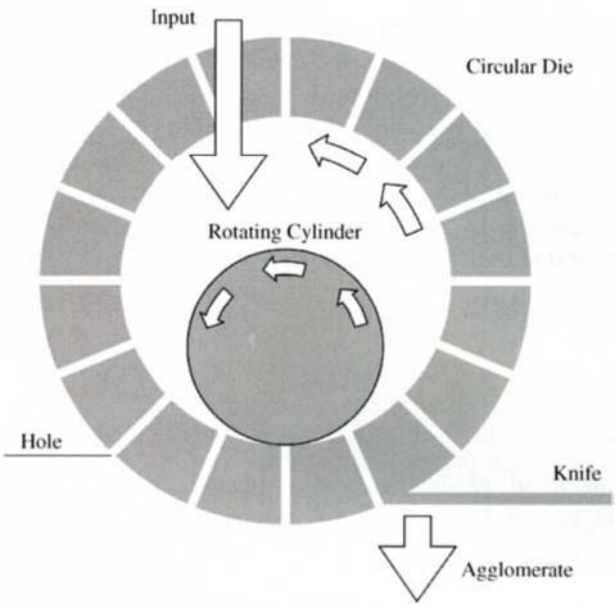


Figure VI.5.6. Circular die (after DSD, 1996).

VI.5.2.5.1. Hydrogenation (VEBA)

Hydrogenation takes place at pressures of about 250 bar requiring plastics to be liquefied before they are processed (Fig. VI.3.7). Liquefaction is achieved by heating plastics for a longer time. After compression to 250 bar in a high-pressure reactor, the plastic liquid is heated to 480°C and mixed with hydrogen. Due to heat and pressure, the carbon chains are split. Supplying hydrogen serves two purposes: carbon chains are split further by the help of hydrogen binding to the breaking points. At the same time detoxification takes place. Reaction products are gases and a synthetic crude oil called "Syncrude" (Table VI.5.6).

Table VI.5.4. Agglomeration.

Step	Remark	Corresponds to specification
Prior crushing	–	–
Segregation of contaminants	By air separator, vibrating riddle, magnet, Eddy current	Reducing of contaminants, dust, ash
Agglomeration		
Cup agglomeration	Rotating knifes producing frictional heat 140°C; caking; cut	Bulk density
Die agglomeration	Plastic particles are pressed through the hole of a die; cut	Particle size, residual moisture

Table VI.5.5. DSD quality requirements for mixed plastics waste (DSD, 1996).

Specification	Requirement
High bulk density	>300 g/l
Particle size	<50 mm
Low content in dust/ash	<4.5%
Low chloride loading	<2%
Low residual moisture	<1%

VI.5.2.6. Gasification (Schwarze Pumpe, high-pressure gasification)

Gasification aims at the production of synthetic gas for other industrial processes. Plastics are mixed with oxygen and steam at 800°C. The gases formed consist mainly of hydrogen and carbon monoxide. Heavy metals and minerals will vitrify in a second step thus forming slag. Condensable intermediates like tar or solids will then be separated for synthetic gas production by means of gasification. Synthetic gas is a basis in the chemical industry, e.g. it is used to produce methanol.

VI.5.2.7. Thermolysis (BASF)

In contrast to hydrogenation, plastics are liquefied at 300°C in vacuum. Without adding hydrogen, plastics are cracked and fractionated to petrochemical basis. Naphtha gases, alpha olefins and oil are formed.

VI.5.2.8. Reduction (Bremer Stahlwerke, blast furnace processing)

Conversion of ore into steel requires deoxygenation. Only recently the traditional reducing agent, crude oil, has partially been replaced by plastic waste in the Bremen steel factory. In principle, plastics could substitute oil completely. To date, 30% of oil is substituted.

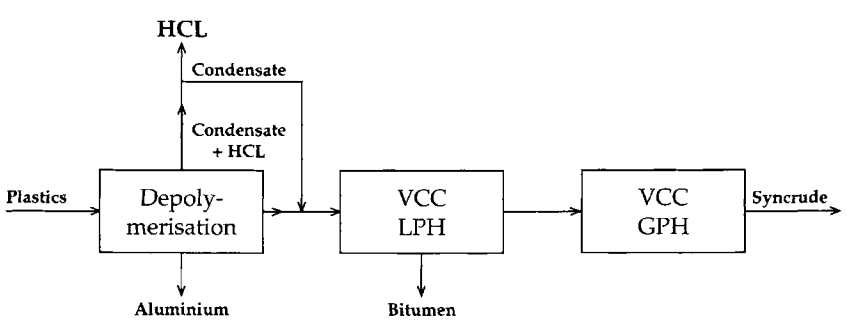


Figure VI.5.7. Recycling of plastic waste by hydrogenation (after Hecka and Niemann, 1996).

Table VI.5.6. Contents and characteristics of hydrogenation main product "Syncrude" (after Korff and Heim, 1989).

Content/ characteristic	Naphthene, paraffin	Ethyl-benzene	Sulfur	Heavy metals	Distillability
Percentage/extent	87%	13%	<0.05%	0% (crude oil: 3%)	Unlimited (crude oil: limited)

Agglomerate is blown into the melting bath at the blast furnace's bottom. Gases formed, thereafter, serve as a reducing agent (DSD, 1996).

VI.5.2.9. Mechanical recycling

In mechanical recycling, refined plastics are melted and processed forming the desired product. In some processes, contaminants and particles of poor melting quality have to be separated from the fusion in order to gain a highly homogenous polymer. If mixed plastics are supplied, e.g. by the DSD, sorting, grinding and agglomeration are required before plastification can start.

The manufacturing process is the same as for new material. Mixed and contaminated plastics are mainly melted and recycled by the following processes.

VI.5.2.9.1. Extrusion

During extrusion, mixed and ground plastic particles are melted together with their contamination forming a fusion that can directly be pressed into a mold by means of a roll extruder. After solidification the product can be taken from the mold.

VI.5.2.9.2. Injection molding

In injection molding, plastics are first melted by heating. Melted plastics are then fed into a cylinder and compressed by means of a piston. They are directly pressed into a mold, whilst the pressing force remains constant until the product is solidified.

VI.5.2.9.3. Sintering

In this process, plastic particles agglomerate in a heated mold first. They are melted due to the high pressures exerted on them. Afterwards, they are directly pressed into a mold.

VI.5.2.9.4. Coextrusion

During coextrusion, multilayer sheets can directly be produced in a single step. Usually a layer of new material will enclose a core consisting of recycled plastics. Granulate is

melted first then pressed through intercalating jets. This technique is applied, e.g. to food packaging since layers of recycled plastic are not supposed to directly enclose food.

VI.5.2.10. Energy recovery

VI.5.2.10.1. Emissions from incineration of plastic waste

Compared to other material with a high calorific value, about 80% of standard plastics (PE, PP, PS) cause lower emissions in incineration plants. Only PVC increases dioxin and furan emissions due to high chloride concentrations. PVC and plastic foams (polystyrene and polyurethane) have to be supplied in a mixture with other fuels due to their negative impact on emissions (Wurm et al., 1996).

VI.5.2.10.2. Combustion in incineration plants for urban waste

According to the packaging waste ordinance, combustion of plastic waste is permitted only if the efficiency of energy recovery is at least 75%. Garbage incineration plants are usually constructed for inertion of waste and not for recovering energy. Thus the efficiency of garbage incineration plants amounts to only 20% compared to 40% for power stations. To date, mechanical and feedstock recycling are subsidized with several hundreds of EURO (€) per ton. Since these recycling methods are too expensive in the long run, supplying garbage incineration plants with plastics waste is being considered. Experiments carried out at a test plant (TAMARA/Karlsruhe) have shown that (Mark et al., 1996):

- mixed plastic waste can be added up to 30% by weight;
- foams can be added up to 3% by weight;
- all halogens (e.g. chlorine from PVC) accumulate in flue gas. They are extracted by flue gas scrubbing.

One limitation arises from the high calorific value of plastic waste. The throughput is reduced by fuels with high calorific value, which could be bypassed if existing plants were modified (Lautenschlager and Mark, 1996).

VI.5.2.10.3. Combustion in cement factories

The cement manufacturing industry is one of the most energy-consuming industries. Therefore, cement factories aim to reduce the energy expenditure by selecting suitable fuels. Cement is produced in three steps: gaining raw cement flour, burning and grinding. Temperatures of about 1450°C are required for burning. Thus fuels with a high calorific value are necessary, e.g. plastic waste. Since fossil fuels became more and more expensive, other fuels have replaced them as shown in Table VI.5.7.

The ordinance on pollution control (17. BImSchV, "Bundesimmissionsschutz-Verordnung"), previously designed for garbage incineration plants only, also applies to cement factories if they are supplied with plastic waste. Threshold values according to this ordinance are fairly low thus hampering energy recovery from plastic waste in cement

Table VI.5.7. Substitution of traditional fuels in the cement industry 1979, 1991, 1997–1999, in percentage (after Knopf, 1995; Bilhard, 1997; VDZ, 1999).

Fuel	1979	1991	1997	1998	1999
Oil	61	9	2	5	6
Gas	14		2	1	1
Coal	25	75	80	75	70
Substitutes (rubber, plastics)	0	16	16	19	23

factories if no exemption permit is granted. Cement quality is not spoiled as long as the amount of plastic waste added to traditional fuels is limited.

In some cement factories, plastic waste granulate is supplied to rotary furnace kilns as fuel substitute. The particle size of the granulate is about 10 mm. Emissions from plastic waste are comparable to those of traditional fuels. However, the amounts of sulfur dioxide emissions are even less.

VI.5.2.10.4. Co-combustion in coal dust incineration plants

According to the Kreislaufwirtschaftsgesetz (German law on waste, enacted 7.10.1996), co-combustion of plastic waste in coal dust incineration plants is permitted if the calorific value of plastic waste is 11 MJ/kg or more, i.e. 30.3 MJ/kg in fact, and the combustion efficiency is at least 75%. It is not permitted according to the ratio formula for plastic waste recycling. Experiments at a test plant (IVD/University of Stuttgart) have shown that (Christill et al., 1996):

- plastics have to be ground to particle sizes between 2 and 10 mm. Additional costs for this treatment amount to 10–15€/t;
- the portion of plastics added can be up to 10% of the furnace power. This would mean energy recovery of 50,000 t plastics waste for 300 MW plants;
- corrosion of the plant does not increase because of fuels with high chlorine concentrations;
- modification of plants does not require a high investment. Operating costs amount to an additional 100€/t.

The use of fly ash and slag in building and construction industry would have to be evaluated again.

VI.5.2.10.5. Monocombustion in fluid bed kiln (rotating)

Whereas garbage incineration plants have an efficiency of 20% for energy recovery, monocombustion of plastic waste reaches up to 40% efficiency in fluid bed kilns – almost comparable to the efficiency of power stations. Compared to coal, plastic waste has a higher calorific value and higher halogen content. Halogens ought to be extracted first in order to avoid high temperature corrosion of the steam boiler, which would result in a lower proportion being converted to current. To avoid this process without dehalogenation, the maximum temperature of the steam boiler would have to be lowered to 380°C,

thus lowering the proportion converted to current from 38 to 20%, at the same time. Dehalogenation reduces profitability of monocombustion. In Ahlstrom, Finland a fluid bed kiln operated at 200–300€/t rendering this process less competitive compared to other combustion technologies (Martin, 1995).

VI.5.2.11. Deposition

According to the Waste Catalogue, plastic waste may be deposited after being treated. Plastic mud or emulsions must not be deposited.

In 1991, about 1.3 Mt of plastics were deposited at landfill sites (Consultic, Marketing und Industrieberatung GmbH, 1995). In the long run, additives (stabilizers, pigments, softeners) could be washed out due to a change of pH during rotting and microbiological processes. These washouts are not considered harmful to the environment. But since the overall capacity of landfill sites is limited, deposition fees are raised, rendering deposition less profitable compared to recycling techniques.

VI.5.2.12. Economics of recycling and markets for recycled plastics

VI.5.2.12.1. General remarks

The utilization of recycling capacities indicates problems and successes in marketing recycled plastics (Table VI.5.8).

The utilization of capacities is low because prices for raw materials are low and they vary greatly due to fluctuations in the markets where raw materials are traded. Fluctuations in the raw materials market directly affect the market for secondary raw materials. Figure VI.5.8 shows the range of fluctuations for raw materials (PE, PP, PVC) in 1986–1991. A similar instability of the plastic market was also observed from 1995 to 2001 (Fig. VI.5.9).

The costs for treating plastic waste by granulation, washing and melting amount to an average of DM 1.50 (0.75€) per kg (Meimberg, 1995) for all thermoplasts. Therefore, recycling of plastics that are cheaper than DM 1.50 (0.75€) per kg is not profitable. Figure VI.5.10 depicts price relations between new and recycled thermoplasts.

Whether recycled plastics will compete successfully in the market not only depends on the price but also or even more so on quality. The higher the purity, the more the characteristics of recycled plastics will become identical with those of newly manufactured plastics and the more marketable recycled plastics will be.

Table VI.5.8. Utilization of capacities for mechanical and feedstock recycling in 1995 (after Lindner, 1996).

Type of recycling	Utilization of capacities (%)
Mechanical	39
Feedstock	45

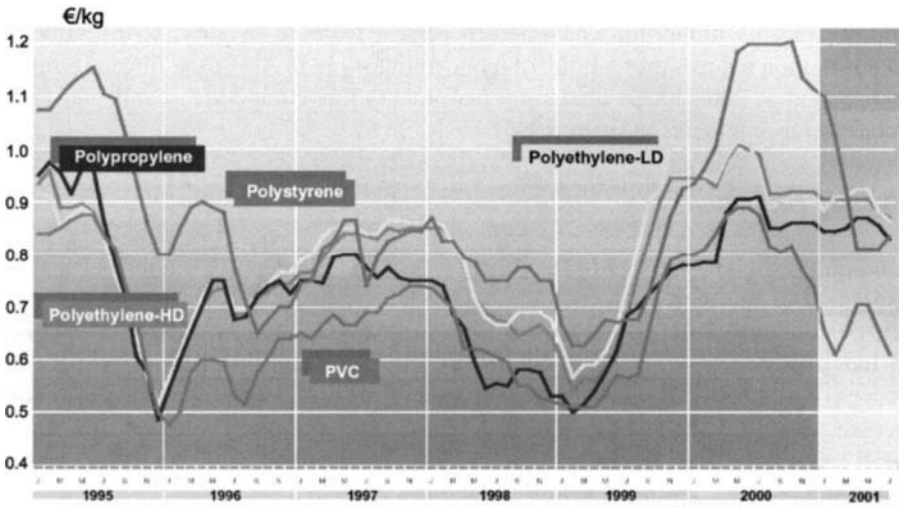


Figure VI.5.8. Price index for PE, PP and PVC 1986–1991 (after Bilitewski et al., 1991) (originally in DM; DM ≈ 0.5€).

VI.5.2.12.1.1. Case study: recycled polyethylene

High-quality recycled PE closely resembles newly manufactured PE. A low price for newly manufactured plastics limits recycling to pure grade PE fraction. During the last decade, recycled plastics were used for applications demanding lower quality standards (Table VI.5.9).

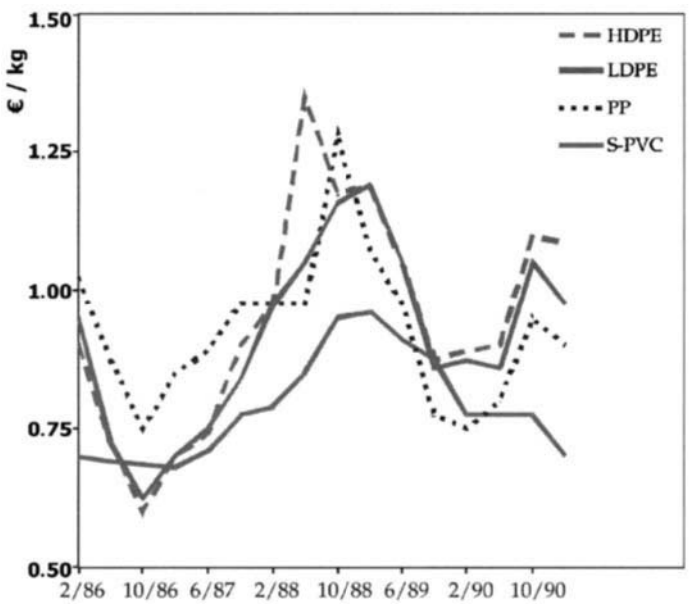


Figure VI.5.9. Price index for PE, PP and PVC 1995–2001 (after VKE, 2002) (originally in DM; DM ≈ 0.5€).

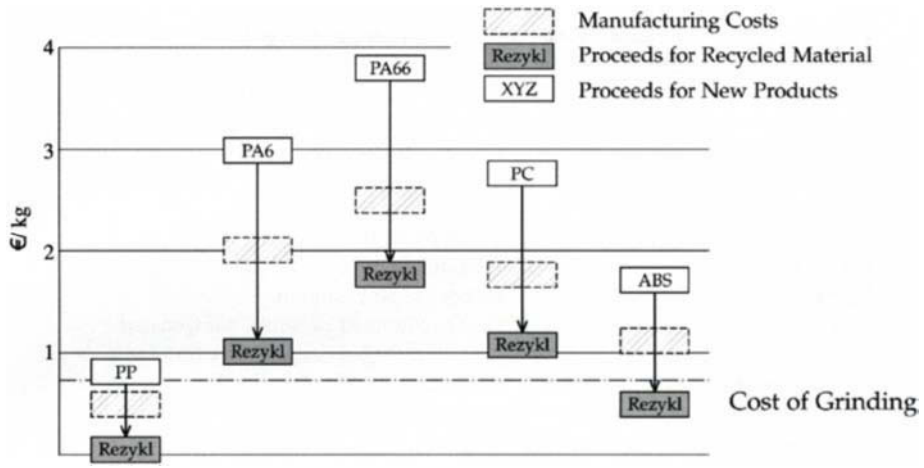


Figure VI.5.10. Proceeds for new and recycled thermoplasts as compared to manufacturing expenditures 1995 (after Meimberg, 1995) (originally in DM; DM ≈ 0.5€).

Another recycling method – coextrusion in hollows manufacturing – is less applied due to reduction of the hollows' weight.

VI.5.2.12.1.2. Influence of additives on the quality of recycled plastics

Plastics are changed by the use of additives to serve different purposes. Additives are mostly composed of halogenated or metallo-organic compounds that are harmful to the environment (Table VI.5.10).

The composition of additives is unknown, for reasons of competitiveness. Therefore, recycled plastics are banned from hygienic applications. Moreover, due to interactions between remaining and newly added additives, the characteristics of recycled plastics cannot be adapted as precise as those of newly manufactured ones. Additives pose a problem in mechanical or feedstock recycling since toxins from additives could contaminate gases.

Table VI.5.9. Application of recycled PE, 1995 (after Hanning and Raddatz, 1995).

Products/use in sector	Tons per year (1995)
Dust bin	5,000
Bottling sector without bottle boxes	10,000
Bottle boxes	35,000
Other	50,000
Sheets	
Bags	
Non-compression-proof pipes	

Table VI.5.10. Toxic contents of additives (after Bilitewski et al., 1991).

Additive	Contents with environmental relevance
Stabilizer	Heavy metals, in particular halogenated lead, cadmium, sulfur, antimony, copper compounds
Lubricant	Heavy metals: lead, zinc
Softener	Chloroparaffin
Fillers and amplifiers	Asbestos
Pigments	Heavy metal: cadmium
Fireproofants	Highly chlorated paraffins, halogenated Antimony 203-synergists, bromine compounds
Flame retardants	Halogens

Granulate from recycled plastics is used for:

- building and construction (forms, isolation, timbering, insulation);
- packaging and transportation (sheets, containers);
- industry (car manufacturers: molds).

VI.5.2.12.2. Mechanical recycling

VI.5.2.12.2.1. Products from injection molding
Injection molding allows a high extent of automation and high throughputs. Due to their fair profitability, products made of mixed plastics compete successfully against traditional materials such as wood or cement. Typical products are forms, tubes, anti-noise sheets, checker bricks or bags (see Table VI.5.15).

VI.5.2.12.3. Feedstock recycling

The basic methods of plastic waste utilization, products generated and potential markets in Germany are shown in Table VI.5.11. If feedstock recycling is preceded by agglomeration a throughput of at least 20,000–30,000 t/year is required to achieve profitability (DKR, 1995).

VI.5.2.12.3.1. Feedstock versus mechanical recycling (DSD et al., 1996)
From the environmental point of view, mechanical recycling should be chosen, if:

1. high purity grades are given;
2. a 100% substitution of primary raw material versus secondary raw material can be achieved.

For mixed plastics, feedstock recycling should be applied according to the following environmental ranking:

1. reduction;
2. thermolysis;
3. gasification.

Table VI.5.11. Feedstock recycling: processing output, products, markets.

Method	Company	Output	Possible products	Markets, reuse in
Hydrogenation	VEBA	Syncrude	Benzene, fuel, diesel fuel	Petrochemistry
		HCl	HCl	Chemical industry
		Bitumen	Asphalt component	Building and construction
Gasification	RWE (Schwarze Pumpe)	Technical gas	e.g. Methanol	Chemical industry
		Cinders	Building material	Building and construction
Thermolysis	BASF	Naphtha	Ethylene, propylene	Plastics industry (PE/PP)
		Technical gas	Various	Chemical industry
		Oil	Methanol	Chemical industry
Use as reducing agent	Steel-factory Bremen	"Reduction"	–	Steel industry

Mechanical and feedstock recyclings are comparable from an economical point of view. The DSD subsidized recycling is given in Table VI.5.12.

Subsidies serve to adapt existing plants to plastic recycling requirements. Subsidy spending will be stopped after amortization of the plants giving way to real pricing. Mechanical recycling is more profitable since it requires less treatment.

Table VI.5.12. Subsidies paid by the DSD for different types of recycling (DSD, 1996).

Operation	Mechanical (€/t)	Feedstock (€/t)
Pre-treatment and sorting	300–400	150–175
Recycling	0	100–250
Proceeds	Variable	Variable
Sum of supplements	300–400	250–425

VI.5.2.12.4. Energy recovery

At present, combustion of plastic waste is forbidden according to the packaging waste ordinance. If the purpose of combustion is any other than inertization, exemption permits can be obtained. Table VI.5.13 shows limitations in thermal treatment of plastic waste.

VI.5.2.12.5. Markets relevant to the various types of plastics

Main materials in plastic waste of different origin are listed in Table VI.5.14.

Table VI.5.15 comprises major products manufactured from recycled plastics.

Table VI.5.13. Legal and economical limitations in thermal treatment of plastic waste.

Combustion in	Legally restricted by	Economics (€/t)	Done?
Garbage incineration plants	Kreislaufwirtschaftsgesetz: energy efficiency	≈150.-	Yes
Cement factories	Requirements 17. BImSchV	≈25.-...125.- (combustion only)	Yes
Coal dust incineration plants	Packaging waste act: quoting	≈125.-	No
Fluid bed kiln (mono)	None	≈200.-...300.-	No

Table VI.5.14. Main materials in plastic waste according to sectors (after VKE and Matthews, 1995).

Origin/sector	Main materials
Farming	PE sheets
Building and construction	PVC, PP, acrylic polymers
End-of-life cars	PE, PP, PA, PVC, polyester resins
Commercials and trades	PE sheets
Domestic waste	PE, PP, PS (DSD)
Conclusion	Most important: PE, PP, PS, PVC

Table VI.5.15. Products manufactured from recycled plastics (DKR, 1995).

Sector	Products
Construction	Waste pipes, drains, sheets, bed plates, curbstones, timbering, insulating materials
Farming	Fences, fixation of river banks, horse-boxes, fish boxes
Commercial products	Bins, bags, coverings
Transportation and traffic	Pallets, noise barriers, side rails, brake pads, landing stages
Home and garden	Flower pots, benches, sand-boxes, composters

VI.5.3. Rubber waste

VI.5.3.1. Rubber

Rubber is produced by vulcanization of caoutchouc, sulfur and other substances. It is mainly used for the production of tires. Table VI.5.16 shows the typical composition of tires.

Table VI.5.16. Typical composition of tires (LENTJES LBL).

Content/characteristics	Unit	Amount
Complete tire		
Carbonization remainders	wt.%	39.0
Calorific value	kJ/kg	30.94
Fe-steel	wt.%	12 (Car-T.)
	wt.%	25 (Lorry-T.)
Rubber part only		
Loss of ignition	wt.%	7.50
C	wt.%	81.00
H	wt.%	6.70
O	wt.%	3.00
N	wt.%	0.30
S	wt.%	1.70
Cl + Br	wt.%	0.15
Cu	wt.%	0.30
Al	wt.%	0.15
Zn	wt.%	1.60
Pb	ppm	70.00
Cd	ppm	8.00

VI.5.3.2. Statistics on rubber waste

In 1994, about 1 Mt of rubber waste had to be recovered or disposed off. Some 400,000 t came from technical products, the remainder being scrapped tires (Gesellschaft für Altgummiverwertungssysteme mbH, 1996). In 2000, this number increased to about 800,000 t/year.

Table VI.5.17 lists the types of tires which are the origin of scrap tires.

VI.5.3.3. Recycling and deposition methods of rubber waste

Rubber waste is unsuitable for deposition at landfill sites because of:

- poor compressibility;
- resilient surfaces;
- extremely long rotting time;
- forming of cavities with air inclusion (scrap tires only).

Therefore, deposition decreases whereas recovery increases as shown in Table VI.5.18 for technical products other than tires.

VI.5.3.3.1. Technical products

See Table VI.5.18.

Table VI.5.17. Origin of scrap tires (after Schmidt-Burr, 1996).

Type of tire	%
Cars	63
Lorries	26
Big tires/full rubber tires	11

VI.5.3.3.2. Scrap tires

Figure VI.5.11 shows the recovery methods and disposal of scrap tires.

VI.5.3.4. Recovery technologies

VI.5.3.4.1. Mechanical recycling

VI.5.3.4.1.1. Remolding

In remolding, the abraised tread is replaced by a new one unless the carcass is damaged. Tires for small vehicles can be remolded once, while tires for larger vehicles can be remolded 3–4 times. During the process, 6 l of crude oil are used, which is one-fifth of the normal quantity required for the production of a new tire (28 l).

The most common process is the retreading by heat. In this process, a new tread and a binding plate are placed. On the carcass, vulcanization takes place at high pressures in a die heated to 160°C.

VI.5.3.4.1.2. Reclaiming

This process works with rubber flour, which is produced from rubber waste through

- cold grinding or
- hot grinding.

Table VI.5.18. Development of deposition and recovery of rubber waste in technical products (Anonymous, 1992/C).

	Amount (1000 t)				
	1990	1993	1995	1997	2000
Thereof deposition	392	400	340	190	–
Thereof utilization	30	45	125	290	500
Granulation	10	15	25	40	50
Depolymerization (e.g. pyrolysis)	–	–	50	200	350
Power stations	–	–	–	–	50
Cement factory	20	30	50	50	50
Total	422	445	465	480	500

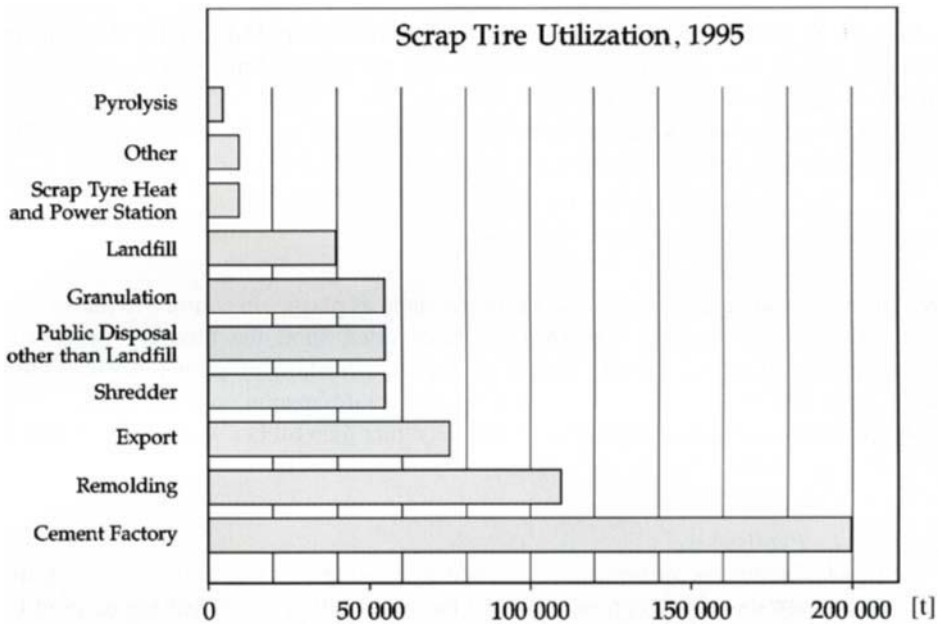


Figure VI.5.11. Utilization and disposal of rubber waste originating from scrap tires (Gesellschaft für Altgummiverwertungssysteme mbH, 1996; Schmidt-Burr, 1996).

Cold grinding process. In this process, rubber waste particles of 100 × 400 mm size are embrittled at −100°C by addition of liquid nitrogen. Rubber flour is produced by stress impact treatment. The expenses will be higher due to the use of liquid nitrogen of about 0.5–1 kg N/kg granulate (EUWID, 1993).

In Germany, there are plants processing 15,000 t of scrap tires per year. Metals are separated with a magnet. Textiles are separated from the rubber by means of a revolving tube.

Hot grinding process. For this process, no liquid nitrogen is required. With the use of two granulators, the rubber waste is fragmented, first at a particle size of 14 mm and after separation of ferrous particles by a magnet, at a particle size between 1 and 6 mm.

Textile parts are separated by air-stream sorting. Compared to the cold grinding process, the treatment described last yields better rubber granulate quality. This process does not require liquid nitrogen and operating expenditures are even less (EUWID, 1993).

As the vulcanization process for rubber waste granulates is not well developed, it will be used for the production of less than 1% by weight of new tires. For this reason, the granulate will be used for construction mats and anti-noise sheets or sporting field surfaces. For these applications, the market for granulate is limited. Another recycling method for granulate is asphalt carpeting. However, substituting the commonly used bitumen with granulate does not make sense from the environmental point of view since bitumen cannot be cracked anymore and there are no appropriate alternative recycling methods for bitumen available (Schmidt-Burr, 1996).

It would be possible to reuse the granulate in the tire industry if the rubber flour quality would be better. This can be achieved by coating the rubber flour with an unsaturated polymer (e.g. polyurethane elastomer).

The tire manufacturer Vredestein considers a percentage of total weight of up to 20% granulates possible without lowering the quality standards, even for high-speed tires.

VI.5.3.4.2. Feedstock recycling

The calorific value of rubber is 31 MJ/kg, or the same as plastic. In contrast to plastics, its composition is well known. Unknown additives often spoil the recovery process of plastics. Recovering technologies aimed at depolymerization of rubber waste require energy input and are therefore unsuitable from the environmental point of view.

Hydrogenation plants are loaded with plastics rather than rubber waste since yield and net profits are higher.

VI.5.3.4.2.1. Pyrolysis

In the pyrolysis process, materials are cracked by heating in vacuum. Even though this process has been developed continuously for more than 20 years, it will not be used for economic reasons.

Pyrolysis yields from 1 t of scrap tires is shown in Table VI.5.19.

VI.5.3.4.2.2. Hydrogenation

Hydrogenation according to the VEBA process requires high pressures of about 250 bar. Therefore, rubber waste has to be liquefied before entering the process. Liquefaction is achieved by heating the rubber waste until elastomer chains will eventually depolymerize to smaller units. Following compression to 250 bar, the liquid material is heated to 480°C in a high-pressure reactor and hydrogen is added. By saturation with hydrogen, the carbon chains are furthermore cracked and at the same time detoxification takes place. In the process, different gases and a synthetic crude oil called "Syncrude" are produced (Table VI.5.20).

Table VI.5.19. Pyrolysis products recovered from 1 t of scrap tires (after Bilitewski et al., 1994).

Output	Amount (kg)
Soot	358
Heavy oil	186
Excess gas	121
Fuel gas	115
Steel	113
Solvents	39
Middle oil	18

Table VI.5.20. Components and characteristics of hydrogenation main product "Syncrude" (VEBA Kohleöl AG, 1996).

Constituent/characteristics	Percentage of weight (wt.%)
Naphthene, paraffin	87
Ethyl benzene	13
Sulfur	<0.05
Heavy metals	0 (crude oil: 3)
Distillability	Unlimited (crude oil: limited)

VI.5.3.4.2.3. Gasification

The main objective of gasification is the production of synthetic gas that can be used in other industrial processes. The rubber waste is mixed with oxygen and steam, at a reaction temperature of about 800°C forming a gas, which contains mostly hydrogen and carbon monoxide. Heavy metals and minerals are melted in the next phase (vitrification), thus forming a slag suitable for construction industries. In the third phase, condensable materials like tar and solid substances are gasified and turned into synthetic gas. Synthetic gas is a universal basis in the chemical industry, e.g. for the production of methanol. The process of high-pressure gasification is applied at the "Sekundärrohstoff-Verwertungszentrum Schwarze Pumpe GmbH"/Berlin.

VI.5.3.4.3. Energy recovery in cement factories

The cement industry is the most important consumer of rubber waste. It uses 236,000 t of scrap tires (26 MJ/kg calorific heat) and 290,000 t of industrial waste (plastic waste, paper, textiles, etc., 22 MJ/kg caloric heat) (VDZ, 1999). Table VI.5.21 shows a comparison of components of traditional fuels and scrap tires.

Table VI.5.21. Comparison of components of traditional fuels and scrap tires for the cement industry (PREAG Continental, 1996).

Contents	Natural gas	Fuel oil		Coal		Tires	
		Light	Heavy	Germany	S. Africa	Whole piece	Cut
C	72.90	86.40	86.30	89.00	82.30	68.00	81.00
H	24.00	13.30	10.80	1.60	5.00	5.60	6.70
O	0.50	–	–	4.00	9.30	2.50	3.00
N	2.60	0.02	–	4.80	1.90	0.25	0.30
S	<0.05	0.15	1.90	1.20	1.20	1.50	1.80
Cl + Br	0.15	–	–	0.17	0.01	0.13	0.15
Energy (kJ/kg)	40.324	42.500	40.500	29.200	25.250	28.800	34.300

In 1999, scrap tires supplied about 6% of the total fuels required (VDZ, 1999). They are fed in whole to the primary entering point of rotary kilns. If sufficient air is provided, complete combustion is achieved without increasing emissions. Sulfur dioxide is absorbed in clinker.

The cost of treatment amounts to about 100€/t rubber waste. For imported coal, the cost is about 80€/t. Therefore, the cement industry charges about 80–130€/t scrap tire to compensate for the difference (Bilhard, 1997).

VI.5.3.5. Markets for rubber waste

The "Gesellschaft für Altgummi-Verwertungssysteme" forecasts an increase in energy recovery from rubber waste, especially in cement factories and scrap tire heat, and power stations (Gesellschaft für Altgummiverwertungssysteme mbH, 1995).

An increased utilization of rubber waste in the production of new tires depends directly on the quality of the vulcanization process. The market share of reconditioned tires is 15% or 110,000 t. Of this number, 68% will be sold by tire dealers, 28% by car dealers, about 8% in gas stations and 4% in supermarkets (Schmidt-Burr, 1996). The quality of reconditioned and new tires is comparable except for high-speed applications (210 km/h or more), where reconditioned tires are not compatible any more.

The markets for insulating and anti-noise sheets are almost saturated.

VI.5.4. End-of-life cars

VI.5.4.1. Legal framework

In June 1993, the German government presented the first draft of an ordinance on end-of-life cars. Substantial issues covered by this draft were:

- the car retailers in the Federal Republic of Germany are held legally and financially responsible for the disposal of end-of-life cars;
- disposed end-of-life cars need to be recycled mechanically;
- new vehicles should be constructed with regard to recycling later on;
- the second draft of this ordinance requires retailers to take end-of-life cars back free of charge. It also stipulates special recycling quotas.

On 21.02.1996, the car manufacturers presented a declaration concerning the removal of end-of-life cars in order to avoid enacting the ordinance second draft. With this declaration, car manufacturers committed themselves to remove for free cars no more than 12 years old through certified recycling companies, to the recycling-oriented construction of new cars, to environmentally compatible disposal of end-of-life cars and to the development and optimization of both material cycles and reprocessing technologies and logistics.

The main objective of the car industry (as stated in the declaration of 21 February, 1996) was the reduction of waste percentage by weight as shown in Table VI.5.22.

Table VI.5.22. Reduction of the percentage of waste by weight according to the Car Manufacturers Declaration of 21 February 1996.

Year	1996	2002	2015
Maximum wt.% of waste	25	15	5

The German Ministry of Environmental Affairs responded by passing a legal regulation, which came into force on 1 April, 1998. The main contents are:

- mandatory registration of each car scrapped;
- specific technical and organizational requirements for construction, technical equipment and operation of buildings such as collection stations, recycling plants and vehicle shredders;
- obligatory annual inspection of the plant by external experts (certification).

The German system has been working satisfactory over the last 4 years. However, some problems still remain.

- Mostly in the first 2 years, a considerable percentage of end-of-life cars were exported to Eastern Europe to circumvent recycling costs. This problem is nowadays partly solved by tighter legal regulations in these countries.
- The external experts used different evaluation standards to certify recycling companies.
- The surveillance by the authorities is not always sufficient: some recycling plants are still operated without permission or certification.

In September 2000, the European Community passed a directive on end-of-life vehicles, which became effective in German law in 2002. The main goals are the following:

- disposal of end-of-life cars free of charge and establishment of a suitable nationwide infrastructure;
- increased recycling rates as compared to the ordinance of 1998;
- prohibition of certain heavy metals in the construction of new cars;
- implementation of comparable and transparent evaluation standards by external experts for the certification of recycling companies.

VI.5.4.1.1. Quantities of end-of-life cars

According to the prognosis of 1991, about 3 million cars would have been disposed each year until the year 2000 (Deutsche Shell, 1991). This estimate was based on the registration statistics, rolling stock and registration of cancels. In 1999, the rolling stock amounted to about 45 million motor vehicles. This number showed an increasing trend as shown in Figure VI.5.12.

The share of cancelled registrations amounts to approximately 6.8%. Thus in 1999, 3.05 million licenses for motor vehicles had been cancelled. In other words: in 1999, 3.05 million motor vehicles were disposed off.

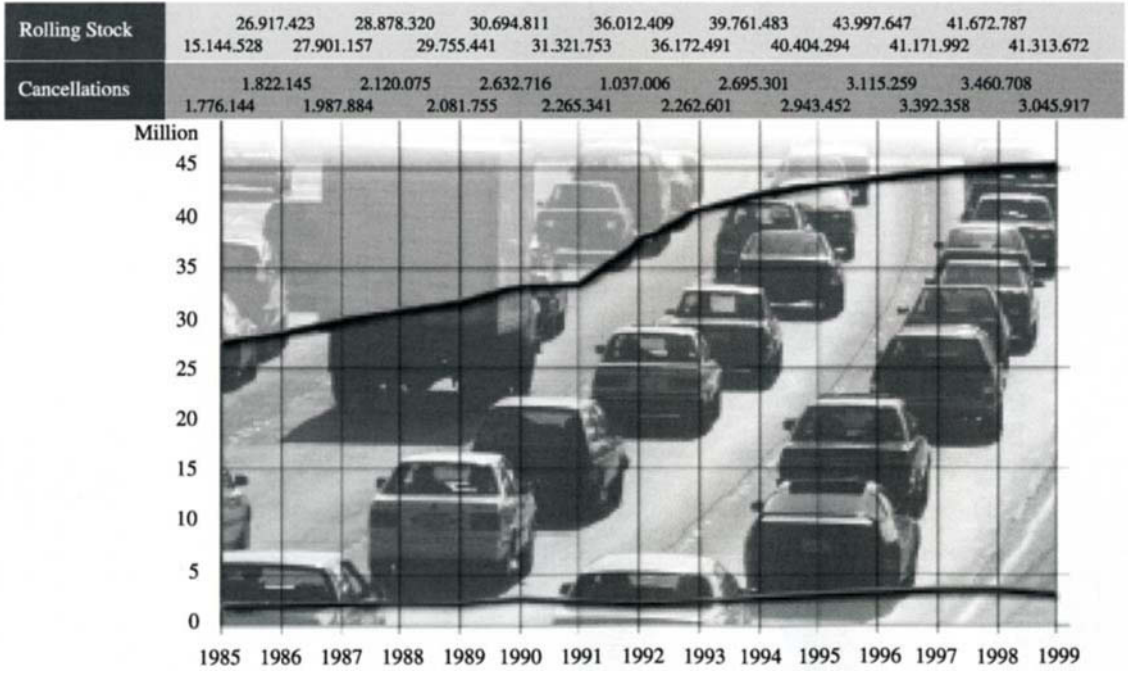


Figure VI.5.12. Rolling stock and cancellations of motor vehicles in the Federal Republic of Germany (after ARGE Altauto, 2000).

Prior to the ordinance of 1998, about 90% of end-of-life cars in Germany was disposed off by either shredding or dismantling and fragmentation. The other 10% was exported. The ADAC, the largest German automobile club, reports that 50% of end-of-life cars will be dismantled before shredding. The latter can be performed at shredding plants, which handle 85% of all disposed cars. The remainder is cut by scrap sheers and compressed in scrap presses (Schmidt, 1993). Today about 1.1–1.7 million (= 36–56% of cancellations) end-of-life cars in Germany are treated first by dismantling and fragmentation in about 1150 licensed recycling plants and, as a second step of treatment, by shredding. The rest will be exported or stolen (ARGE Altauto, 2000).

In 1993, 50 shredding plants handled 1.7 Mt of end-of-life cars (Anonymous, 1993b). Since 1993, a rising demand in shredding plants can be observed, as a shortage of capacity to handle about 200,000 t of end-of-life cars existed. In 2000, 57 licensed shredding plants (41 in Germany, 16 in other countries) were in operation (ARGE Altauto, 2000).

VI.5.4.1.2. Make up of components in end-of-life cars

The make up of the components in end-of-life cars has changed over the last years. The use of plastic instead of metal parts has increased (Table VI.5.23).

The use of plastics has notably increased, as they are not corrosive and are easier to manufacture. The development of highly stress-resistant plastics broadened the field of applications thus allowing the use of plastics in the engine compartment or for primary structures such as doors and fender wings.

Of about 40 different types of plastics used in the car industry (Fig. VI.5.13), the mainly used are given in Table VI.5.24.

As the weight percentage of plastics used in car manufacturing increases, the Automobile Industry League (VDA in German) recommended the identification of parts according to DIN 7728-Part 1, in order to improve recycling feasibility.

Table VI.5.23. Changes in the composition of end-of-life cars (after Härdtle, 1989).

Material	Year of scrapping					
	1980/85		1990/95		2000	
	kg	wt.%	kg	wt.%	kg	wt.%
Steel	560	55.1	535	53.0	465	47.0
Cast iron	142	14.0	126	12.5	109	11.0
NF metals	45	4.5	53	5.2	59	6.0
Rubber	53	5.2	51	5.0	50	5.0
Plastics	45	4.5	91	9.0	158	16.0
Glass	40	3.9	40	4.0	40	4.0
Other	130	12.8	114	11.3	109	11.0
Total	1015	100.0	1010	100.0	990	100.0

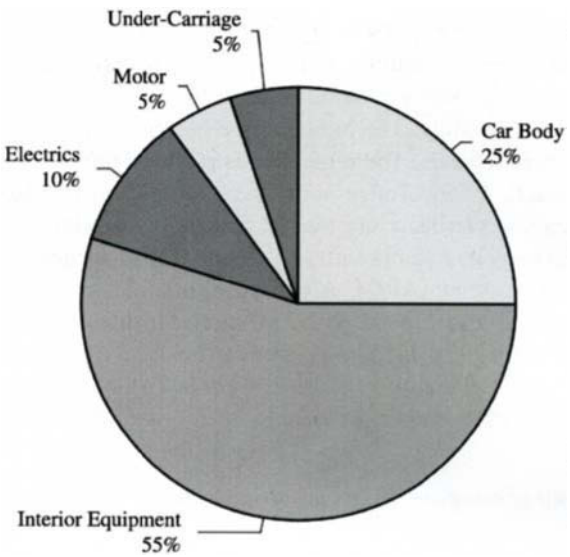


Figure VI.5.13. Use of plastics in motor vehicles: types of plastic (after Schmidt, 1992).

To improve the recycling technologies, the automobile industry developed the software tool "IDIS" (International Dismantling Information System), which contains information regarding materials and dismantling technologies for the most important types of cars. The licensed recycling plants can obtain it free of charge (Fig. VI.5.14).

Besides the above-mentioned solids, end-of-life cars contain operating fluids. Each car contains about 28 l. Because of the risk potential and danger of pollution, they have to be removed before the start of the recycling process. This has been a legal requirement since 1998. A special practical problem is posed by the resilient isolators because of the very small amount of oil and the time needed to tap it.

Table VI.5.24. Use of plastics in motor vehicles: types of plastic (after Schmidt, 1992).

Type of plastic	%	Example
PUR	22	Seats, noise isolation
PVC	23	Sheets, undersealant
ABS, PS	16	Damper, outside mirror
PP	16	Heating
PE	6	Fuel container, radiator
PA	6	Hubcap, paneling
Duroplasts	3	Motor-electrics, isolation
PMMA	2	Rear lamps

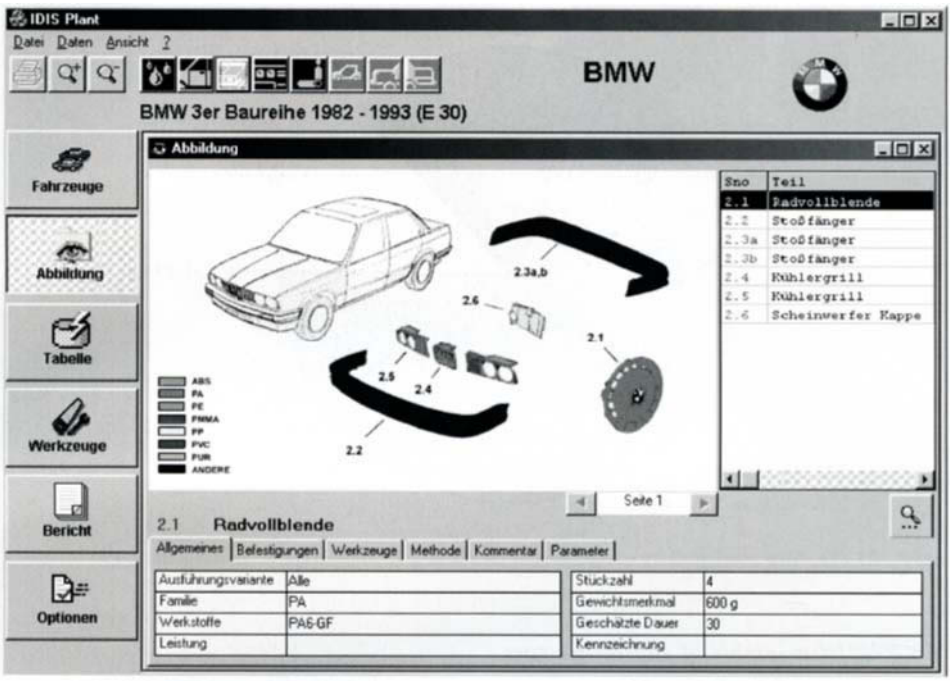


Figure VI.5.14. International Dismantling Information System (IDIS).

Table VI.5.25 shows the type and average quantity of operating fluids remaining in one used car.

In addition, end-of-life cars contain a considerable amount of non-ferrous metals (Fig. VI.5.15).

Table VI.5.25. Type and quantities of operating fluids remaining in an end-of-life car (after Bilitewski, 1992).

Operating fluid	Amount (l)
Fuels	3
Refrigerant	7
Motor oil	4
Washer water	3
Gear oil	2
Grease	1
Brake fluid	0.7
Differential oil	0.5
Total	21.2

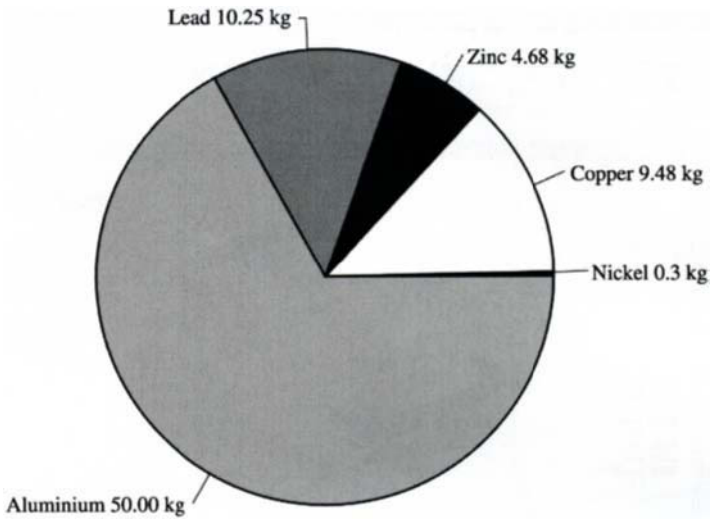


Figure VI.5.15. Share and quantity of non-ferrous metals in a middle-class car (after Schmidt, 1993).

VI.5.4.2. Disassembly of end-of-life cars

The main objective of dismantling end-of-life cars is the separation of the car's constituents into pure grade components. Thus the maximum degree of recycling is achieved. These are the advantages:

- materials and spare parts can be recycled;
- operating fluids can be removed safely during the draining;
- the amount of waste that can spoil the shredding process is reduced;
- deposition of the remaining waste at landfill sites is much easier since it is not contaminated with operating fluids (from 2005 onwards all waste to be disposed of at landfill sites will have to be pretreated thermally);
- the required energy input for shredding is less;
- the quality of the steel scrap is improved.

Figure VI.5.16 shows the main steps of dismantling.

VI.5.4.3. Shredding of end-of-life cars

The objective of shredding is the fragmentation of complete car bodies into particles sized between 50 and 150 mm. In Germany, shredding is mostly carried out using a shredder, which works like a hammer mill-crusher. Materials supplied are torn and ground until the desired particle size is obtained. Then, lighter particles will be separated by air stream sorting. Ferrous metals will be separated by a magnet. The process flow chart is shown in Figure VI.5.17.

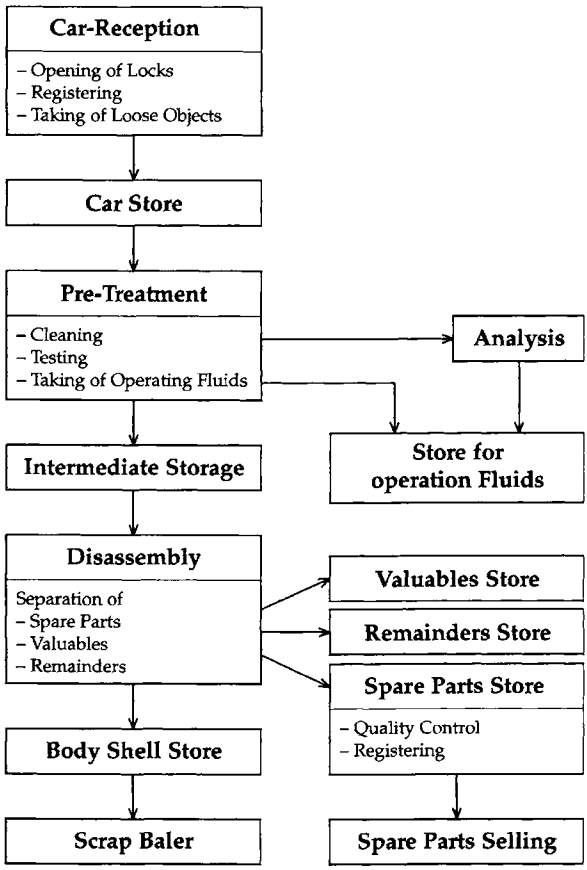


Figure VI.5.16. Dismantling steps in ELV recycling (after Bilitewski et al., 1994).

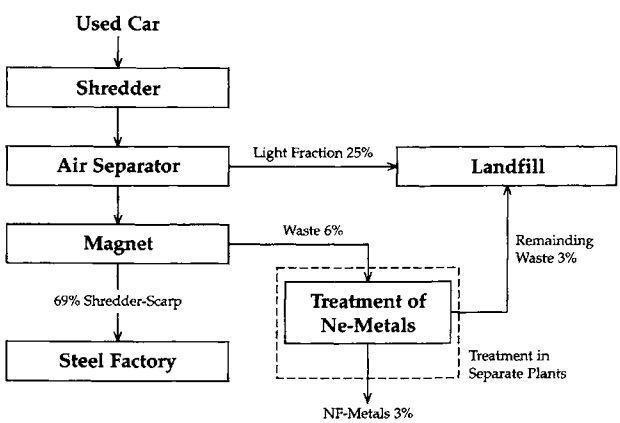


Figure VI.5.17. Flow chart of shredding ELV (after Bilitewski et al., 1994).

Table VI.5.26. Constituents of the heavy fraction (after Oetjen-Dehne and Ries, 1992).

Material	wt.%
Aluminum	41.2
Zinc	28.7
Copper	5.0
Lead	1.8
Other	23.3

After shredding, three fractions remain (weight percentages in parenthesis):

- steel scrap fraction (69%);
- heavy fraction (6%);
- light fraction (25%).

VI.5.4.3.1. Steel scrap fraction (69%)

The steel scrap complies with the requirements of the steel industry. It can be directly used. Of the end-of-life cars, steel scrap (69%) is 96% steel by weight. This presents a fair recycling share.

VI.5.4.3.2. Heavy fraction (6%)

Table VI.5.26 presents the composition of the heavy fraction.

These components can be separated by:

- separation in water;
- dry separation.

VI.5.4.3.2.1. Separation in water

First, all impurities are separated by washing. Second, the remaining ferrous metals are separated with a magnet. Third, in a float-sink process rubber, plastic and magnesium stay at the surface of ferrosilicon froth while non-ferrous metals sink. Through consecutive froth flotation, non-ferrous metals can be further separated. The separation efficiency is 93%. Although operating process waters run in closed circuits, the use of ferrosilicon requires excessive wastewater treatment, which renders this process too expensive in the long run.

VI.5.4.3.2.2. Dry separation

Dry separation is a multilevel process consisting of air-stream sorting and vibrating screens. Materials to be recovered are identified by:

- atomic emission spectroscopy,
- X-ray fluorescence analysis,

which control a sorting device.

Table VI.5.27. Composition of the light fraction (after Goldmann and Fröhlich, 1991).

Waste fraction		Light fraction	
Material	wt.%	Material	wt.%
Aluminum	41.2	Elastomeres (rubber)	23
Zinc	28.7	Cl-free thermoplasts	13
Copper	5.0	Glass, ceramics	13
Lead	1.8	Iron	13
Other	23.3	Fibers, cellulose	10
		Foams (PUR)	7
		PVC	6
		Varnish	3
		Aluminum	3
		Copper	1
		Other	8

Another means is a one-step identification and sorting by Eddy current. Eddy currents induce magnetic fields in non-ferrous metals. Since non-ferrous metals differ in their conductivity, the intensity of the magnetic field induced also differs. Hence a magnetic field of opposite direction allows the separation easily. The break-even point for sorting by Eddy current is 60,000 t/year (Sattler, 1991).

VI.5.4.3.3. Light fraction (25%)

Recycling of the light fraction is still unprofitable. Therefore, the light fraction is normally disposed at landfill sites (Table VI.5.27).

To reach the recycling rates of the European directory, it is necessary to decrease the amount of the light fraction to recover parts of it. A process for the handling of the light fraction has been developed. A pilot plant has been working since April 2000 (Fig. VI.5.18). The fractions are iron/steel, copper of a good quality, a mixture of metals and minerals and an organic fraction, which will be recovered in incineration plants.

VI.5.4.4. Treatment and recovery of remainders

VI.5.4.4.1. Remaining materials

During the dismantling process, the following materials are recovered:

- steel scrap, non-ferrous metals and noble metals;
- high-quality parts;
- plastics and polyurethane foam seats;
- tires;
- glass;
- operating fluids.

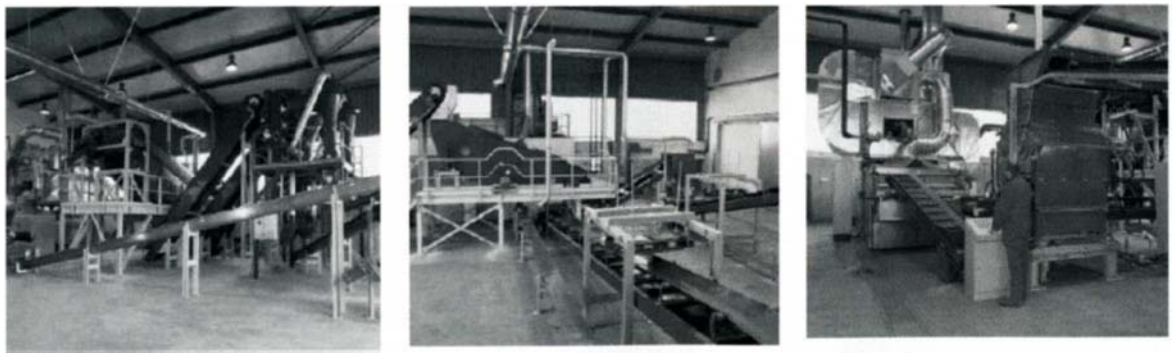
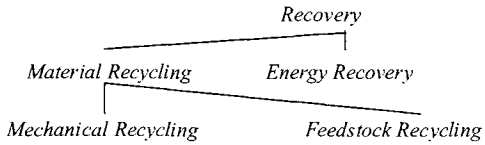


Figure VI.5.18. Pilot plant for the treatment of the shredder light fraction (ARGE Altauto, 2000).

There are several recovering options in principle:



The engines, drive trains and other valuable components can be used again after repairing and reconditioning (mechanical recycling). Plastics can be chemically recycled and reused in similar production processes (feedstock recycling).

VI.5.4.4.2. Steel scrap

The steel scrap will be used for the production of new steel. The more intense the dismantling, especially the separation of main contaminants: copper, nickel, chromium and molybdenum, the better the quality of the steel scrap. According to the Association of Iron and Steel Industries, steel scrap from end-of-life cars is classified type 4 steel-scrap index (Association of Steel Manufacturers, 1997).

VI.5.4.4.3. Non-ferrous metals

The most important components of the heavy fraction – aluminum, zinc and copper – will be 90% recyclable. These materials will be melted in special smelters. They are further used in applications with the same quality requirements as the original material. For example, aluminum will be used as secondary aluminum in the engine compartment. Copper will be reused in cable manufacturing.

VI.5.4.4.4. Precious metals and catalysts

In 1993, the regulations for vehicles emissions were changed radically in Europe. Compliance with regulations can only be achieved by using catalysts. Limited resources of precious metals and the high value of precious metals forced recycling of used catalytic converters in order to recover platinum, palladium and rhodium.

Recovery of these materials is achieved by disassembly of the catalytic ceramic unit, followed by obtaining a ceramic powder with homogenous precious metal quantities through grinding, filtration and mixing and finally by treating the ceramic powder chemically or by applying pyrometallurgy. A share of recovery up to 98% (platinum) or 80% (rhodium) can be achieved without lowering the quality of recovered precious metals (Stoll, 1991).

VI.5.4.4.5. Plastics

Plastics have been exposed to high stress (mechanical and chemical) in end-of-life cars. About 120 kg plastics of poor quality can be recovered per used car (Richter and Lotz, 1996). Plastics account for about 30% of the shredded light fraction. Since recycling does not yet pay off, these plastics are deposited at landfill sites together with other components of the shredded light fraction. Plastics recycling is therefore close to 0%.

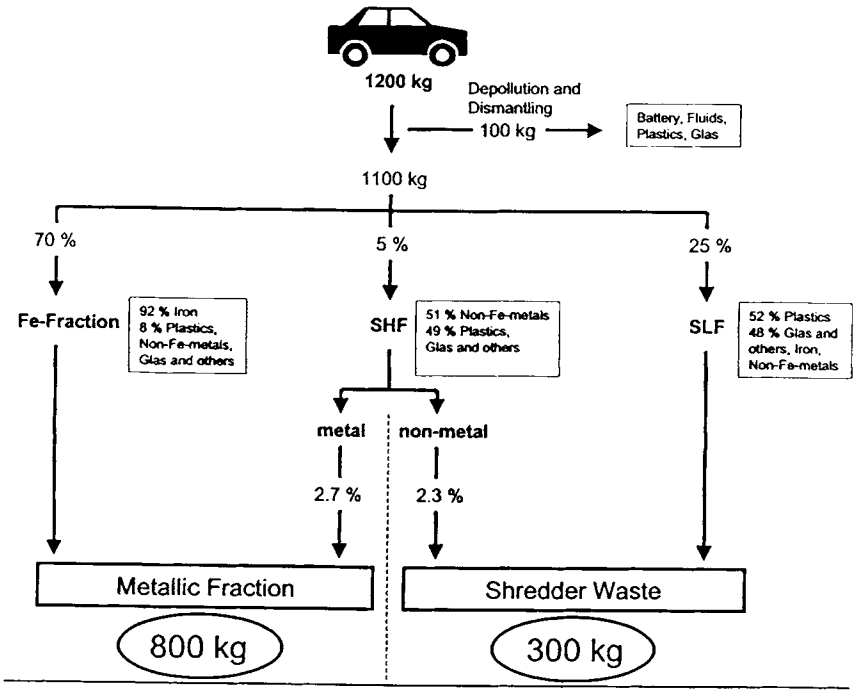


Figure VI.5.19. Material flow in the car shredding process (Lohse et al., 2001).

Although deposition of 120 kg of plastics per used car is negligible considering the total weight, shredding companies can significantly reduce deposition costs if they do not need to make use of deposition. Recycling methods depend on the purity grade of plastics (Fig. VI.5.19).

There are three basic recovery options: energy recovery, mechanical recycling and feedstock recycling. Energy recovery in gasification plants or combined heat and power stations is applied to compounds and bigger parts albeit to a minor extent. PUR-foam seats are burned in power stations replacing up to 20% of traditional fuels (Weigand et al., 1996). Costs are incurred mainly for disassembly and transportation.

Mechanical recycling and feedstock recycling require high purity grades to guarantee compatibility of secondary plastics with primary products. Advanced sorting techniques in order to gain high purity grades are not profitable yet. Figure VI.5.20 explains why.

The working group *End-of-life Cars Recycling of German car manufacturers (PRAVDA)* aims to use recycled plastics as grinding stock additives if the safety requirements allow this. As for mechanical recycling, duroplasts are ground to 2–4 mm particle size and added as filler in the duroplast manufacturing process. For instance, the plastics portions of the former GDR cars "Trabant" have been transformed into insulating sheets and anti-noise sheets using this process.

Plastics recycling is successfully applied to polypropylene shock absorbers. They are easily accessible for dismantling. They are composed completely of polypropylene, which

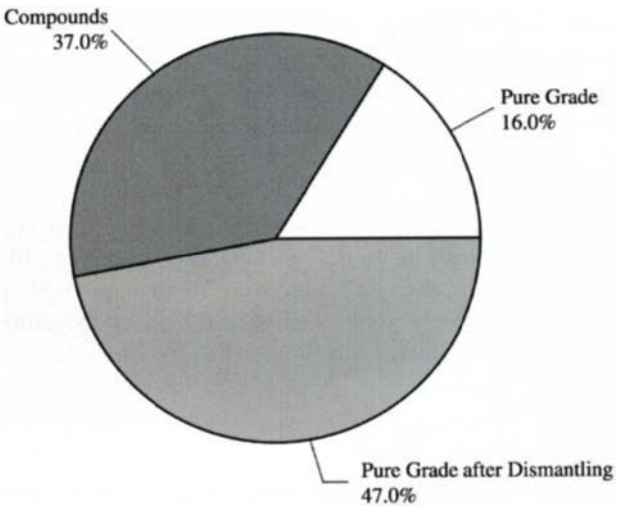


Figure VI.5.20. Purity grade of plastics from ELV after disassembly (after Richter and Lotz, 1996).

complies with high purity demands and only has to be devarnished before grinding. The same characteristics apply to petrol containers.

Nevertheless, recycling of plastics is not economical yet. Therefore, automatic detectors for the separation of the different plastic types are necessary. BMW is developing such a technique.

VI.5.4.4.6. Glass

Every year about 60,000 t of flat glass, from end-of-life cars must be processed (Anonymous, 1991). Each car contains an average of 4% of its weight or 40 kg flat glass. The main portion is deposited as waste. The rest will be used for isolation glass, hollow glass and cast glass. A secondary usage in car manufacturing is impossible due to the high-quality standards. Especially the glass of the windscreen and the side windows cannot be recovered in a common process.

VI.5.4.4.7. Operating fluids

VI.5.4.4.7.1. Oil

Oil from oil changes or operating fluids taken during end-of-life cars disassembly, comply with the requirements for processing as second class refine according to used oil ordinance/category I. Processing and retailing is carried out by the recycling industry and petrol industry.

An important part of the used oil is recovered as a carrier of carbon and is used as energy in blast furnaces in the steel producing industry.

VI.5.4.4.7.2. Fuels

The fuels taken are sometimes contaminated by either solvents or water. In this case, they cannot be recycled and thus have to be disposed off. The main portion of recovered fuel, however, can be used in vehicles of the recycling plant after having been tested.

VI.5.4.4.7.3. Coolant

A few years ago, coolants had to be disposed off in special plants. In recent years, a new process for the recovery of the glycol portion of coolants by means of a film evaporator has become more and more important. Glycol is recovered with up to 99.5% purity. Therefore contracts on delivery of secondary glycol had been signed by recycling companies and coolant manufacturers. Today more than 90% of the coolant is recycled in several specialized plants.

VI.5.4.4.7.4. Brake fluid

Previously, brake fluids were burned in hazardous waste incineration plants. Since 1992, they can be re-esterified in a plant in Schleswig-Holstein, where the boron portion of the glycol ether is separated to distill the glycol ether in a second step. Eventually, the separated boron portion and the distilled pure glycol ether are esterified into brake fluid again. The treatment procedure recovers 95% of the brake fluids' main components (Bilitewski et al., 1994). Nowadays the most important part of the brake fluid is recovered in similar plants.

VI.5.4.4.8. High-quality spare parts from end-of-life cars

Spare parts from end-of-life cars have long been recycled. Especially abrasive parts are exchanged for repaired spare parts from end-of-life cars, e.g.:

- engine, gears, axle;
- starter, generator;
- carburetor, fuel pump;
- radiator, wheels.

Spare part sales are still the most important source of revenue for recycling plants.

VI.5.4.4.9. Batteries

The average life span of batteries is about 5 years. 90% of worn batteries are recycled. First, the sulfuric acid is removed and recycled. Then the battery is crushed in a roller crusher. Ferrous particles are extracted by a magnet, plastics separated by sink-float sorting. The lead portion gained thereby is refined and sold as commercial lead. This technique is both economically and ecologically acceptable.

VI.5.4.4.10. Waste flows in used car recycling

Figure VI.5.21 shows the waste flow in end-of-life cars' recycling (new techniques for the handling of the shredder light fraction are not considered yet).

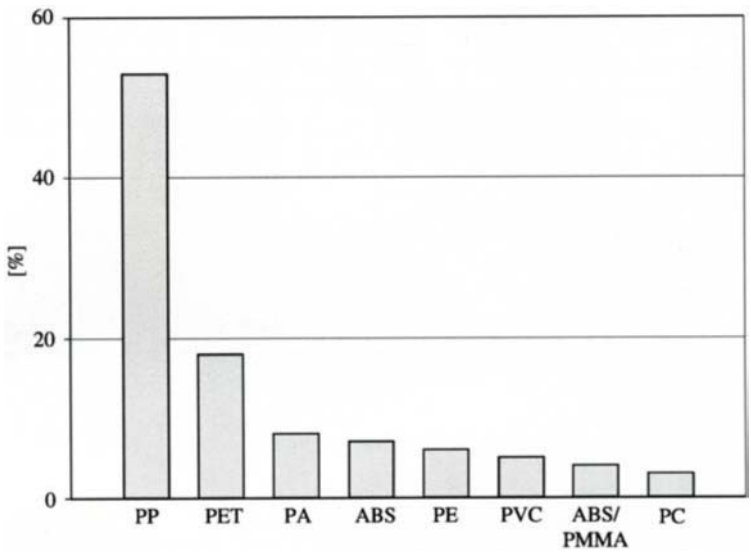


Figure VI.5.21. Distribution of types of plastics in the "high purity grade fraction" (after Richter and Lotz, 1996).

VI.5.4.5. Economics of end-of-life car recycling

VI.5.4.5.1. Basic considerations

The profitability of end-of-life car recycling depends directly on the age of vehicles. The older a spare part or material, the less its value. Usually, a market for recycled spare parts exists as long as the type of vehicle is still manufactured. The size of the market depends on its rolling stock. That does not apply to spare parts limited to a special type of vehicle, for instance, starters or generators. Also technical development accounts for reduced profitability of spare parts recovery and retailing, apart from wear and corrosion.

In theory, profitability could be raised if waste flows are scaled up in a recycling alliance. Nevertheless, high-quality recycling would result in losses up to DM 300–400 (150–200€) per car according to an investigation (ORG-Consult, 1992). Limiting factors are the extent of disassembly and recovery.

Recovery could principally be performed with or without disassembly preceding shredding. For energetic reasons, disassembly became a standard recovery step and a legal requirement as explained in Table VI.5.28.

It can be concluded that through prior disassembly about 2–13 kW h of energy per ton can be saved. Besides the energy saving aspect, removing the light fraction is quite costly, whereas retailing spare parts is considered profitable. Expenditure for light fraction removal is even higher if shredding is not preceded by disassembly, rendering the light fraction much more contaminated (Table VI.5.29).

But to get this system working, economical ways for the recovery of plastics, glass, rubber and other non-metal materials have to be developed and established.

Table VI.5.28. Energy requirements for shredding of end-of-life cars with and without prior disassembly (after Adolph, 1992).

Shredding	Energy demand shredding (kW h/t)	Energy demand processing (kW h/t)	Savings
With prior disassembly	25–28	10–13	
Without prior disassembly	20–23	8–10	
Energy savings if cars are disassembled first	Min. 2	Min. 0	∑Min. = 2
	Max. 8	Max. 5	∑Max. = 13

VI.5.4.5.2. Profitability of end-of-life cars disassembly

Proceeds from the retailing of spare parts are estimated to reach DM 270–300 (135–150€) per car (Schmidt, 1993). Proceeds depend mainly on age and condition of the vehicles. Disassembly time is 180 min on average (Fig. VI.5.22).

The graph also applies to the disassembly of other materials. Figure VI.5.23 shows disassembly expenditures of different recycling companies.

The costs range between DM 250 (125€) and DM 400 (200€) per vehicle. They depend on the vehicle's age and state and the number of end-of-life cars processed.

VI.5.4.5.3. Profitability of shredding

Treatment expenditures for shredding are distributed as shown in Table VI.5.30.

In 1991, shredding expenditures amounted to an average of DM 130 (65€) per ton. Main expenditures and main proceeds in used car recycling are summarized in Table VI.5.31.

VI.5.4.5.4. Steel scrap

Proceeds from steel scrap depend on its quality. The quality is related to the extent of the necessary disassembly, the latter being the most expensive step in end-of-life cars' recycling. This limits the profitability. Interdependencies of steel scrap retailing are shown in Figure VI.5.24.

Profitability was found the best at 60% extent of disassembly (UMBERA, 1992).

Table VI.5.29. PCB loading of shredding waste depending on prior treatment (UBA, 1991).

Shredding	PCB loading, mg/kg of shredding waste
Without prior disassembly	150
With prior disassembly	< 10

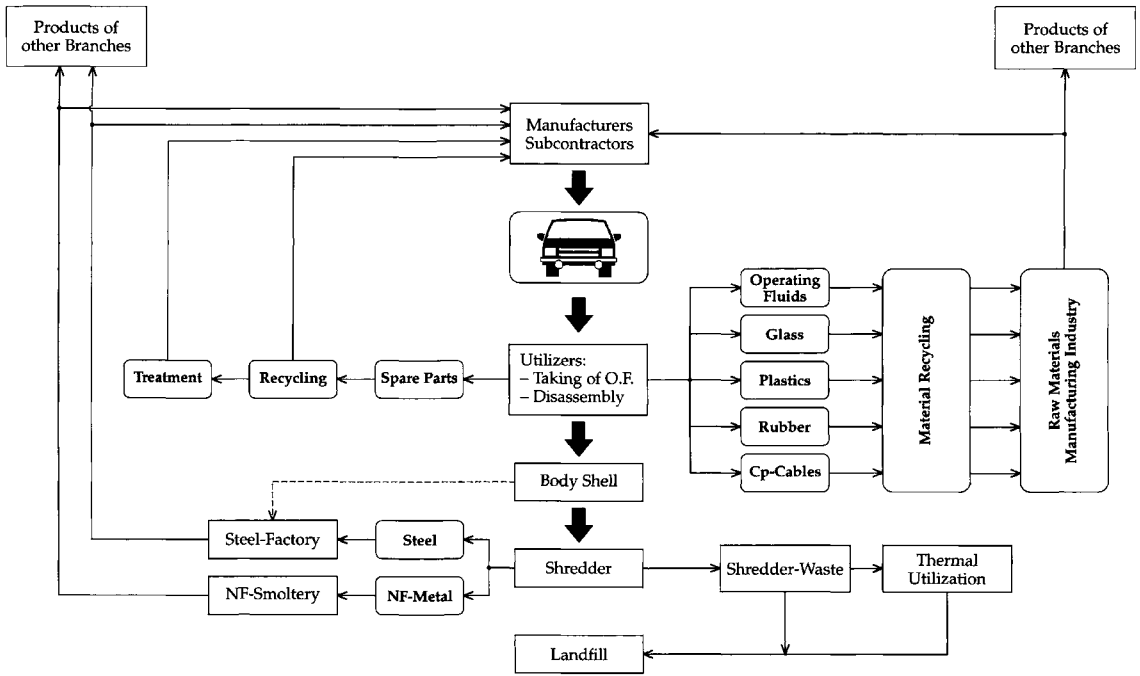


Figure VI.5.22. Waste flow in recycling (after Bilitewski et al., 1994).

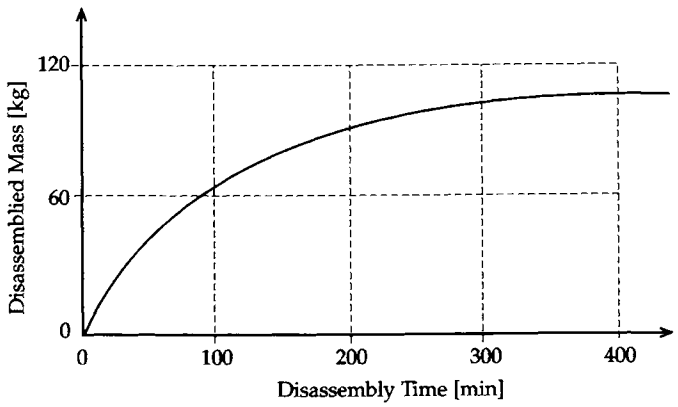


Figure VI.5.23. Correlation between disassembly time and yield (after Richter and Lotz, 1996).

VI.5.4.6. Markets

VI.5.4.6.1. Steel scrap

In 1992, 39.8 Mt of raw steel was manufactured with almost one-third or 12.8 Mt generated from steel scrap. Steel scrap originates from end-of-life cars recycling, demolition waste, incineration plants, steel swarf and sheet scrap (Bundesverband deutscher Stahlunternehmen, 1993) (Fig. VI.5.25).

VI.5.4.6.2. Non-ferrous metals

Aluminum is the most important non-ferrous metal recovered in used car recycling. As the share of aluminum in the car bodies will be increasing and 95% of the energy can be saved in contrast to producing primary aluminum by using secondary aluminum with its low melting point of 660°C, the automobile industry appears to be a promising market.

Table VI.5.30. Distribution of treatment expenditures: shredding (Anonymous, 1992).

Item	Percentage of total expenditure (%)
Disposal of remaining waste	30–40
Plant maintenance	22
Personnel	15
Energy consumption	10
Others	10–23

Table VI.5.31. Main expenditures and main proceeds in end-of-life car recycling.

Process	Main expenditures	Main proceeds	Variable
Disassembly	Personnel	Spare parts	Extent of disassembly
Shredding	Disposal R-waste	Steel scrap	Extent of disassembly → purity
			Separation of NE metals

VI.5.4.6.3. Plastics

See Section VI.5.2.

VI.5.4.6.4. Precious metals from catalytic converters

Precious metals from catalytic converters can be used again in the manufacturing of new catalytic converters. About 0.3 g of rhodium and 1.5 g of platinum are required per catalytic converter. Due to improved emission rules in the European Union, an estimated additional 20 million catalytic converters will be produced.

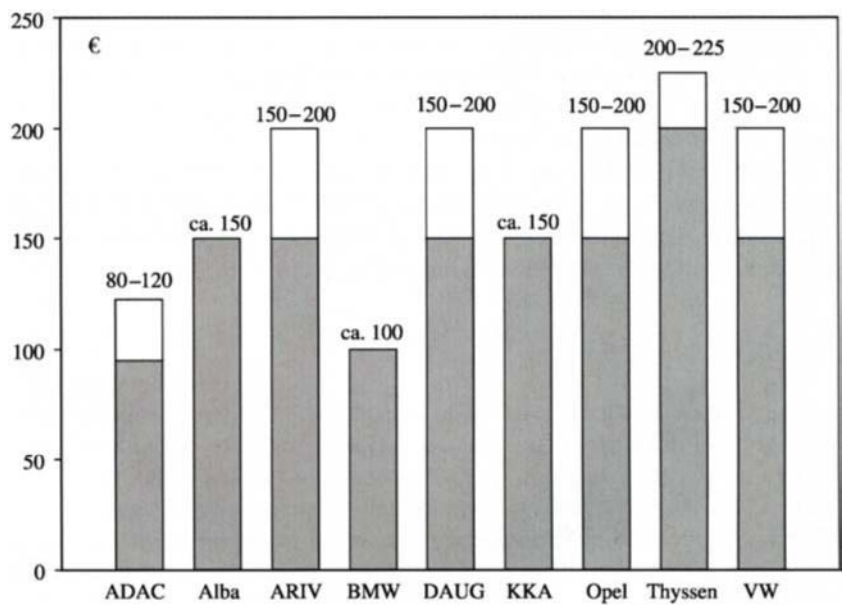


Figure VI.5.24. Main expenditures and main proceeds in end-of-life car recycling (originally in DM; DM ≈ 0.5€).

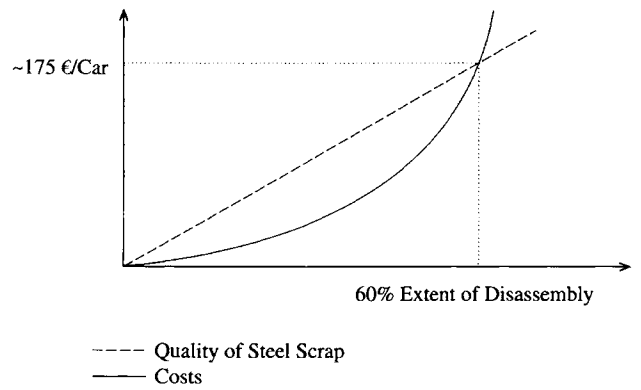


Figure VI.5.25. Profitability of steel scrap recycling related to steel scrap quality and extent of disassembly.

VI.5.4.6.5. Spare parts

In Germany, approximately 250 companies are involved in recondition and retail spare parts from end-of-life cars. The market for spare parts is consolidated.

VI.5.4.6.6. Tires

Remolded tires compete with new tires in the market. They hold a 15% share of the market, which is about 110,000 tires. Of this, 68% will be sold by tire retailers, 28% by car retailers, 8% by gas stations and 4% by supermarkets (Schmidt-Burr, 1996). Retreading requires only 6 l of oil compared to 28 l for new tires. The quality of retread and newly manufactured tires is almost the same except for high-speed applications (210 km/h or more) where retread tires cannot compete.

Used tires are also burned in cement factories in order to recover their energy. There are even special tire power stations in operation. If submitted to material recycling, tires are either applied to feedstock recycling in the petrol industry or to mechanical recycling, yielding rubber granulate in the rubber industry (see Section VI.5.3).

VI.5.4.7. Concluding remark

This brief overview of the current practice and assessment of technical, environmental and economic aspects of the applied recycling technologies for three large and still growing complex streams of consumer waste in Germany shows, on one hand, that one of the targets of the European Community waste management strategy that is complete or partial waste recycling in order to reduce amount of waste to be disposed off and use of raw materials, and, in some cases, to recover energy from waste material through using it as a fuel, might be successfully pursued. On the other hand, these technologies should be economically viable and competitive in the market. For this, further legal and economic structural arrangements are needed, both at the Community and the national level.

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VI.6
High-volume mining waste disposal

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V1.6.1. Introduction

Mining waste disposal permanently brings about a contamination threat to groundwater of unprotected aquifers and surfacewater in dumping sites all over the world. As was shown in Chapter III.6, even a non-hazardous coal mining waste layer of 1.5-m thickness can be a persistent source of deterioration of the aquatic environment lasting for decades. Use of mining waste in civil engineering as fill and earthworks material should thus be considered as a potential source of long-term water contamination.

The mining waste burden and management problems are particularly important due to the high volume of material disposed. According to the Central Statistical Office (2002), the total amount of mining waste (including tailings from preparation plants) generated in 2000 in Poland was as high as 73.6 million tons (Mt), i.e. 59.5% of the total waste generated in the country. Annual generation of hard coal mining waste in 2001 accounted for 38.4 Mt and waste from ore mining, almost entirely tailings, accounted for 29.9 Mt. Current percentage of mining waste use was relatively high and accounted for 91.0% of generated coal mining waste and 75.1% of ore mining and processing. The total amount of hard coal and ore mining and processing waste laying in dumps at the end of 2000 was 1253.5 Mt that was 63.4% of total amount of all wastes disposed throughout the country. Of that, hard coal mining waste comprised 53.3% and metal ore (copper) mining and processing, 46.7%. The area of each dump ranges from about 10 to >200 ha for large central dumping sites where waste from several mines has been disposed. Reused material, predominantly applied at the surface in civil engineering as common fill, e.g. for land leveling, road and embankment construction, is also exposed to the atmospheric conditions. In 1995–1996, only 12.1% of the reused coal mining waste was applied underground in mine workings, while 87.9% was used for engineering construction at the surface (State Inspectorate of the Environmental Protection, 1997). These data clearly illustrate the range of the problem (for data on the global mineral extraction and mining waste generation, see Chapter III.6).

At the stage preceding the design and construction of a dump or earthworks, the reliable evaluation of pollution potential to ground- and surfacewater from waste, as well as

the prognosis of the life-cycle leaching behavior and of impact on the aquatic environment in the area of the prospective waste disposal should be the basis for the dump location permit, rejection or acceptance of a material for civil engineering constructions and protective measures to be applied. In this case, false-positive or false-negative errors in the long-term risk assessment have direct economic or environmental consequences, and thus the evaluation should be carried out particularly carefully.

Concentration of large volumes of mining waste in a relatively small area, the mechanism of pore solution formation in the anthropogenic and natural vadose zone in the disposal site, transport of contaminants from the source to the receiving aquatic environment and the resultant impact on the groundwater of the saturated zone and surfacewater in the vicinity of dumping site within its life cycle have to be considered. In general, risk management approach with respect to sulfidic mining waste is fixed on the acid rock drainage (ARD) formation and control strategies (Hutchinson and Ellison, 1992; Environment Australia, 1997; EPA/DOE, 2000), in order to prevent toxic metal mobilization at low pH. The experience of the authors with coal mining waste (Twardowska, 1981; Szczepańska and Twardowska, 1987, 1999; Twardowska et al., 1988; Twardowska and Szczepańska, 1990) discussed in Chapter III.6 shows that also non-acid leachate from the dump can cause severe degradation of the groundwater quality in the saturated zone just due to the high concentration of chlorides at the first stage of leaching and sulfates in long-term perspective. The sulfate ions are generated from the same process of sulfide oxidation that causes ARD formation and occur in leachate from buffered waste. The sulfate ions are balanced either by the Ca^{2+} and Mg^{2+} cations at the concentration level constrained by equilibrium with gypsum, or by Na^{+} ions. In this case, the TDS concentration is limited entirely by the sulfate generation rate and the vertical redistribution of loads, discussed earlier (see Chapter III.6). Therefore, not only low-buffered acid generating (AG) waste dumps, but also buffered non-acid mining waste disposal sites should not be neglected as a source of groundwater deterioration. It is obvious that ARD poses potentially a very high risk to water quality.

The general best practice principles of risk management from sulfidic waste, including coal and ore mining waste, comprise four major steps: (i) life-cycle prognosis of leaching behavior of waste material exposed to atmospheric conditions for the analyzed variants of the dump or civil engineering construction under consideration; (ii) developing preventive planning, design and disposal operation practices for the waste material, which is adequate to the assessed risk; (iii) dump rehabilitation in operational and post-closure periods; and (iv) life-cycle monitoring of the vadose and saturated zones within the area of the dump or civil engineering construction impact on groundwater quality to provide an early alert for taking remedial actions before significant degradation of recoverable groundwater resources occurs.

In this chapter, a risk management approach to the contamination caused by high-volume mining waste disposal has been exemplified in the current disposal strategies and practices with respect to coal mining waste in the Upper Silesia coal basin (USCB) in Poland. Mine waste management practices in Australia and USA also have been discussed.

V1.6.2. Long-term prognosis of leaching behavior of mining waste and its effect on the aquatic environment

V.1.6.2.1. Site selection and prognosis of leaching behavior

In every case of dumping site selection, and dump construction, an optimization analysis of pollution potential to the aquatic environment should be carried out. The site most advantageous with respect to the aquatic environmental protection requirements is often not in compliance with other optimization parameters, e.g. with the distance from the mine(s) or the system of waste transport. At the preliminary stage, several variants of the site location should be analyzed for selection of the optimum one, being consistent with all economic and technical criteria, but preferring environmental protection requirements of sustainable development.

The extent of hazard from the dump leachate to the aquatic environment should be evaluated on the basis of the long-term prognosis (no less than 25 years). The minimum time period for prognosis depends on the volume and duration of the dump construction, as well as on the occurrence in the planned dumping area of unconfined water resources of particular value. The flow diagram of evaluation is given in Figure VI.6.1. The correct assessment of input data is of a special importance for the accuracy of prognosis. The computer simulation should be thus preceded by the detailed testing of the disposed material properties, short-term and long-term static and geochemical dynamic tests discussed in Chapter III.6, and validated by long-term field experiments (e.g. lysimetric) or studies in existing old disposal sites of the same or similar waste (from the same seams) if such sites already exist. Hydrogeologic, hydrologic and climatic conditions in the planned dumping area are another set of input data for the prognosis of contaminant migration in the groundwater. The input data based on analogy can be used entirely for the preliminary assessment of the dump impact on the aquatic environment. The long-term prognosis of leaching behavior and acid generation potential of waste material, besides being of importance in deciding the dumping site location, also suggests the appropriate management strategy.

The case study exemplified in Environment Australia series (Environment Australia, 1997) as an approach to ARD assessments for new and existing mines along with waste dump planning, presents a similar procedure, with particular regard to ARD generation potential (Fig. VI.6.2). The same source (Environment Australia, 1997) identifies five main rock material types with different management prescriptions: IA, IB, IC — non-acid forming material of low to extreme salinity; II — potentially acid forming material of low risk; III — potentially acid forming material of high risk, based on evaluating net acid generation (NAG). It should be mentioned that such differentiation, though convenient, is somewhat artificial, in particular with respect to the range limits and threshold values.

The recognition of ARD potential as a key issue in the project planning and management in many areas such as mine waste testing procedure, mine planning, designing of tailing storage and waste rock dump (including water treatment facility if needed), reclamation and closure planning, or using waste material for construction was a basis of another similar approach in estimating ARD potential of waste rock by block modeling (Downing and Giroux, 1993; Downing and Madeisky, 1996; Bennett et al., 1997; Bursey et al., 1997; Downing and Giroux, 2000). The authors consider the diversity

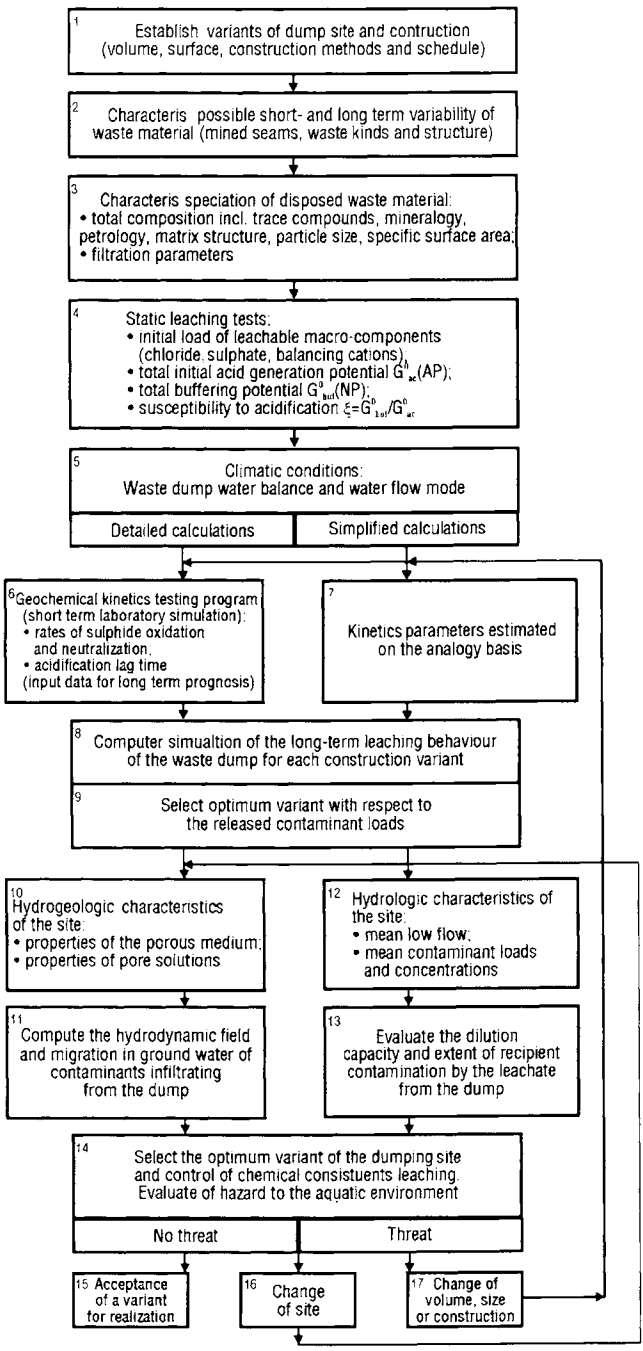


Figure VI.6.1. Flow diagram of a risk assessment to the aquatic environment from the mining waste reuse or disposal, and selecting optimum variant of a dumping site.

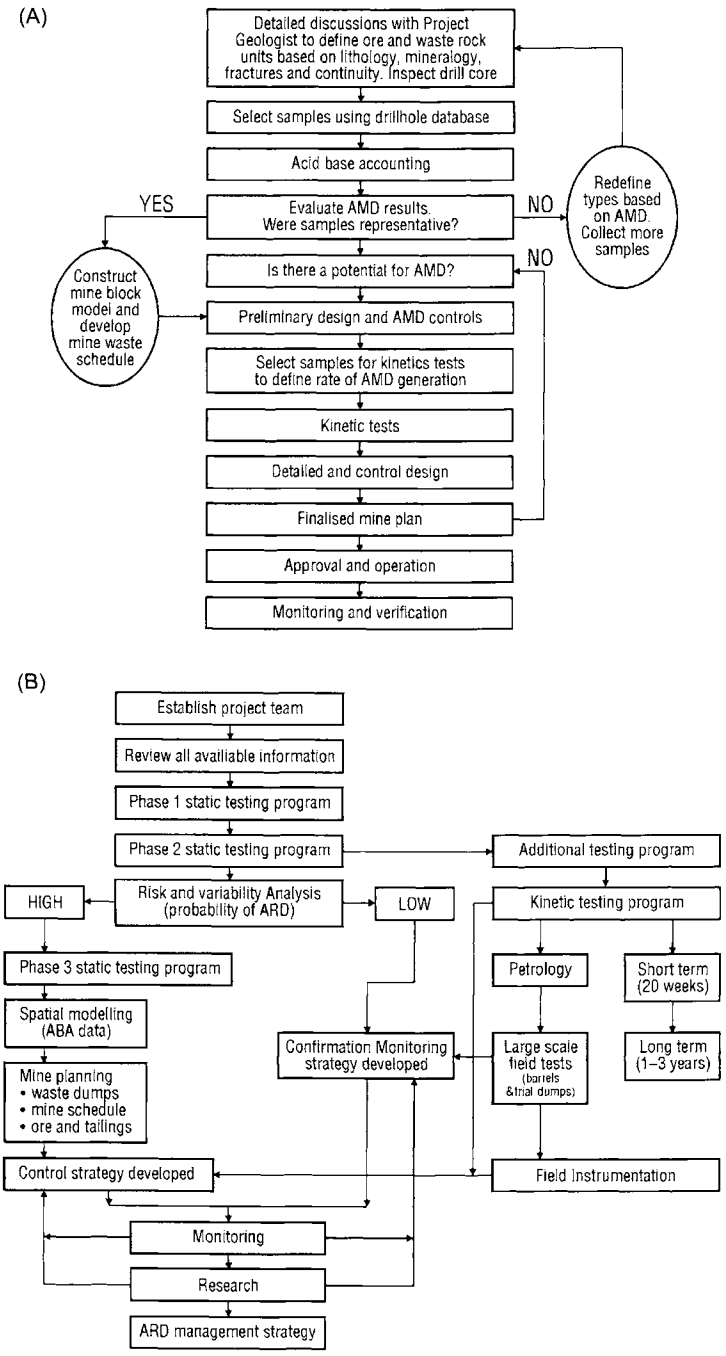


Figure VI.6.2. Approach to AMD/ARD assessments of new (A) and existing (B) mines (Placer Pacific Ltd., after Environment Australia, 1997). AMD is acid mine drainage and ARD, acid rock drainage.

of acidifying/buffering capacity of a heterogeneous rock material within the mined ore deposits and define two major components of the block model estimating the extent of hazard to the environment: (i) the acid generation potential and (ii) the metal and trace metal components of rock material that would impact the metal leaching from acid waste rock (ML/ARD). A waste material has been proposed to be classified (ABA classification) as an integral part of a geostatistical resource estimate study (through drilling in blocks $10 \times 10 \times 10$ m^3) as AG, potentially acid generating (PAG), potentially acid consuming (PAC) or potentially neutral (PN) on the basis of a ratio Ca–Mg carbonates/total sulfur = neutralization potential/maximum potential acidity (NP/MPA). The criteria of classification were given as follows:

- PAG: NP/MPA ≤ 1.0
- PN: $1.0 >$ NP/MPA < 3.0
- PAC: NP/MPA ≥ 3.0

This classification corresponds with the criteria of evaluating acidification/buffering capacity presented in Chapter III.6 and is an attempt of its practical application on site, as it is presented in Figure VI.6.3.

ARD-generating waste material from ore mining (PAG) produces hazardous metal-rich acid leachate; though it does not imply that mine rock classified as PN or PAC is environmentally neutral.

For high-volume dumping sites active for many years before site closure and capping, and in deep mining regions often sited in subsidence-affected areas, the construction period is particularly critical and environmentally problematic. The general approach is to evaluate the risk to the aquatic environment from the waste dump as a result of: (i) geochemical characteristics of material implying contaminant generation and release rates (primary contaminant load, sulfide oxidation kinetics, equilibria constraints); (ii) dump construction, volume, development in time determining the total potential load of contaminants and its temporal and spatial distribution; and (iii) hydrogeological and hydrological conditions, which determine the ability of the vadose zone to attenuate or increase contamination and of recipients (ground- and surfacewater) to dilute the contaminants load to the environmentally acceptable level. As has been shown in Chapter III.6, not only ARD, but also leachate from buffered waste material can create a substantial problem for groundwater and make it unfit for any use for a period of decades.

VI.6.2.2. Models for long-term prognosis of contaminant leaching and transport

Long-term impact assessment of mining waste disposal sites and engineering constructions on the aquatic environment constitutes a basis for the step-by-step approach to the decisions concerning optimum dump location and construction, as well as preventive or remedial measures for control of contaminant leaching from new and old dumping sites and engineering constructions. For this purpose, the software packages have to be composed of two major integrated parts: (i) a model for hydrogeochemical calculations of generation, leaching and transport of species within the waste dump and (ii) a model of water flow and contaminant transport in

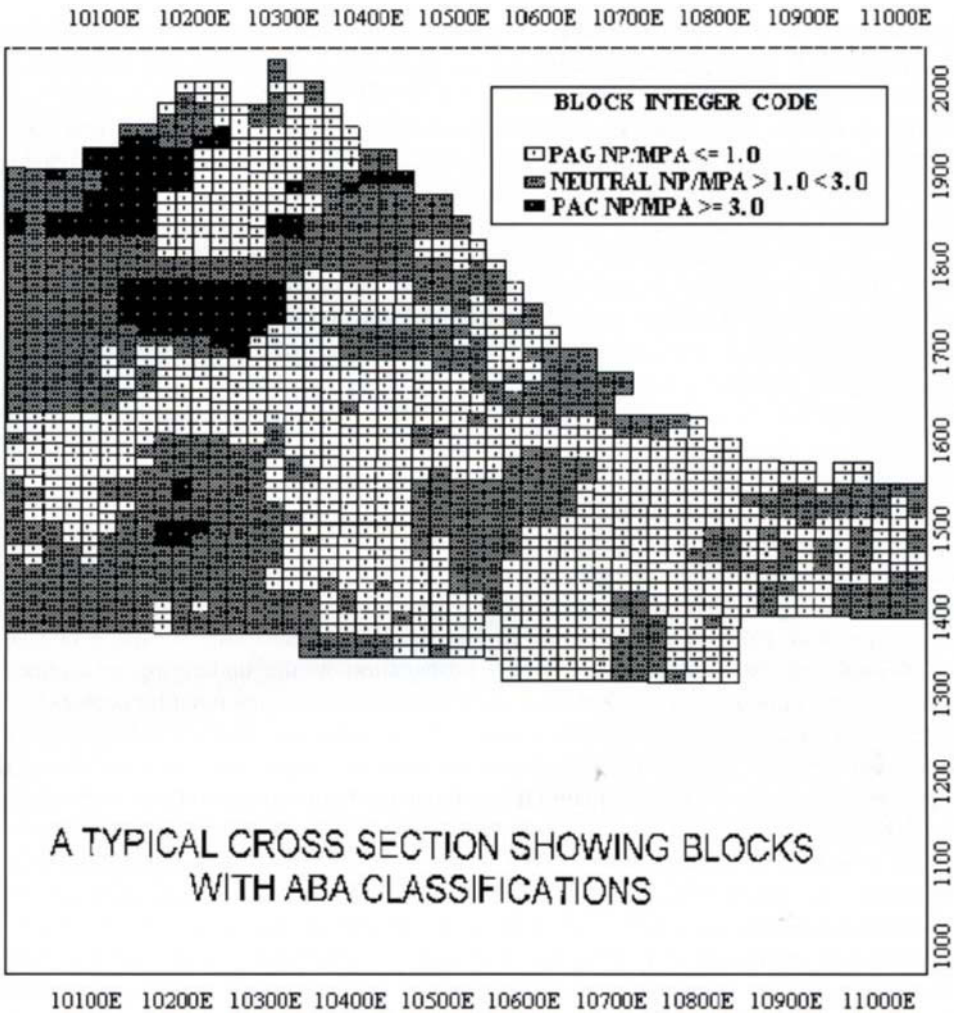


Figure VI.6.3. Example level plan showing blocks with ABA classification (after Downing and Giroux, 2000). AG is acid generating rock; PAG, potentially acid generating rock; PAC, potentially acid consuming rock; and PN, potentially neutral rock.

groundwater in the waste dump site, and eventually also in the receiving surfacewater. The local groundwater quality monitoring (LGQM) database for existing dumping sites of waste from the same mines and seams may be helpful for the prognosis and input data *in situ* verification.

Input data should include: (i) mining waste characterization related to the initial content, generation and leaching of soluble constituents; (ii) waste disposal site construction and its temporal and spatial development (consecutive waste layers formation program); and (iii) hydrologic, hydrogeological and meteorological data for the waste

disposal area. In the prognosis, both macro-constituents of importance (chloride, sulfate, TDS), as well as ARD and mobilizable trace elements that may cause quality degradation of receiving waters should be considered.

The up-to-date developments in numerical modeling of hydrogeochemical reactions, contaminant transport in saturated–unsaturated media, and groundwater flow provide a number of sophisticated software packages that give an opportunity of a reliable long-term prognosis in accordance with the above scheme (SSG, 2003; Waterloo Hydrogeologic, 2003). The HYDROGEOCHEM 2 coupled model of HYDROlogic transport and GEOCHEMical reactions in saturated–unsaturated media, which contains two basic modules: the transport module and the geochemical reaction module, is particularly well suited for simulating processes of species generation, release and transport within the mine waste dump as an anthropogenic vadose zone, natural vadose zone and in saturated zone. For groundwater flow and contaminant transport modeling, several other effective software programs can be used, depending upon the complexity of the hydrogeological conditions and transport problems, e.g. from easy-to-use KYSPILL 2.0 (Anonymous, 1997; Serrano, 1997) tested by American Institute of Hydrology or FLONET/TRANS (Waterloo Hydrogeologic, 2003), through MODFLOW-SURFACT and 3DFEMFAT software packages to GMS 4.0 (Anonymous, 1999; SSG, 2003, Waterloo Hydrogeologic, 2003). Of the mentioned software KYSPILL (Anonymous, 1997; Serrano, 1997) is the scale-dependent groundwater pollution model capable of predicting 3D dispersion of contaminants in the vadose zone and 2D propagation in the underlying unconfined heterogeneous aquifers. It considers both point and non-point contamination sources and reactive or degradable contaminants, and is applicable for dump leachates as a contaminant source. Due to simplicity, it has serious limitations, e.g. does not consider continuous input of a contaminant from non-point sources, or multi-component transport. FLONET/TRANS is a 2D finite-element groundwater flow and contaminant transport model, which allows prediction of contaminant plume migration from waste dumps, by simulation of steady-state flow and time-varying transport in leaky, confined, or unconfined aquifers with heterogeneous and anisotropic properties. MODFLOW-SURFACT is the upgraded version of a widely used MODFLOW program (McDonald and Harbaugh, 1999) with the modeling capability of vadose and fully and variably saturated zone flow, and multiphase multi-component contaminant transport. It considers seepage and delayed yield conditions, parent and transformation product transport modeling, as well as linear or non-linear retardation for each species, and thus allows correct long-term flow and contaminant transport prediction from new and old dumping sites. 3DFEMFAT is a 3D finite-element model of flow and transport through saturated–unsaturated, heterogeneous and anisotropic media. This model can use a very large time step, and among other capabilities, considers spatially and temporally dependent element and point sources/sinks, a prescribed initial condition or the simulated steady-state solution as the initial condition, as well as iteratively determined infiltration, seepage, and/or evaporation boundaries, which is advantageous for application to seepage from mining waste dumps. Of these packages, groundwater modeling system (GMS) and its latest version 4.0 is the most sophisticated and comprehensive groundwater modeling environment (Anonymous, 1999; SSG, 2003). GMS supports several finite-difference and finite-element packages in 2D and 3D that provide site characterization, simulate flow and contaminant transport in saturated and unsaturated zones, bioremediation and natural

attenuation and include MODFLOW, MODPATH, MT3DMS/RT3D, SEEP2D, SEAM3D (Widdowson, 2002), UTCHEM and FEMWATER. MODFLOW 2000 — the U.S. Geological Survey modular groundwater model support in GMS 4.0 is the latest and the most advanced MODFLOW version that includes the new HUF, LPF and ADV packages (Harbaugh et al., 2000; Hill et al., 2000; Clement, 2001; Mehl and Hill, 2001; Zheng et al., 2001). Due to complexity, GMS modeling system has the tools for a variety of modeling needs: the predictive analysis of mining waste dump environmental impact is one of them.

There are a number of other software packages that can be applied for predicting groundwater flow and contaminant transport from dumping sites. They have specific capabilities, e.g. Visual HELP (based on the U.S. EPA's Hydrologic Evaluation of Landfill Performance, 1984) for modeling landfill hydrology, estimating groundwater recharge rates and determining the effectiveness of capping; AquaChem package for geochemical modeling and managing water quality data with use of PHREEQC, or CVFlux 2D and ChemFlux 2D packages that are widely used for predicting the movement of contaminants from tailings, pits and earth containment facilities. Of these models, PHREEQC — a computer program for speciation, reaction-path, advective transport, and inverse geochemical calculations (Parkhurst, 1995; Charlton et al., 1997; Vrabel and Glynn, 1998; Parkhurst and Appelo, 1999; Charlton and Parkhurst, 2002; Merkel and Planer-Friedrich, 2002; Zhu and Anderson, 2002) in particular the latest version PHREEQC Interactive 2.8.0.0 (2003) is the most applicable for geochemical calculations involving reactions and contaminant transport occurring in sulfidic waste (Parkhurst, 1997; Appelo et al., 1998). The correct prediction of contaminant generation and transport with use of even the most sophisticated models highly depends upon the reliability of input data. In the case of coarse heterogeneous sulfidic waste, the critical parameters include, besides total sulfur and total carbonate contents, also spatially, vertically and temporally influenced kinetics of sulfide oxidation and availability of buffering agents under actual conditions of their exposure. The assessment of these parameters is generally particularly problematic, as laboratory exposure conditions differ substantially from those in the real field conditions.

Surfacewater quality is less impacted from mining waste dumping sites than the shallow unconfined aquifers. Nevertheless, environmental impact assessment (EIA) requirements consider evaluation of contamination threat also for surfacewater recharged by groundwater or directly from dumping site drainage system. For this purpose, several surfacewater flow and contaminant transport models might be used, e.g. GFlow 2000, flow model and solute transport system in saturated zone that supports also conjunctive surfacewater and groundwater modeling or AQUASEA upgraded software package, which consists of the hydrodynamic flow model that can simulate water level variations and flows, and the transport–dispersion model that simulates the spreading of a pollutant of any kind under the influence of the flow and existing dispersion processes (SSG, 2003; Waterloo Hydrogeologic, 2003).

The contaminant transport modeling and application of computer models for a regional prediction of the contaminants transport from the non-point source or waste disposal site in soils and groundwater has also been discussed in Chapter V and is exemplified in the case study presented in Chapter V.4.

V1.6.3. The basic tasks of mining waste dumps rehabilitation

Under the actual conditions of the thickly populated mining areas such as the USCB in Poland, the rehabilitation of mining waste dumps is a task of a particular importance. According to the definition, these tasks should be realized through the technical, agrotechnical and biological actions enabling economical and environmental restoration of the degraded areas. These measures comprise the land reshaping, dump sealing, improvement of soil properties, regulation of water balance, and installation of a monitoring network in the site area (Directive of the Minister of Environment, 2002). Polish Environment Protection Act (2001) with regard to land surface protection defines rehabilitation tasks as the optimum landscape reshaping, restoration of quality parameters of soil according to the standards and economical reuse of the derelict land. Due to the limited availability of land for locating dumps, and technical and economical limitations of waste reuse for stowing in mine workings, the requirement of land surface rehabilitation should not be treated as an exact restoration of the primary landscape and area use, but as an optimum solution, which ensures also the maximum volume of waste to be disposed in the site. In general, in the USCB conditions, it means the construction of high flat waste dumps, as a temporary (so called "forestall reclamation" in the subsidence area) or final solution. This means, in fact, the creation of a new landscape, which should fulfill the following prerequisites:

1. Life-cycle environment pollution control during dump construction and after site closure.
2. Maximum disposal volume, under the prerequisite (1).
3. Acceptable landscape planning, under the prerequisites (1), (2) and (4).
4. Optimum economic reuse of a site, under the prerequisite (1)–(3).

In general, the first two prerequisites are of superior significance, while the other two are of a subordinate weight. Independent of the gradation, all these prerequisites should be unconditionally fulfilled, though the first two (environmental protection and maximum volume) dictate the solutions for landscape planning and land use. The applied methods of biological reclamation should constitute an integral part of tasks (3) and (4), provided that the major prerequisite (1) is fulfilled. Rehabilitation of the dumping site should start from the land preparation for dumping and be continued until the dump construction is completed, finally shaped and adequately used. Rehabilitation actions should be conducted in parallel with the dump construction as temporary (transitional) and final measures.

V1.6.4. Aquatic environment protection strategies in mining waste dumping sites

V1.6.4.1. General assumptions

The availability of areas suitable for dump location due to the favorable hydrogeological conditions is generally extremely limited. Mining waste dumps are invariably located on land that is considered to have little or no value for other use, such as abandoned sand and gravel pits, areas of continuous surface deformations due to subsidence caused by

underground mining, etc. These areas usually have a disturbed vadose zone and stripped soil layer that could have played the role of a protective barrier. They are therefore susceptible to groundwater contamination. A number of old dumps of a high long-term pollution potential are sited over unconfined aquifers being a valuable resource of drinking water, or along the river beds.

A high volume of sulfidic mining waste output implies the need to search for cost-effective and efficient control strategies for minimizing generation, release and discharge of contaminant loads to the aquatic environment. The most efficient and practicable way of reducing a potential risk is the prevention of atmospheric oxygen and water penetration through the waste layer, in order to:

- control sulfide oxidation, acid generation and trace metal release occurring in wastes and in the dump bedrock;
- reduce the waste volume exposed to leaching;
- increase the buffering capacity of low-buffered AG material.

The above control measures can be achieved by the appropriate construction of a dump (Twardowska et al., 1988; Twardowska, 1990, 1993; Szczepańska and Twardowska, 1999). The waste disposal strategy presented here is based mainly on the authors' experience and solutions applied in dumping sites of coal mining waste in the USCB in Poland that are not considered hazardous (2000/532/EC; 2001/118/EC). The discussion also comprises the review of management and disposal strategies for ARD generating wastes from the mineral industry (coal, uranium, base metal and precious metal projects) in Australia (Environment Australia, 1997) and in the USA.

The general principle to be followed in the mining waste disposal practice is a site-specific approach to each waste disposal site, resulting from significant differences and variability of waste rock properties, site characteristics, dump development, volume, construction period, geology, petrology, hydrogeology, hydrology and climate, in spite of the similarities in the basic mechanisms of pollutant generation and release (see Chapter III.6).

V1.6.4.2. Dump construction

V1.6.4.2.1. Minimization of the exposed surface

The dump final shape and the construction period should ensure minimization of its exposed surface, which determines the amount of infiltration water and waste rock in the uppermost layer where processes of contaminants generation and leaching are the most active. This requirement may be met by the construction of high dumps in layers of a terrace form, which provides the lowest surface area: dump volume ratio, the best utilization of a site for collection of the maximum volume of wastes and reduction of water precipitation infiltrating to the dump. To constrain side air penetration and enable fast rehabilitation and biological reclamation of the construction, the dump external batters and terraces should be formed first, in heavily compacted thin layers (~ 0.5 m) and shaped according to the final designed form and slope. Next, the internal parts of the dump should be filled in thicker compacted layers (up to 6 m) in sections, up to the final level, adequately constructed to prevent or reduce infiltration of precipitation water.

VI.6.4.2.2. Reduction of waste contact with infiltration water and controlled water discharge from the dump

This may be accomplished by: (i) application of a surface or shallow sub-surface drainage system at the top and terraces of the dump, placed at the low-permeable base layer of low hydraulic conductivity ($k < 10^{-10}$ m/s) and (ii) the double surface drainage ditches at the dump toe for separate uptake and discharge of unpolluted water from the adjacent catchment area and leachate/drainage/run-off water from the dump (Fig. VI.6.4).

Sub-surface drainage of the dump prevents the vertical percolation of atmospheric precipitation through the dump and limits the infiltration entirely to the top cover layer. The bulk of the disposed waste will be thus eliminated from the process of contaminant leaching, which greatly reduces the pollution potential from the dump. During the dump construction, temporary open drainage ditches should be applied at the top of every intermediate layer.

The double system of surface ditches at the dump toe eliminates the contact of natural water from adjacent area with effluents from the dump and the direct contact with the disposed wastes. This reduces the volume of polluted water and provides discharge of natural waters to the nearest recipient, while polluted water, through the retention pond, can be periodically discharged to the collector of saline waters, to the closed circle of a washery or in portions to the recipient receiving water body during the period of high water flow if these waters contain no hazardous constituents in concentrations exceeding maximum concentration limit (MCL). Hazardous ARD should be up taken and treated before discharge to the receiving waters.

VI.6.4.2.3. Rendering the dump air- and water-tight

Restriction of air penetration prevents sulfide oxidation that causes generation of ARD and mobilization of pollutants from the waste rock. Reduction of water infiltration, besides control of sulfide oxidation, attenuates contaminant leaching from the dump. The top and slope protection against erosion is also of importance.

This can be achieved by the construction of the external dump batters and the internal part of the dump in compacted layers of different thickness and application of the air-tight material with high water retention capacity at the top of each internal layer (Figs. VI.6.5 and VI.6.6). Such properties have some fine-grained tailings from washeries and dense coal combustion fly ash (FA): water mixture. The dense FA: mine water mixture displays the greatest penetration resistance to air ($R = 1100-1200$ kPa/cm^2), about an order of magnitude higher than natural cohesive soils, and high residual water retention capacity, though its hydraulic conductivity is rather high ($k > 10^{-6}-10^{-8}$ m/s), within the range of non-insulating or very weakly insulating material (see Chapters III.7 and VI.8). Some fine-grained argillaceous tailings show better barrier properties with respect to water, within the range of medium permeable material ($k < 10^{-8}$ m/s). Significantly lower permeability of tailings to water and adequate buffering capacity of alkaline FA with respect to potential ARD leachate from the overlaid layers are the additional protective factors that can be utilized for rendering the mining waste dump air- and water-tight. For optimum use, the blanket layers of dense FA: mine water mixture can be placed on the intermediate internal layers of sulfidic mining waste to control ARD, while argillaceous

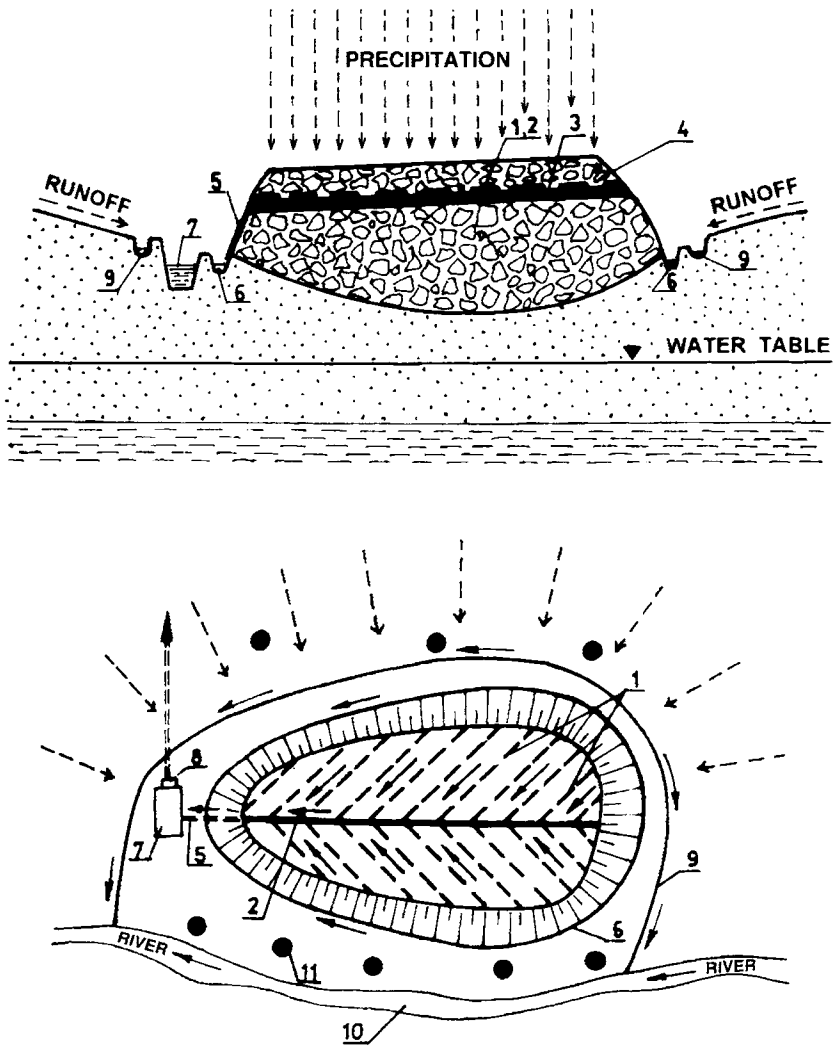


Figure VI.6.4. Schematics of mining waste dump dewatering system. Surface drainage system of mining waste dump to attenuate contaminant leaching (1,2); surface drainage system at the top layer placed at a barrier layer (3); (4) top "neutral" vegetative waste layer or topsoil; (5) drainage collector; (6) toe ditch for collecting run-off and drainage from the dump; (7) retention/evaporation pond; (8) pump; (9) exterior barrier ditch; (10) stream receiving natural runoff from the adjoining area; and (11) monitoring wells. Slope no less than 1:2.5.

tailings may be utilized as a transitional drainage-bed at the temporary top of a compacted waste layer during the dump construction. Due to susceptibility of fine-grained material to erosion, both tailings and FA mixtures should not be introduced into the external surface parts of batters. Dump closure will require construction of a permanent drainage at the dump top cover layer on a low-permeable bed, along with a system of slope ditches, toe collectors, and retention ponds.

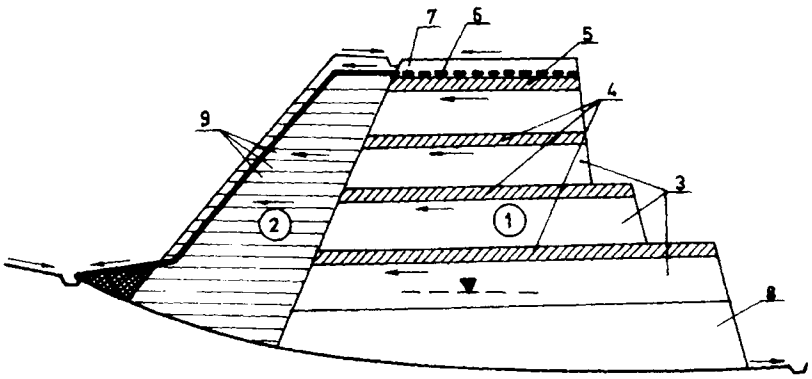


Figure VI.6.5. Mining waste dump construction with barrier layers of dewatered fine-grained tailings. (1) Internal part of the dump; (2) batters (slope min. 1:2.5); (3) compacted layers of mining waste; (4) barrier layers of dewatered fine tailings; (5) barrier layer; (6) drainage system of the top layer + capillary break (sand, gravel); (7) vegetative layer; (8) bottom layer, possible gradual inundation; and (9) batters constructed of mining waste compacted in thin layers.

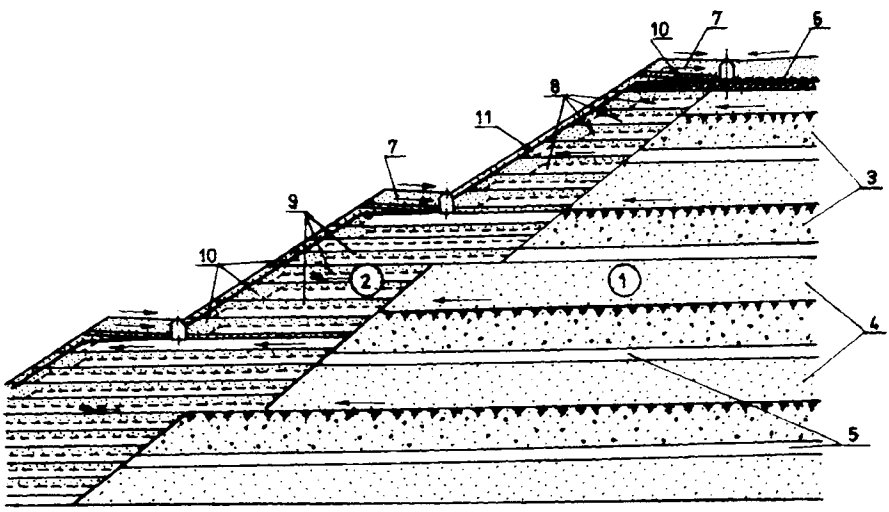


Figure VI.6.6. Construction of mining waste dump with use of dense coal combustion FA: water mixture as air-protective layers. (1) Internal part of the dump; (2) batters (slope min. 1:2.5, bench/terrace slope 1:5 to 1:10); (3) heavily compacted mining wastes; (4) moderately compacted mining wastes; (5) dense FA: water mixture; (6) surface drainage + capillary break (sand, gravel) + infiltration barrier layer (dewatered fine tailings, clay + [optionally] geomembrane); (7) vegetative layer; (8) layers of dense FA: water mixture or dewatered fine tailings ≤ 0.25 m; (9) mining waste compacted in thin layers (≤ 0.5 m); (10) external part of batters (compacted mining waste only); and (11) drainage collector (open ditches or/and pipes).

The slopes and gradients of compacted layers should facilitate water flux to the drainage collectors and prevent vertical percolation (Figs. VI.6.5 and VI.6.6). The average slope of the dump should not be steeper than 1:2 to reduce the potential for erosion, allowing safe slope formation and convenient maintenance of vegetation.

One more protective option is the bottom lining of a dump base. In case of high-volume coarse-grained mining waste disposal in large-area dumping sites, in particular in the areas affected by subsidence, use of bottom liners is usually ineffective, unreliable (cracking), expensive and limited by the availability of a material for liners. This measure should be thus considered only for low-volume dumping sites of high-risk material, such as sulfidic metalliferous ore mining waste of high ARD potential.

VI.6.4.2.4. Minimization of contaminant loads discharged from the top cover of the dump

Despite excluding the bulk of a waste dump from generation and leaching of contaminants, the mining waste dump can still pose a serious threat to the aquatic environment, as these processes are particularly active in the surface layer. Consequently, in the case of mining waste disposal of a high contamination potential (high reactive sulfide content, low buffering capacity and thus high ARD, high heavy metal content) and unfavorable hydrogeological and hydrologic conditions in the area, additional measures for minimization of contaminant release from the exposed surface layer, which serves also for introduction of a vegetative cover, could be required. They comprise: (i) selective disposal in the top layer of low-saline and low-sulfide, low-reactive, non-acid generating waste; (ii) minimization of the vegetative layer thickness; as this parameter is determined by the depth of a root system penetration, the herbaceous carpet cover with a shallow root system is preferable; (iii) minimization of infiltration rate by the selection of plants assuring high evapotranspiration (this method is, though, limited to the vegetation period); (iv) enhancing waste properties by blending with material of high buffering capacity; and (v) reduction of air penetration to the vegetative layer, through selecting for this layer a waste material of appropriate particle size, compacted to the extent not affecting adversely the vegetation.

Due to the observed weak role of *T. ferrooxidans* in sulfide oxidation in coal mining waste dumps in the USCB area, no control measures for these bacteria have been considered. In ore mining areas of high ARD potential, these bacteria can, though, substantially accelerate and intensify the process of ARD generation (see Chapter III.6) In this case, bactericide addition or amendment of a top cover layer with high calcite or/and dolomite material for neutralization of rock and thus for suppression of the activity of these bacteria susceptible to pH changes beyond the optimum range, might be required.

VI.6.4.2.5. Minimization of contaminant concentrations in the saturated zone

In general, most dumps may be considered as an anthropogenic vadose zone. Some of these constructions are of a mixed type, the dump toe being waterlogged. In many cases of dumping site location in the area of deep coal mining, the gradual inundation of a dump toe occurs due to subsidence.

The source of groundwater contamination in the saturated zone is the release of soluble constituents from the waterlogged material, infiltration of water percolating through the upper unsaturated part of the dump and surface run-off from the batters' slopes. The critical conditions are formed in the border layer as a result of the variability of the water table.

The concept of water quality protection in the saturated toe part of the dump is based on the following assumptions:

- In the saturated zone there are practically no conditions for the generation of new contaminant loads resulting from sulfide decomposition. The kinetics of sulfide oxidation in the saturated waste layer is very low due to the negligible availability of oxygen; therefore, mining waste stored under water is chemically non-reactive.
- Release of contaminants contained in the waste material is of a short-term nature. Soluble constituents occurring in the material at the moment of inundation are transferred to the solution. After washing out the contaminant load occurring in the material during inundation, it becomes harmless to the aquatic environment provided the storage mode is not changed.
- The amount of water in the waterlogged layer is limited to the voids between the waste particles.

If the contaminants released from the gradually inundated layer pose even a short-term threat to the groundwater quality used for water supply, e.g. highly saline wastes, the pollution potential of the waste can be substantially reduced by a single thorough exchange of water in the layer. Periodic forced discharge of saline water to the saline mine water pipeline from the relief wells can be applied until the subsidence ceases and permanent reduction of chloride salinity or other contaminants to the acceptable level occurs. The dump batters along with relief wells can be used also as a protective barrier against inundation of the external area in the vicinity of the dump (Fig. VI.6.7).

VI.6.4.2.6. Further developments

The current status of groundwater protection from contaminant leaching from sulfide mining waste dumping sites cannot be yet defined as being satisfactory and needs new solutions, particularly in the most critical period of a waste dump construction that usually lasts for years. During this time, both soluble contaminant leaching and generation of new contaminant loads occur. These processes have detrimental impacts on the groundwater quality down-gradient of the dump that results in deterioration of Quaternary aquifer observed in the most cases in the USCB area, and in other dumping sites. The solutions being under development utilize ability of some other abundant waste materials to act as water-permeable barriers having required properties for attenuation of contaminant generation or migration, e.g.:

- Air-tight material for prevention of sulfide oxidation within the waste layer and thus generation of ARD.
- Material showing neutralizing properties to prevent heavy metal mobilization.
- Material of high sorption capacity for metals and some toxic organic compounds.

All these materials are considered to be used as preventive barrier layers, in particular, in the critical transitional stage of dump construction prior to capping. According to

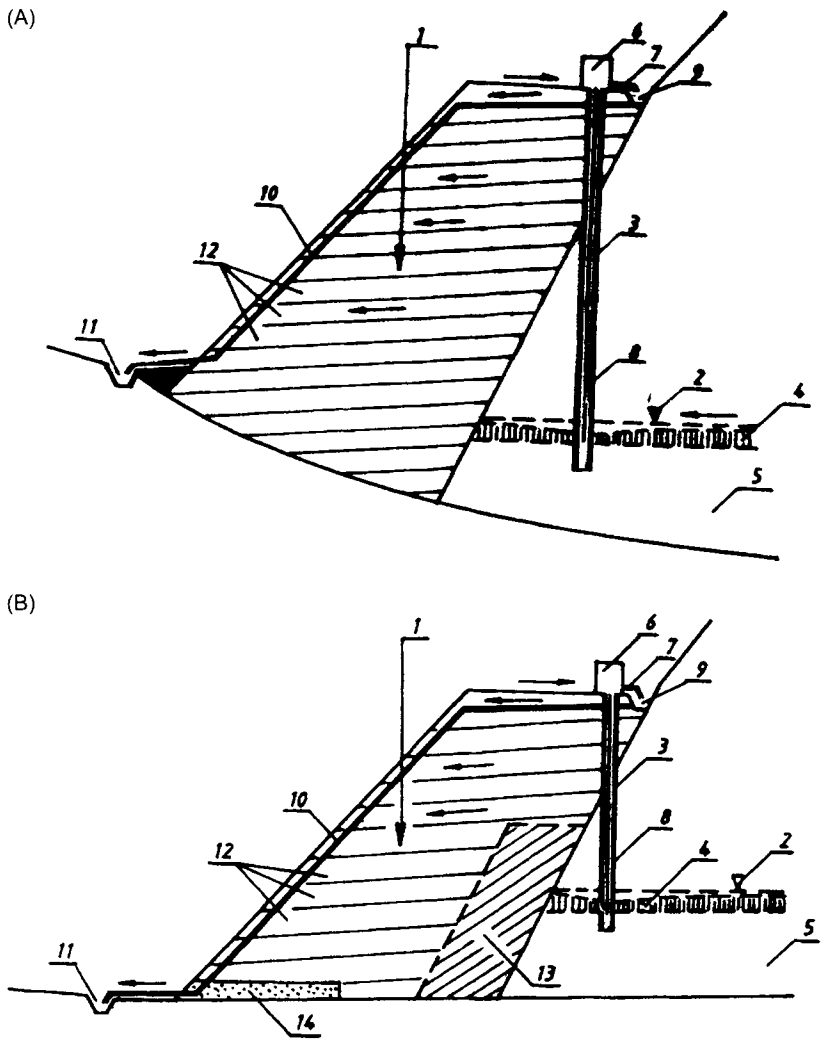


Figure VI.6.7. Construction of mining waste dump in the zone of a gradual inundation due to subsidence without (A) or with internal sealing screen (B). Batters; (2) inundation level; (3,6,8) relief wells with filter packs and a pump; (4) upper layer of inundated part of a dump; (5) inundated zone; (7) discharge from a pump; (9) collecting ditch at the batter terrace; (10) surface drainage collectors; (11) dump toe ditch; (12) mining waste compacted in thin layers; (13) impermeable screen; and (14) longitudinal strip drain.

the experience of the authors, the material of adequate air-tightness (high penetration resistance coefficient) and temporary neutralizing capacity is a dense mixture of saline water with coal combustion FA, in particular enriched in carbonatic material, e.g. containing products from lime desulfurization process (see also Chapter VI.8). To make it effective, the protection layer should be of a blanket-type placed at the top of a mine waste layer and solidified, as it has been already described (Fig. VI.6.6).

High sorption capacity for metals and organics show stabilized sewage sludge and composts rich in humic substances (HS) that can be utilized in dumped ARD-generating mine waste material as permeable barriers in a way similar to that presented in Figure VI.6.6 for dense FA: water mixture. The use of both kinds of protective barriers in one dump alternately may significantly enhance metal immobilization in waste material. The above protective measures are particularly attractive due to low capital costs and their passive character that means no running costs and no need of after-care and maintenance. Only in case of serious unpredictable surface deformations, e.g. due to accidental subsidence, when continuity of the layer is damaged, some extra repair would be needed where possible.

The possibility of solubilized HS application as permeable barriers for *in situ* remediation of contaminated aquifers from organic and inorganic pollutants has been also reported (Georgi et al., 2002). The HS barrier is proposed to be constructed by injection of HS solution, which is subsequently immobilized onto the aquifer materials optionally by: (i) coating of the mineral surfaces with Fe^{3+}/Fe^{2+} precipitates in order to produce positively charged surface sites prior to the injection of HS; (ii) flocculation of HS in the interstitial pore volume using polyvalent cations, e.g. Ca^{2+} (Fig. VI.6.8).

This active-care and much more expensive method is of a prospective use for groundwater remediation in old dumping sites where contamination of aquifer has already occurred. It has been successfully tested in a bench scale; its construction and effectiveness will be investigated in a field study.

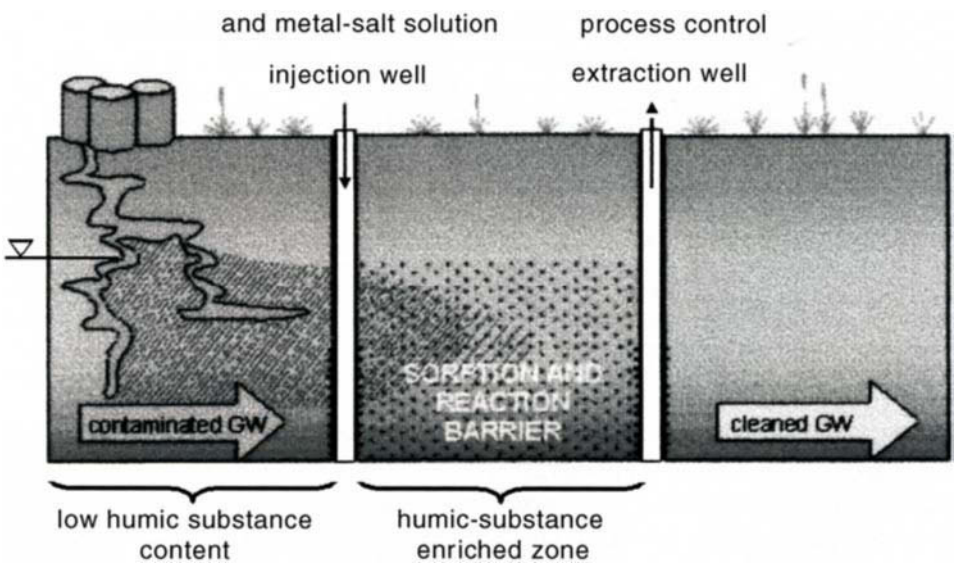


Figure VI.6.8. Construction of a humic substance barrier in a contaminated aquifer (after Georgi et al., 2002).

The dump construction and rehabilitation strategy in other countries, which are facing problems of ARD in mining areas, is based on the same approach as discussed above. The practical implementation of this approach and engineering options to manage ARD for mining waste dumps differs in details dictated by the site-specific conditions and properties of the material that exclude unified rigorous routine practices and implies the need to search for an individual optimum solution for each dumping site. A compendium of ARD management options in dumping sites is exemplified below by the practice and activity of several of Australia's best-performing minerals mining companies (Environment Australia, 1997).

VI.6.4.3. Rehabilitation strategy for mining waste dumps in Australia

The rehabilitation strategy for the waste dump construction in Australia is directed mainly to minimize the potential for ARD and considers the control of the same parameters as discussed above, i.e. sulfide oxidation and acid generation rates, water percolation through the waste layer along with control of alkalinity and acidity balance of the material. A hierarchy of appropriate management strategies is as follows:

- minimize oxidation rate;
- reduce potential for transport of oxidation products to the recipients;
- contain and treat acid drainage.

A summary of engineering options to manage ARD comprises a set of proactive preventive and reactive remedial measures (Environment Australia, 1997):

Preventive measures include (Figs. VI.6.9 and VI.6.10): (i) selective handling/encapsulation of high ARD generating waste with benign material; (ii) in-pit disposal (if available), similar to encapsulation; surface cover may be provided either by water or compacted fill cover; (iii) blending/mixing/co-disposal of ARD wastes with benign non-acid producing or acid neutralizing materials; (iv) micro-encapsulation through leaching the ARD waste with a phosphate solution with hydrogen peroxide, to form a passive surface coating of phosphate precipitate over the waste rock fragments; and (v) uncontrolled placement of low ARD generating waste with downstream collection and treatment of water; collection systems include catchment ponds, drains, trenches, groundwater boreholes; treatment/disposal systems include chemical treatment (e.g. lime dosing), controlled release and dilution by adjacent streams, evaporative disposal, process reuse and wetland filter treatment.

Remedial measures comprise (Fig. VI.6.10): (i) subsurface sealing or surface covering with a low-permeable benign material to control water and air penetration into the dump; (ii) downstream collection and treatment of water, as in option (v) of *Preventive measures*; and (iii) removal of high ARD waste, an option usually not considered because of the costs involved.

The above options, in general, are of a less complex character, and consider mainly ARD waste encapsulation and blending in order to reduce acid generation potential, without control of leached loads transported to receiving waters. They also assume availability of excess land for dumping, benign/acid consuming material for ARD waste insulation/sealing (e.g. porphyry), and also adequately high capacity of receiving waters to dilute the contaminant loads transported in non-acid leachate.

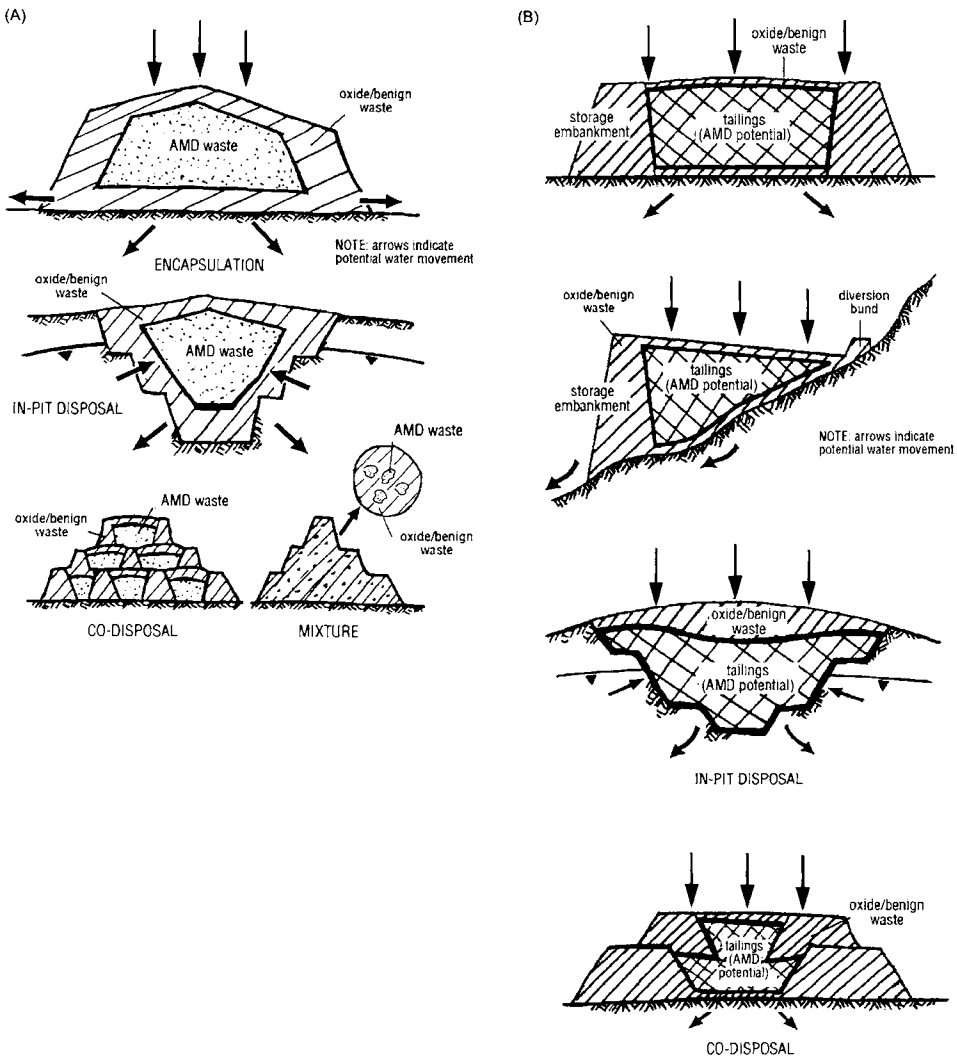


Figure VI.6.9. Methods for ARD control using a range of encapsulation and co-disposal options (A) in waste rock dumps; (B) in tailing storages (from Environment Australia, 1997, after Marszalek, 1996).

The construction of dumps using double or single insulation of ARD waste with primarily non- and low-sulfur material (Fig. VI.6.11(A,B)) prior to formation of a compacted external porphyry seal shaped as a terraced landform with an average slope angle 1:4 (Fig.VI.6.12) may be a viable option provided the feasibility analysis confirms availability of both insulating material and land for dumping.

The rehabilitation strategy focused on reducing both infiltration through the dump and convective/diffusive transport of oxygen, which is shown in Figure VI.6.13, is the closest to the approach considered by the authors of this Chapter as the most effective. Sealing

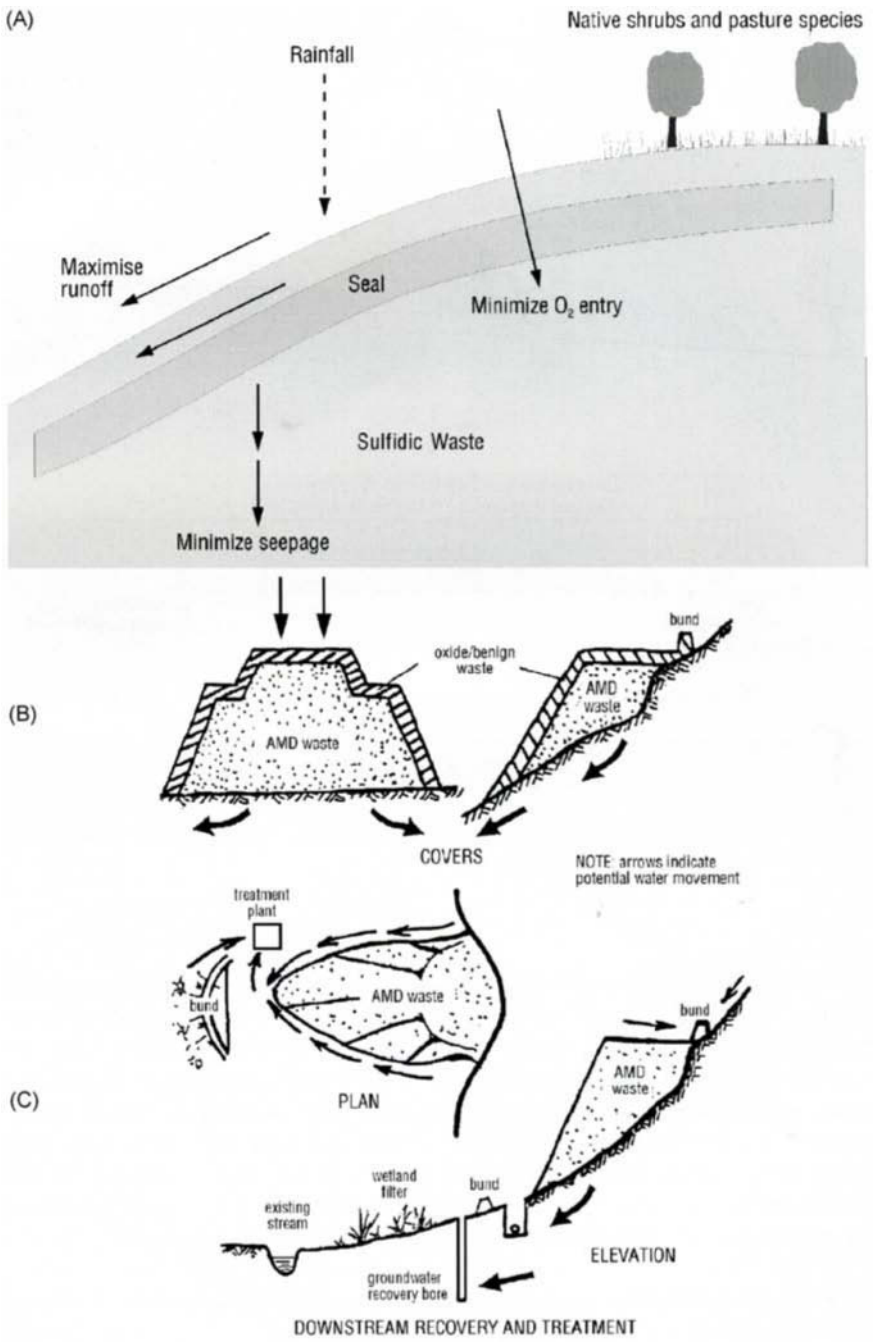


Figure VI.6.10. Methods of ARD control in waste rock dumps using subsurface air- and water-tight seal (A), surface cover with oxide/benign waste (B) or downstream collection and treatment of water (C) (after Environment Australia, 1997).

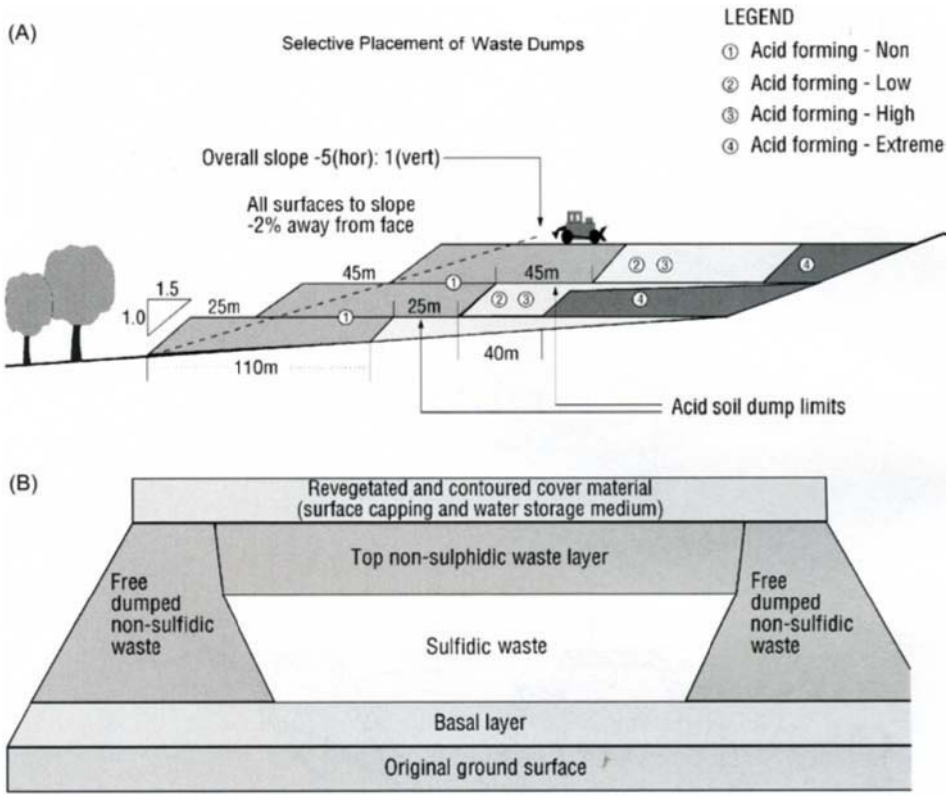


Figure VI.6.11. Formation of dumps with use of double (A) or single (B) insulation of ARD waste with non- and low-sulfur material (after Environment Australia, 1997).

covers may comprise compacted low-sulfide waste rock, oxide wastes, soil cover or multi-layer cover incorporating soil layers (sometimes combined with geomembranes) of different properties acting as a capillary break, water retention base layer, water storage zone, surface barrier and vegetation layers, as is schematically shown in Figure VI.6.13. Synthetic membranes, despite high efficiency in water exclusion, are generally not applicable for high-volume mining waste sealing although they have been used for protection of low-grade ore stockpiles and other high-risk wastes. Among the specific measures is the development of bactericides to prevent the catalytic role of *T. ferrooxidans* mainly with respect to high ARD generating waste at pH < 4.

VI.6.4.4. The rehabilitation strategy for the mining waste dumps in the USA

VI.6.4.4.1. The routine solutions

The routine strategy of mining waste management in the USA is based on a similar, but much wider general approach than ARD control and is focused on attenuation of chemical

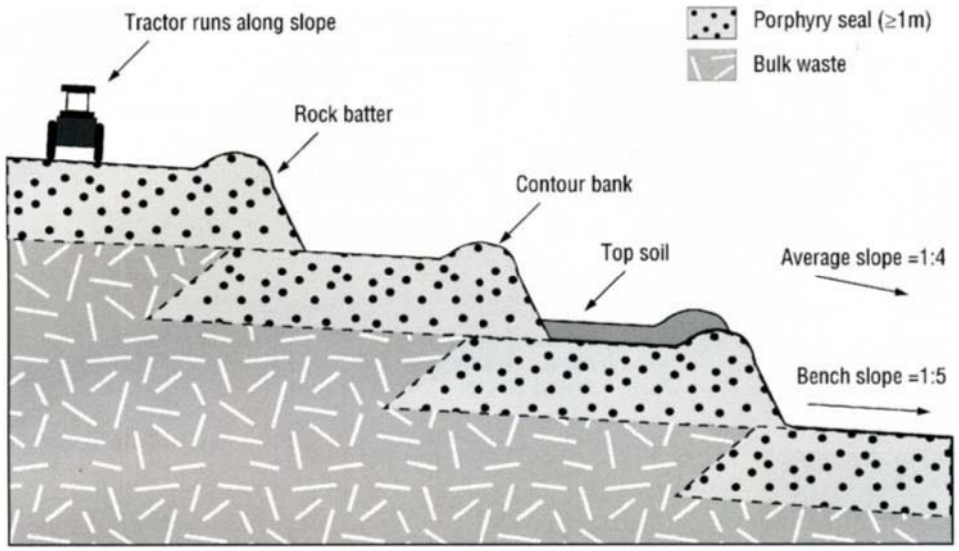


Figure VI.6.12. Detail of construction of dump batter (after Environment Australia, 1997).

constituents, as well as controlling, besides leachate, also wind and surfacewater erosion. These issues are thoroughly discussed by Hutchinson and Ellison (1992). The study focuses mainly on the safe disposal of non-hazardous mining waste regulated under RCRA, Subtitle D, but many of the aspects are applicable also to hazardous waste disposal under RCRA, Subtitle C. This study, covering a wide range of subjects concerning environmentally safe management of mining wastes, is strongly recommended as a valuable review of modern mine waste management units and requirements.

The major assumption is the disequilibration and change of mining waste properties with time. This is in agreement with the authors' approach to this material, presented in Chapter III.6 and in earlier publications (e.g. Twardowska et al., 1988; Twardowska and Szczepańska, 1990; Szczepańska and Twardowska, 1999). The geochemical changes are divided into four major stages, different for various waste materials and involving: (i) a mining process-controlled stage; (ii) acid generation-controlled stage for ARD wastes; (iii) re-solution phase for non-acid generating waste; and (iv) long-term degradation of more resistant minerals.

Attenuation of contaminant migration is thus also strongly dependent on the waste and site characteristics; its required extent is determined by federal and state regulations and groundwater quality standards with respect to the different potentially mobile chemicals of concern (macro- and trace metal and non-metallic species/complexes, asbestos, metal cations, major anions, and cyanides). In general, four types of attenuation mechanisms are considered: (i) physical (filtration, dispersion, dilution, and volatilization); (ii) physiochemical (adsorption and fixation); (iii) chemical (precipitation, hydrolysis, complexation, oxidation, and reduction); and (iv) biological (biodegradation, bacterial consumption, and cellular uptake by plants). Additional factors of importance for evaluating the applicability of the particular attenuation method on a site-specific basis

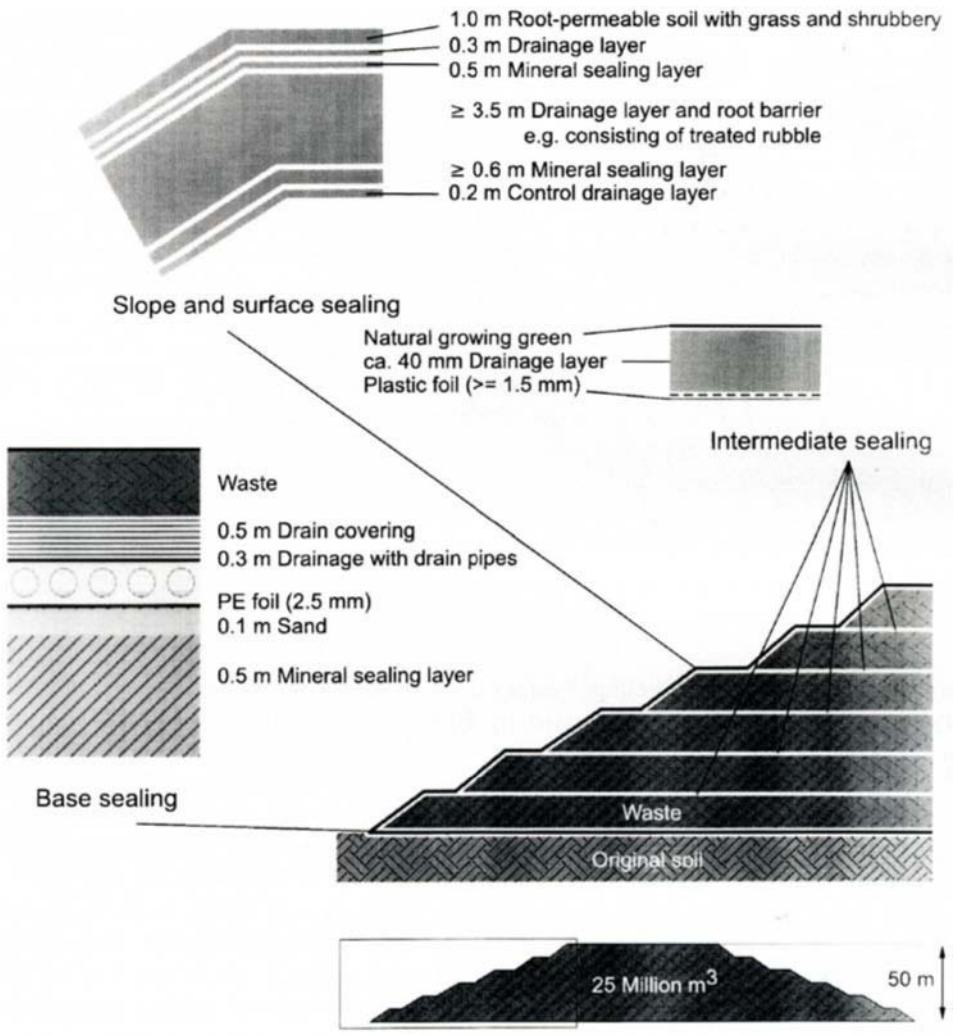


Figure VI.6.13. Schematics of insulation strategies (after Environment Australia, 1997).

include climatic and vadose zone conditions, attenuation capacity and waste unit management practices. The last factor incorporates direct and indirect activities aimed at improving the potential for attenuation, e.g. providing a lining with good attenuation properties; combining wastes with appropriately different chemical or physical properties, or locating certain wastes within specific areas having conditions adequate for attenuation to occur (direct activities). Indirect activities may include, e.g. controlling of the amount of liquid contacting the waste.

The prerequisite for selecting an optimum method for the attenuation of chemical constituents, is an application of appropriate level of verification, based on technology,

prior experience and testing, as well as modeling and field demonstration to determine the attenuation capacity and verification of the predicted behavior of the chemicals of interest.

Much attention in mine waste management is paid to the bottom liner system design and closure requirements. Due to an unfavorable location of some mine waste disposal facilities close to valuable surface or groundwater resources, the liner system involving material of low hydraulic conductivity could be required to avoid an unacceptable threat to groundwater. Considering the different levels of hazard presented by different wastes, a wide variation in physical and chemical properties, as well as often very large sizes of the mine waste disposal units and long period of their development, some lining systems can be economically or technically unfeasible. As a result of the lack of natural soils of low hydraulic conductivity close to the disposal sites, the geosynthetic material application for liners in North America is increasing dramatically. It should be, though, mentioned that due to specific geological conditions of mining and location of waste dumps in areas of progressive subsidence, the efficiency of bottom liners use for large area- and volume-units could be problematic. Much more efficient and cost-effective management practices are aimed to risk reduction. In the USA, such practices comprise mainly bottom non-liner barriers, such as placement of under-drains, cut-off walls, sub-aqueous deposition, etc.

The authors' approach is focused rather on preventing generation of pollutants and their transport to groundwater, i.e. reduction of an exposed surface and disposed waste volume subjected to leaching, and limitation of operation time before the permanent closure of the dump section, along with the construction of durable surface facilities for long-term water protection.

With respect to the life-cycle protection of the aquatic environment, closure requirements for controlling the seepage migration to the receiving waters, as well as the wind and surfacewater erosion, are of particular importance. In the North American practice, the emphasis is put on "passive-care" approaches such as the provision of a durable long-life cover requiring minimum maintenance. "Active-care" approaches, e.g. collection and chemical treatment of contaminated water are considered unfavorable, and should be replaced finally by passive-care activities. The technologies and design elements, which are recommended for different solid mining waste types, comprise, in general, a similar set of alternatives, as discussed earlier. A choice of action depends upon the life-cycle evaluation of threat to the beneficial use of surface or groundwater. It may thus include several options, such as: (i) "no action"; (ii) institutional controls; (iii) conditioning or treatment (physical, chemical, biological); (iv) encapsulation (surface or subsurface); and (iv) waste removal for off-site disposal. Of these technologies, effective encapsulation appears to be the most appropriate passive-care approach.

The key routine elements of this technology include cover layers (single or multi-layered: top, drainage, capillary break), barrier and special layers, depending upon the threat posed to the environment (EPA, 1989). The EPA basic waste management unit requirements are incorporated in a vast list of guidance documents, applicable to mining wastes (EPA, 1979, 1982, 1983a,b, 1985, 1987a,b, 1989). The manner in which various types of wastes are managed depends upon the type and environmental behavior of the particular material. The detailed discussion of these requirements, as has been pointed out at the beginning of this chapter, is provided by the comprehensive study of Hutchinson and Ellison (1992).

VI.6.4.4.2. Novel mine waste technologies

Sulfidic mine wastes have been found to have severe detrimental impacts on the environment and ecosystems due to combination of acidity, heavy metals and sediments in the West of the USA (see Chapter VI.6). The technologies for ARD control being currently under testing in the USA within EPA/DOE Mine Waste Technology Program (2000) consider the following priority areas (Wilmoth, 2000):

- Source controls, including *in situ* treatments and predictive techniques to provide a permanent long-term solution.
- Treatment technologies for providing immediate (short-term) alleviation of the most severe environmental problems.
- Resource recovery (heavy metal extraction) from mining wastes in order to help offset remedial costs.

The at-source controls technologies of the first priority consider use of sulfate-reducing bacteria (SRB) method; biocyanide oxidation for heap leach piles; transport control/pathway interruption techniques, including infiltration control, sealing, grouting, and plugging by ultramicrobiological systems.

SRB: among these technologies, particular attention has been paid to use anaerobic SRB to significantly retard or prevent acid generation at affected mining sites. With respect to ARD generated in mining waste piles, it can be used to reduce the contamination of acid high-metal leachate in three ways: (1) dissolved sulfate is reduced to hydrogen sulfide through metabolic action by the SRB; (2) the hydrogen sulfide reacts with dissolved metals forming insoluble metal sulfides; and (3) the SRB metabolism of the added organic nutrient produces bicarbonate that increases pH of the solution and thus limits further metal dissolution.

In the SRB bioreactors constructed at the Calliope abandoned mine site in order to treat the metal-rich leachate with pH 2.6 from waste rock pile within EPA/DOE Program (2000) (Fig. VI.6.14A,B), a combination of organic carbon (cow manure), cobbles and crushed limestone was used as a fill to provide nutrient and stable substrate, and to adjust pH for bacterial growth. For the metal concentrations present in the ARD in the site, at SRB population from above 10^3 to 10^6 cells/ml and residence time of ARD for 4.5–5.5 days in the reactors, which were run from 1998 to 2001 throughout these years, the metals were removed to threshold levels 800 μg Zn/l, 80 μg Cu/l, and 5 μg Cd/l.

The successful application of SRB in a field scale for ARD and AMD remediation under EPA/DOE program (2000) has given rise to studies and applications of this promising and efficient technology in various projects on eliminating ARD and AMD (Diels et al., 2002; Ibeanusi and Archibold, 2002; Ngwenya et al., 2002; Zaluski et al., 2002) also with biorecovery of metals (Tabak and Govind, 2002). The obtained efficiencies of metal removal in different projects and a diverse scale of application are within the range reported above. Though most of the SRB projects are allocated in the USA, this technology becomes increasingly popular also in Europe, where several research centers are currently involved in SRB studies and upscaling of applications (Johnson and Hallberg, 2002; Piet et al., 2002; Geller et al., 2002).

The recent experiments on using an integrated mixed metal-tolerant microbial system to enhance the removal of multiple metals from coal pile run-off and their subsequent

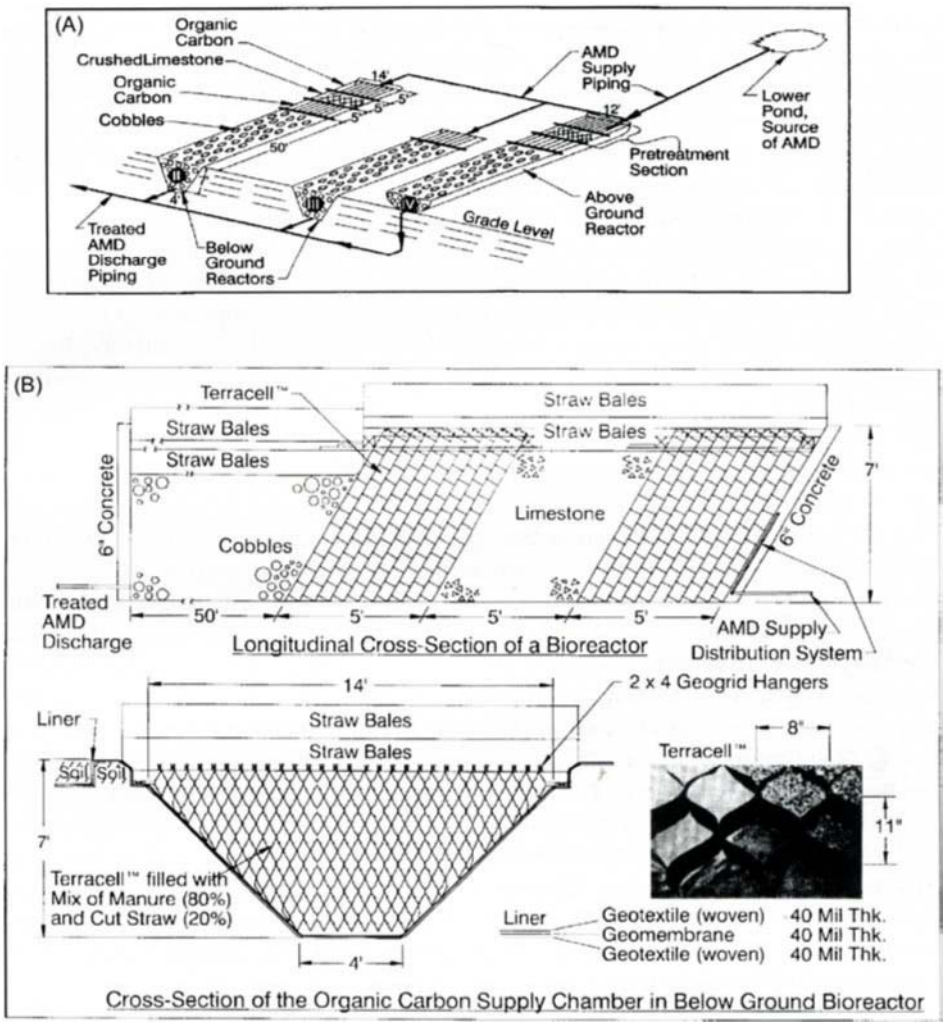


Figure VI.6.14. Layout (A) and design (B) of sulfate-reducing bacteria (SRB) bioreactors in Calliope Mine, Montana, USA (after EPA/DOE, 2000).

recovery in the bacterial biomass showed a high removal range of 83–100% and a recovery of 38–58% of Al, As, Cd, Cr, Cu, Fe, Pb, Se and Zn occurring in concentrations typical for coal pile leachate (Ni showed lower recovery rate of 15%) (Ibeanusi et al., 2003). The reported data prove high effectiveness of the mixed microbial system in metal removal and recovery process from ARD and demonstrates possibility of the prospective wide use in this field.

Source control technologies are in compliance with the methods described earlier as "rendering the dump air- and water-tight". They are focused on the new technical solutions for tasks well known for a long time, one of them is elimination or reduction of

precipitation infiltration and groundwater flow through the waste piles, including those from historical mining activity that generate acidic, metal-laden ARD. These solutions consist of developing new water-insulating grouting materials coupled with drain system to hydraulically control the water flow at the site. Source control material undergoes testing for impermeability for water once it is emplaced onto the surface waste pile, for acid resistance, as well as for wet/dry and freeze/thaw cycling.

One of these projects under EPA/DOE program comprised successful testing of a spray-applied flexible, urethane grout called KOBAthane 4990 used at the surface mine waste pile to prevent infiltration. To transport groundwater away from the AG material, the French drain was placed up-gradient of the pile. The technology emplacement resulted in the significant improvement of water quality down-gradient of the pile: dissolved metal concentrations decreased below MCL for drinking water. Other spray-applied, modified chemical grouts that incorporate the tailing material as a filter are under testing at the ore tailing site. This technology might be efficient and cost-effective for source control of relatively small size piles sited in the remote unpopulated areas, where aesthetic values and possibility of vandalism are of a lower importance.

Another group of new solutions is directed to attenuating processes of chemical and biochemical sulfide oxidation that are responsible for generating ARD within the waste pile. The methods presented in this chapter consisted of application of barrier layers of air-tight material permeable to water. Under EPA/DOE Project (2000), so-called "biological cover" to control pyrite oxidation has been tested as an innovative technology for cost-effective remediation of acid-generating abandoned mine tailings by means of establishing and maintaining a biologically active subsurface and near-surface microbial barrier that consume dissolved oxygen from the water infiltration into the pile and thereby reduce the generation of ARD. The oxygen permeability reduction of five orders of magnitude was reported in laboratory- and field-scale experiments as a result of establishing a biologically active zone by adding low-cost nutrient solution that served as a source of carbon, nitrogen, phosphorus, and micronutrients for stimulation of indigenous oxygen-consuming microorganisms and SRB growth. Overall, further laboratory and field testing showed unstable results that suggested the necessity of defining critical parameters for formulating an appropriate nutrient mixture.

Heavy metal in situ stabilization technologies: a number of projects has been conducted under EPA/DOE Mine Waste Technology Program in order to identify technologies for *in situ* treatment/stabilization of particularly problematic toxic metals such as mercury and lead as a cost-effective alternative to excavation and removal of hazardous mine waste and metal-contaminated soils to a waste repository; e.g. for lead, the remedial approach consists of phosphate stabilization of mine waste contaminated soils by mixing commercial grade phosphoric acid and a trace of KCl into the soil followed by liming for pH adjustment that results in conversion of lead into a highly insoluble pyromorphite.

ARD treatment: several technologies are being focused on development of effective ARD/AMD treatment systems for removing toxic, dissolved metallic and anionic constituents from the leachate *in situ* and increasing the pH of effluents to near neutral values using biological and/or chemical treatment processes. Integrated passive biological reactor utilizes both SRB (anaerobic treatment) and aerobic bacteria (aerobic reactor) in a series of biological processes for the complete mitigation of ARD with precipitation of metal ions as insoluble sulfides (most metals) or oxides (Fe, Mn).

For removal of selenium from Se-bearing leachate to the level of 50 μg/l (ppb) under the US National Primary Drinking Water Regulation Limit, four technologies have been successfully tested: (i) best demonstrated available technology (BDAT) for coprecipitation of selenium using ferryhydrite; (ii) catalyzed cementation of Se by adsorption onto iron surface regardless of its valence state (Se^{4+} or Se^{6+}); (iii) biological Se reduction to elemental selenium by specially developed biofilms containing specific microorganisms using baffled anaerobic solids bed reactors (BASBR); and (iv) enzymatic reduction of selenium based on proprietary enzyme extraction/purification method combined with immobilization/encapsulation techniques that keep the selenium reducing enzymes in a functional arrangement within an immobilized/encapsulated matrix. All these technologies removed Se below the MCL, of them BASBR appeared to be the most consistent process tested, with the majority of results below the detection limit 2 μg Se/l (ppb).

Biological destruction of weak acid dissociable (WAD) cyanide occurring in cyanide solution heap leaching of sulfide ores of precious metals in concentrations 500–600 mg CN/l along with other contaminants such as As, Cu, Hg, Ag, Zn was found to be an efficient process for cyanide reduction to <2 mg CN/l. The indigenous aerobic and anaerobic organisms capable of effectively degrading cyanides were isolated during the bioaugmentation phase, and used in the subsequent aerobic and anaerobic reactors, and in final aerobic step. Cyanide and heavy metals were substantially removed and pH consistently neutralized in a more cost-effective way than in conventional processes. The remediation of metal-complexed cyanide has been also investigated using several photolytic methods (direct photolysis and homogenous photolysis) to enhance naturally occurring remediation processes.

To remove from ARD/AMD trivalent arsenic As^{3+} that has been reported to be more toxic than As^{5+} forms and much more difficult to remove from solution, photochemical oxidation process was used effectively for conversion of As^{3+} to As^{5+}. Removing As^{5+} was next accomplished using adsorption onto ferric iron (U.S. EPA accepted method). Other arsenic removal technologies were tested to reduce its concentration from approximately 500 to <50 μg/l that comprised: (i) mineral-like precipitation by substituting arsenate into an apatite structure; (ii) aluminum oxide adsorption; and (iii) ferryhydrite adsorption (BDAT technology). All three technologies showed favorable results.

For thallium removal from ARD/AMD to levels of <1.7 μg/l, two technologies are considered: (i) adsorption onto manganese dioxide (available as a waste from zinc electrowinning process) and (ii) reductive cementation of thallium with use of elemental iron (available in scrap form).

Under Mine Waste Technology Program, an extensive search to evaluate innovative nitrate removal technologies was undertaken. Of the 20 technologies screened, 3 were selected as the most promising economically and environmentally: (i) ion exchange with nitrate-selective resin; (ii) biological denitrification; and (iii) electrochemical ion exchange (EIX).

At present, numerous technologies are available for remediation of ARD. These technologies include biosorption, mineral/resin adsorption, chemical precipitation (e.g. lime precipitation), ion exchange, freeze crystallization, evaporation and many others. The status of development and application of these techniques can be followed in the websites of U.S. Geological Survey (USGS), U.S. EPA and some other sources given as a reference

material for further information at the end of this chapter. Remediation methods are usually site-specific, thus both conventional and novel processes have to be carefully analyzed with respect to feasibility and applicability, and possibly modified to meet the requirements.

VI.6.4.5. Other rehabilitation technologies for the mining waste dumps

A potential for ARD/AMD attenuation and remediation show also other recent studies carried out in different countries.

An interesting technology of using steel manufacturing by-products incorporated into the funnel-and-gate system, which is one of the applications of permeable reactive barriers (Powell et al., 1998), for controlling mine tailing leachate with high As concentration has been proposed by Korean authors (Ahn et al., 2003). Besides elemental iron, these materials contain various compositions of Fe oxides and Ca–Fe oxides that are adsorption sites for both As^{5+} and As^{3+}, while Ca hydroxides can also neutralize acidic leachate and promote precipitation of dissolved heavy metals. Of the tested material, evaporation cooler dust (ECD) was found to be the most efficient material to remove As and dissolved metals, and to increase pH; oxygen gas sludge (OGS) and basic oxygen furnace slag (BFOS) also showed high efficiency. This technology is particularly attractive due to utilization of low-cost materials as permeable reactive barrier media in mine tailing containments.

Other investigations propose a galvanic suppression technique of pyrite oxidation and restricting further oxidation of Fe^{2+} by molecular oxygen using minerals with lower rest potentials (E^0), and *in situ* precipitation of calcite for ARD/AMD remediation (Noecker et al., 2003). The mineral with a lower potential acts as the anode (oxidation and dissolution of that mineral) and the mineral with the higher potential acting as the cathode is protected from dissolution (Holmes and Grundwell, 1995). Preliminary results showed that metallic Cr(c) in particular, and also Zn(c) and Al(c), all effectively reduced the oxidation of pyrite in aqueous solutions, while the reaction of CaO and pyrite produced a calcite precipitation when CO_2 was added. The authors have suggested that mobility of As, Se, Cu and Pb in ARD/AMD can be effectively reduced by precipitation of calcite, although current *in situ* immobilization techniques with use of FA and limestone as sorbents require extensive subsurface disturbances. At the reported stage, the feasibility of both methods, i.e. of galvanic suppression and *in situ* precipitation of calcite for AMD remediation seems to be low: introducing environmentally problematic metals or FA into acidic leachate/drainage in real systems might rather create more new hazards than positive effects, while water cover of sulfidic waste in natural conditions is in itself an effective protection against pyrite oxidation.

A substantial sorption capacity of different organic materials, including organogenic waste, for metals and metalloids has been reported by many authors (Shuman, 1999; Madejon et al., 2003; Twardowska and Kyziol, 2003; Twardowska et al., 2003). Madejon et al. (2003) found out that the affinity of metals and As for binding onto municipal waste compost, leonardite and forest litter followed the order Pb > Cd ≥ Cu > Mn ≥ Zn > As. Of these materials, municipal waste compost appeared to show the highest sorption capacity for heavy metals, while binding of As directly related to the humic acid (HA)/fulvic acid FA ratio and was the highest for leonardite. The formation of soluble

metal–organic chelates was low. These properties suggest the potential of using organogenic waste and natural material in permeable reactive barriers for metal removal from acidic leachate in mining waste dumps.

The above studies exemplify some research directions in seeking new opportunities for application of low-cost waste materials as metal sorbents from ARD.

V1.6.5. Landscape formation and land use in a dump site

The problem, which requires attention, is a need for the change of the primary landscape and land use in the dumping site. It arises on one hand from the severe land shortage in many mining areas, and on the other hand from the basic requirement of a maximum, environmentally safe use of the site area for waste disposal. As a result, high dumps are being constructed in a primarily flat area. Therefore, a new landscape and new way of land use is formed, which has to fulfill the above requirements, and not to be the aim by itself. Not always is a correct order of priorities followed. An example of an interesting, but not rational solution is the Paciorkowiec coal mining dump (Piast colliery, USCB, Poland), where the landscape became a superior target (Fig. VI.6.15). Forming the dump surface in the shape of free standing conic tips, creates high development of a surface vs. volume,

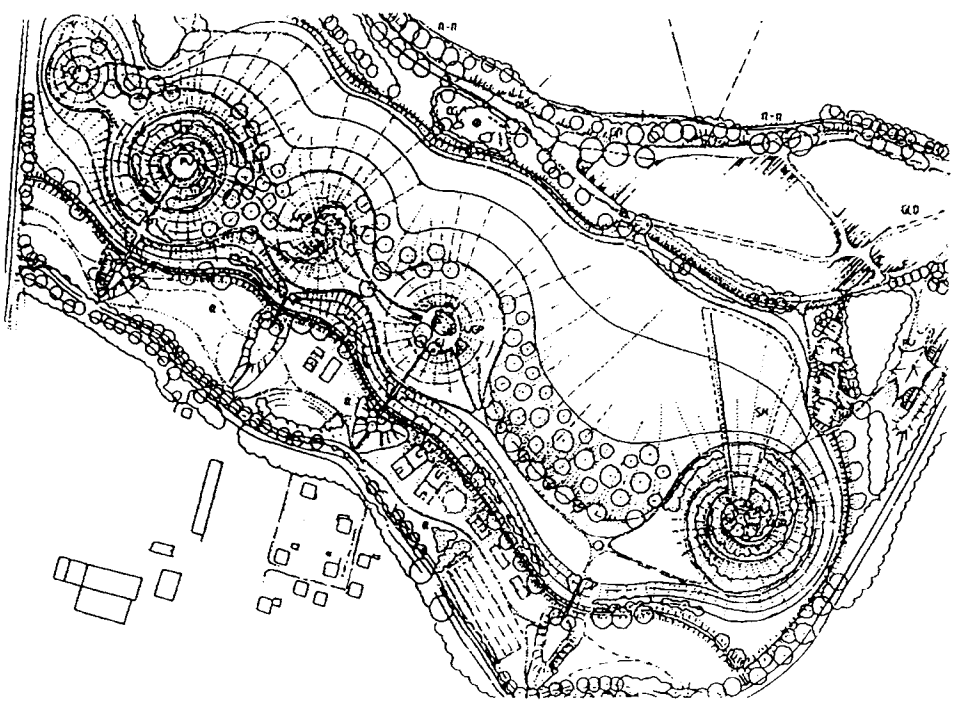


Figure VI.6.15. Paciorkowiec coal mining waste dump (Piast colliery, USCB, Poland). Construction of the dump as a recreation area with toboggan slides (architects: Bogdanowski, J.; Myczkowski, Z.).

reduces the disposal area, increases the threat of self-ignition and thus compels high-cost tips formed in thin heavily compacted layers. This solution, though, shows that the dumps can become a part of a new landscape and be used as a recreation and sports grounds, and be visually attractive and accepted by a local community. Many later landscape architecture solutions in mining waste sites designed as recreational areas avoid such extravagances (e.g. Debiensko or Bukow sites, USCB, Poland).

An unquestionably good example is an adaptation of the coal mining Janina dump as a recreation and park area (USCB, Poland). The construction of the dump was completed in 1995; its volume is 11.5 million m^3, average height 22 m, surface area 62 ha, enlarged for further 15 ha. The table-shape of a dump creates convenient conditions for disposal of high-volume wastes, is easily maintained and is suitable for siting of sports facilities (bicycle paths, tennis courts, picnic areas). The recreation and sport creates a good chance for rational and pro-ecological use of mining waste dumps, which fulfill the basic goal, i.e. waste rock disposal.

V1.6.6. Biological rehabilitation: concepts, solutions, and aims

An important role in mining waste dumps management belongs to the vegetation cover of a dump surface. For a long time this element of mine waste management was a synonym of a term "reclamation". The perception of the dump top layer as a place for growth and endurance of the introduced vegetation is still widely prevalent among specialists from this field. They usually do not consider that vegetation has to fulfill similar tasks, as other elements of rehabilitation, i.e. environmentally safe solid waste disposal, along with prevention of wind and water erosion of a dump surface. In a dump construction method, which starts from the final formation of batters and its slopes and next filling the internal part of the dump, the role of vegetation cover is particularly important both as an element of environment protection and landscape planning. Here, though, inconsistency of approaches and laws between European countries and the USA exists. The biological reclamation guidelines in Poland follow the German reclamation laws, where most frequently aforestation is the ultimate goal. Due to the lack of adequate knowledge, the complex approach to environmentally safe mine waste management and the ground and surfacewater protection as the first priority was not considered when these laws were developed, mainly by the traditional agronomists and forest specialists. The outdated guidelines, unfortunately, often correspond to the requirement of restoring primary use and high productivity of dumping areas, and are literally treated by the regional ecological administration.

In order to obtain rapid vegetative cover on mine waste, planting of trees at close spacing is still practiced and prescribed in Germany and Poland (Hutnik and Davis, 1978; Harabin and Strzyszcz, 1993; Neumann-Malkau, 1993). The emphasis on an instant exterior effect occurs also in the Czech Republic, and even in the UK, where up to the last decade of 20th century herbaceous cover had been preferred. At the same time, a number of authors report failures in establishment of trees, severe plant losses and their weak growth at the reclaimed mining waste dumps due to various reasons, such as adverse physical and chemical properties of waste material as a substrate for plant growth, low nutrient availability, unstable composition, coarse grain size, inappropriate water balance

and waste acidification (Hutnik and Davis, 1978; Kerth, 1988; Kerth and Wiggering, 1990; Neumann-Malkau, 1993). This disqualifies dumping sites as areas of productive wood resources. The satisfactory insulation role of the top encapsulation against water and air penetration into the dump, as well as against water and wind erosion, and its cost-effectiveness, requires minimization of the vegetative layer thickness, which is not suitable for the root system of high plants. In general, topsoil cover for vegetation support is not available; therefore the plants have to be introduced directly on the waste material, which in the exposed, not heavily compacted top layer is particularly susceptible to adverse transformations and acidification. This suggests an application of herbaceous cover, in particular for support of natural processes of soil formation, prevention of erosion and reduction of water infiltration (through evapotranspiration). In biological reclamation practice, a parallel application of sodding and trees planting in the same area is quite frequent, which creates an inappropriate competition. The natural invasion and succession of high pioneer species, which could damage the drainage or the infiltration barrier, should be taken into account in the design and construction of cover layers. The designed vegetation should thus consider the prospective status with respect to the environmental safety and fire control requirements (for coal mining waste) towards encapsulation tightness for water and air. Unsealing of the dump cover by the deep penetrating root system threatens also the plant due to easy access of reagents, i.e. air and water, for acid generation and self-ignition of coal mining waste as a result of the exothermic process of sulfide oxidation. Some proposed methods either reduce the risk of self-ignition of coal mining waste (e.g. compaction in squares) or vegetative layer acidification by addition of buffering materials, but do not control infiltration and acidification of the deeper waste layers. In each case, the selection of plant species should be waste-, site- and use-specific and consider also both negative and positive role of the naturally invading plant species. They are generally in much better shape, than varieties planted with or without use of topsoil. In Polish climatic conditions the natural invaders comprise *Betula* sp., *Populus tremula* L., *Salix* sp. and *Robinia* sp., which effectively compete with planted species (Patrzalek et al., 1993). The present state of reclamation practice shows that stress on returning the land to a high rate of productivity and the primary mode of use is generally unrealistic, expensive and often environmentally unsafe.

The biological reclamation regulations and practice in the United States are, to a much greater degree, incorporated into the complex mine waste management activities focused on minimization of the damage to the environment. The restoration of high productivity or a primary use is not a priority. Vegetation is considered as a component of the top layer of the surface encapsulation; in the inappropriate climate conditions the alternative can be an armoring layer of gravel-size material.

The EPA provides information concerning plant species, cultivation and areas of adaptation (EPA, 1983c) that are still in force. The general requirements reflect the approach to tasks and the function of the introduced vegetation (Hutchinson and Ellison, 1992):

- perennial, locally adapted and resistant to the unfavorable conditions (temperature extremes, low-nutrient soil, little or no maintenance),
- of sufficient density to minimize cover erosion,
- with the shallow root system that will not disrupt the drainage or the infiltration barrier.

For this reason, the use of tall plants (shrubs or trees) is not recommended due to deep penetration of a root system and a threat of drainage and barrier layer damage. In contrast to planting trees at close spacing practiced in Germany and still being in wide use in Poland, the perennial herbaceous cover, sometimes in combination with wider spacing of trees where applicable, is a common practice in mining waste dumping sites in the USA. It should be added, that also in Poland, the establishing herbaceous cover at the dump surface (predominantly without topsoil) as a cost-effective, efficient and environmentally sound solution gradually became a common dump re-vegetation practice, though still not without problems of a different kind.

V1.6.7. Monitoring strategies

Monitoring is an essential part of management of mining waste units. As ground and surfacewater are the most endangered compartment of the environment in the area of dumping sites, every mining waste dump or other industrial waste disposal facility, in particular the dumps sited in the area of the major groundwater basins (MGWB) and usable horizons of groundwater (UHGW) and in the river valleys, should have an adequate groundwater and/or surfacewater life-cycle monitoring program. Such programs should be capable of early detection of the threat to the beneficial use of water resources and provide documentation about the extent of the threat before it actually occurs. This concept provides an early alert for taking remedial actions, which greatly reduces the potential for loss of recoverable water resources. Besides water, other compartments of the environment should also be included in the monitoring program, if a proven risk occurs.

Essential components of the aquatic environment monitoring program are: (i) background studies to identify the primary environmental parameters and define the environmental values to be protected in the dumping site area, in particular water resources. The results of the studies serve as reference values in case of newly established dumping sites; (ii) the vadose zone life-cycle monitoring/screening to provide early means to detect a risk, and subsequently, undertake a remedial action before the contaminants degrade the recoverable water resources; and (iii) the saturated zone life-cycle monitoring up-gradient and down-gradient of the dump to determine site impacts, validate short- and long-term prognosis and effectiveness of prevention/remediation strategies in the dumping site. The scope of parameters to be incorporated into the monitoring program should be based: (i) on the waste characteristics determining potential for the receiving water deterioration from macro- and trace component generation and release from the disposed mining waste and (ii) the pathways of the constituents generation, interaction and migration in the anthropogenic (dump) and natural (bedrock) vadose and saturated zones in the actual hydrogeological and hydrologic conditions.

The guidelines for the design and operation of the monitoring systems for the vadose and saturated zones presented in comprehensive handbooks, are recommended for further reading (EPA, 1986; Hutchinson and Ellison, 1992; Sara, 1994; Wilson, 1995; Wilson et al., 1995; Looney and Falta, 2000; Nielsen, 2000; Boulding and Ginn, 2003). These books discuss basic principles of vadose and saturated zone hydrology, prevailing monitoring techniques and installation of monitoring devices, as well as operational and analytical details. The design of direct (sampling) and indirect (non-sampling) monitoring

systems specific for mine waste management units, including in-waste, vadose zone and groundwater monitoring is discussed in the guidelines edited by Hutchinson and Ellison (1992). The monitoring issues addressed there focus on locating monitoring points in the monitored media, selecting monitoring equipment and determining monitoring parameters required to provide an early alert for assessment of threat and taking remedial actions, along with limitations of the methods. The prevalent methods are focused on obtaining a profile of soil moisture content, suction and other details of water balance and transport within the dump. A limitation of the in-waste and natural vadose zone monitoring is a high probability of false-negative readings in all point- and non-point sampling methods. False-positive readings are evaluated as of a low probability, or even unlikely (for direct point sampling methods). Also field sampling, which entails drilling for core samples and subjecting them to laboratory tests to determine density, void ratio, soil moisture content and soil moisture suction is considered as an alternative. To determine chemistry of seepage, batch or column leach laboratory testing methods are recommended.

The authors of this chapter (Twardowska et al., 1988; Twardowska and Szczepańska, 1990; Szczepańska and Twardowska, 1999) have, for a more than decade, routinely used drilling and core sampling along the dump for screening the water balance, and also for pressure extraction (under nitrogen) of pore solution from the core. The pore solution is analyzed for its chemical composition by ICP-OES or ICP-MS. For the high-volume non-hazardous waste dumping sites, where no surface synthetic liners are used, we regard this method as highly reliable and informative. It provides direct data on the vertical redistribution of contaminant loads in the vadose zone and transformations of chemical composition of pore solution vs. water exchange rate in the waste layers. Several examples of basic hydrochemical profiles of pore solutions at different characteristic coal mining dumping sites have been presented and discussed in Chapter III.6. On the basis of own experience, the authors recommend this method for wide use for in-site screening (see also Chapter IV.5).

The application of commonly used biological test systems for the environmental monitoring of waters affected by the leachate from mining waste is not possible due to often high acidity and iron content, and lack of nutrients. Nevertheless, successful development of new bioassays based on organisms native to acidic mining lakes has been recently reported (Picki et al., 2003). This opens the prospects of extending biological testing on this specific kind of waste, provided that these organisms are adequately sensitive to typical pollutants occurring in ARD-affected waters.

With respect to the major parameters to be analyzed in sulfidic mining wastes, pH and sulfate concentrations in the pore solution are the basic indicators of acid generation, while concentrations of calcium and magnesium indicate buffering capacity of the material. Chloride balanced by sodium is the major indicator of the water-exchange process in the dump constructed from waste of high or moderate salinity. Aluminum is a common ion in the first stage of waste acidification, while silica along with re-appeared alkalis indicate deep acidification of the material. Of trace metals, iron, manganese and zinc are abundant components of the pore solution of poorly buffered waste. Zinc frequently becomes a macro component of ARD. Other compounds commonly present in acid pore solution of mining waste in higher concentrations include lead, copper, cadmium, arsenic and selenium, and other heavy metals specific for a mined metalliferous ore or coal. These compounds, in addition to pH, Eh and conductivity should be analyzed in a life-cycle

monitoring of the vadose and saturated zone in the vicinity of a dump. The practice of monitoring shows that the highest pollution potential from the mining waste dump to the aquatic environment caused by acidification and high heavy metal release commonly lags behind the start of acid generation and sulfate release and occurs in the post-closure period. This confirms the requirement for life-cycle vadose zone and groundwater monitoring in the vicinity of the mining waste dump.

Formerly, this delayed adverse environmental impact was not taken into consideration in Polish mining areas, therefore monitoring terminated after the dump closure. The monitoring itself was rare, if any, in the vicinity of non-hazardous mining waste dumps, which were considered harmless on the basis of compound concentrations in 1:10 water extract from freshly generated waste. Currently, as a result of the growing consciousness of the delayed and non-linear increase of pollution potential from these facilities, the life-cycle monitoring becomes an obligatory component of the dumping site project and maintenance that comprises also 30 years' post-closure period (Directive of the Minister of Environment, 2002).

More detailed discussion of monitoring issues related to mining waste is addressed in Chapter IV.5.

V1.6.8. Public opinion

Due to the precondition of acceptance of a local community for getting a localization permit for a waste disposal site from the Environmental Departments of the district administration, the role of public opinion has a substantial impact on siting a project (Environment Protection Act, 2001). Thickly populated mining areas and severe shortage of places for waste landfilling brought about the necessity of dump location in close proximity to settlements and farms. Though the members of the local communities are traditionally connected with mining, the "not-in-my-backyard" syndrome makes requirements for siting, constructing and managing dumping areas more stringent. Public opinion is extremely sensitive to aesthetics and to the way a facility is used. In general, there is no interest and firm rejection by the former owners, and lack of potential new candidates for continuation of the primary production in the rehabilitated formerly agricultural land. The final shape of batter re-vegetated as a first stage with herbaceous cover and a target use of a disposal area for recreation or even as aesthetic barrens become the preferable way of high-volume mining waste disposal site management in Poland.

V1.6.9. Underground disposal and reuse

V1.6.9.1. Disposal strategies

In recent years, a shortage of available land for high-volume mining waste disposal, and its environmental burden, as well as high economic and social costs, have resulted in an increasing pressure of administration and public opinion against the surface methods of waste landfilling. Simultaneously, a concern about severe surface deformations in

a thickly populated area caused by subsidence brings about the need of stowing underground mine workings. This promotes a long-known method of mining waste use for filling goafs, disused mine workings and abandoned mines as an ideal solution. The additional pro-environmental aspect of this method is a decrease of the land damage by quarrying natural material (sand, gravel) used for backfilling (stowing), besides an adequate reduction of mining waste disposal at the surface and control of subsidence. In the Polish environmental strategy, increase of stowing of underground workings with use of coal mining waste is considered as a priority for mining waste management in the USCB. The amount of mining waste used underground by the end of 1994 was estimated to be at least 100 Mt. The annual amount of mining waste utilized underground as an additive to the sand stowing in 65 collieries of the USCB in 1990, 1993 and 1994 was 4.2–5.1 Mt or ~23% of the total mining waste reuse and it did not show an increasing trend (State Inspectorate of Environmental Protection, 1995). In 1994–1995, a regress of this way of coal mining waste use occurred. The annual rate of mining waste use underground dropped to 3.1–3.8 Mt, which amounted to 12.1% of the total amount utilized. The rate of coal mining waste directed for stowing did not exceed 7.4% of the total amount generated by coal mining, while the amount of mining waste utilized at the surface was continuously growing (State Inspectorate of Environmental Protection, 1997). In 1998, the rate of mining waste utilization reached 69.5% of the total amount generated (Central Statistical Office, 1999), while in 2001 it was already 89.1%, of this coal mining waste were used in 91.0% (Central Statistical Office, 2002). The predominant field of mining waste use is in engineering construction as common fill, where these wastes are often even more vulnerable to the adverse weathering processes than in the dumping sites. The major reason for limited use of mining waste underground is that the coal companies responsible for the environmental strategy of mines, consider costs of mining waste use for backfilling of mine workings still too high compared to surface utilization and disposal (State Inspectorate of Environmental Protection, 1997). An additional technical reason for limited use of mining waste for backfilling is its relatively high compressibility compared to sand (Skarżyńska, 1995); therefore it can be used as an additive to sand in proportions up to 30–40% wt.

V1.6.9.2. Legislative and regulatory framework

In general, Polish regulations and the Geological and Mining Law of 1994 amended in 2001 do not restrict use, disposal and storage in mine workings of any waste that is not qualified as hazardous, if the environmental and technological requirements are fulfilled, a legal permit for use, disposal or storage is obtained and adequate fees for disposal and storage paid (waste use underground is free of charge). Technological requirements are defined in the Polish Standards PN-93/G-11010 "Mining. Materials for Hydraulic Filling. Specifications and Tests" (PKN, 1994). Environmental requirements, also with respect to the mining waste, comprise the compulsory EIA. Unfortunately, up to now there is no standard testing procedure for evaluating a potential risk to the environment during the reuse or disposal of waste materials. This results in a frequently simplified approach to the evaluation of waste leaching behavior, which is based on the analysis of water extracts according to compliance tests (EN 12457-1/2/3/4). An up-to-date approach to

characterization of waste leaching behavior discussed in Chapter III.1 considers the use of a complex testing procedure, which much better reflects the short- and long-term risk from waste to the aquatic environment. After final development by CEN/TC 292 of a standard testing procedure for environmental risk assessment from granular wastes and its approval as a European Standard, it will have the status of a national standard without any alteration in the CEN members and affiliated countries, among them Poland. This should greatly improve the reliability of the risk evaluation, provided these Standards will be acknowledged to be obligatory for use by an adequate governmental Directive. At the present stage, the confidence in the environmental risk assessment from the disposed waste based on the water extract is highly problematic.

Mining waste disposal at the surface is covered in Poland by the Waste Act of 2001, and the relevant regulations.

According to the USA regulations, the mining waste backfilling falls under the US-EPA Underground Injection Control (UIC) Regulatory Program of 1981 and the SDWA — Safe Drinking Water Act of 1974.

At the European Union, there is no specific Mining Law or legislation on waste from mining and processing of minerals, thus all relevant directives and regulations on waste are applicable also to mining waste, while the Member States use their national legislation. Recent mining accidents in Spain (Aznalcòllar accident in 1998) and in Romania (Baia Mare accident in 2000) that endangered aquatic and terrestrial environment, have induced the European Commission to issue a document COM(2000)624 final that sets priority actions related to the safety of mines, management of mining waste and integrated pollution prevention and control. These actions comprise the following initiatives:

- Amend the Seveso II Directive to include mineral processing of ores and in particular, tailing ponds and dams used in connection with mineral processing of ores.
- Develop guidelines on management of mining waste covering the environmental issues as well as the best practices, which could prevent environmental damage during the waste management phase.
- Develop a best available techniques reference document (BREF) on waste management to reduce current pollution and to prevent or mitigate accidents in the mining sector.

On the basis of these initiatives, the EC Environment Directorate General started a public consultation process on a working document related to the management of waste resulting from prospecting, extraction, treatment and storage of mineral resources (EC DG ENV A2/LM, 2002).

More information on these initiatives can be found in the EU websites listed in the references. It should be added that though the EU plays a modest role in the global mineral mining industry, it still has 1872 inventoried mining sites, of that 347 for non-ferrous metal extraction, most of them in France, and 578 coal mines, mostly in Belgium (all closed) (BRGM, 2001). Despite the fact that only 917 sites, i.e. 49% are still under operation, closed mines and waste dumping sites often continue to generate contaminants.

The EU legislation relevant to mining and environmental aspects of these activities, and the regulations of several other countries with developed mining industry (Canada, the USA, Australia, Mexico, Malaysia) are referred in BRGM report (2001).

V1.6.9.3. Environmental implications

Proponents of utilization mining waste for mine backfilling, besides stressing the environmentally beneficial protection of the surface against damage due to the structural support of undermined areas and reduction of surface waste disposal, also stress on the returning of the rock material to its original environment. It should be taken into consideration that during mining and processing, rock material undergoes significant physical and chemical transformations (decrease of grain size, increase of the exposed surface and hydraulic conductivity, temporary exposure to oxic conditions and high humidity). These can result in a higher degree of decomposition of unstable minerals (e.g. sulfides) and enhance material susceptibility to contaminant leaching.

The results of studies reported by Levens and Boldt (1994), indeed showed definitely higher concentrations of almost all dissolved elements in leachate from lead–zinc mine waste backfill compared to the recharge water quality. Some of them occasionally or permanently exceeded MCL, set forth in the Safe Drinking Water Act (As, Fe, Mn, Pb, SO_4), but were lower than concentrations detected in the worst acid drainage of the mine. Concentrations of major ions (SO_4^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}) in leachate, in conjunction with near-neutral pH values (pH 6.89–7.79) gave evidence of sulfide oxidation and acid generation, buffered by carbonate dissolution. Due to buffering, only SO_4^{2-} concentrations (340.0–1140.6 mg/l) consistently exceeded the MCL values (250 mg/l), while contents of heavy metals were low. The authors assume, that after the mine closure when the backfilled stope is flooded, the rate of oxidation of sulfide minerals and associated mineral dissolution will be much lower. Therefore, the contamination potential of the backfill will be greatly reduced, though metals already contained in secondary minerals may be released after the backfill is submerged. The overall impact of this specific backfilled stope has been evaluated as small.

Another example referred to the dual beneficial effects of using colliery spoil rock paste to fill the collapsing limestone mines, which has given rise to a general subsidence or localized surface damage (Jarvis and Braithwaite, 1994).

These examples indeed prove the benefits from reuse of mining waste material for the bulk backfilling (stowing) of underground mine workings. At the same time they also show the need of the site-specific approach to the reuse of mining waste underground, to avoid any threat of contamination of the groundwater by the material, which might be geochemically unstable.

V1.6.10. Conclusions

The environmental implications and practices of mine waste disposal lead to the following general conclusions:

1. Mining waste disposal sites, due to the concentration of large volumes of geochemically unstable (mainly sulfidic) material in relatively limited areas, and usually a long period of construction, should be treated as a potential source of a long-term aquatic environment contamination, which may display non-linear, time-delayed maximum release of contaminants in the post-closure period. The dumping site design should thus be based on the long-term prognosis and ensure reliability and persistence

of environmental protection measures during construction and after closure with little or no maintenance for an adequately long period.

2. The design of waste disposal units should be waste-specific and consider also site-specific conditions, such as climate, hydrogeological conditions and site factors, defining the categorical design criteria and environmental protection measures.
3. The sulfidic waste dump design during construction and after closure should be focused on the prevention of air penetration and water infiltration through the dump and limitation of waste exposure to the atmosphere. The management practices of all kinds, from the methods of placement and schedule to the top layer re-vegetation have to be in concert and consider predominantly surface interception, a passive-care approach and use of adequate chemical or/and physical properties of the waste to reduce risk to the environment. Bottom liners and active-care approach should be applied only in exceptional situations.
4. Engineering constructions from mining waste exposed to the atmospheric conditions should be treated the same way as waste disposal units with respect to EIA, preventive measures and monitoring requirements.
5. Monitoring systems have to provide an early alert for taking remedial actions: the potential costs and degradation of recoverable water resources can be thus greatly reduced. One of the best direct sources of information on actual contaminant generation and transport is quantitative and qualitative analysis of pore solution along the dump and a bedrock profile (anthropogenic and natural vadose zone).
6. The reuse of mining waste for backfilling of underground mine workings provides a triple benefit of reducing surface waste disposal, protecting against deterioration of recoverable groundwater resources and conservation of the undermined land endangered by subsidence. Due to transformation of physiochemical properties of the rock material due to crushing and exposure for some time to the atmospheric conditions, even in the case of returning waste rock to the original excavation, the assessment of potential impact of backfilling material on the groundwater quality should precede its reuse.

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VI.7

Use of selected waste materials and biofertilizers for industrial solid waste reclamation

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VI.7.1. Introduction

Industrial projects have profound influence on society and environment, resulting in benefits, risks and hazards. They bring in their wake the concomitant ills of environmental pollution, depletion of resources, overcrowding, effects on human health, desecration of forests and aesthetic nuisance.

During the last decade there has been increasing concern regarding the disposal of industrial solid wastes at landfill sites. Capital costs and uncertain markets have limited prospects for use of solid wastes for other purposes. Due to the high content of organic matter in some industrial solid wastes only composting and land application are attractive alternatives for their disposal. Organic constituents in these waste materials are potential soil conditioners. The use of these solid waste materials as organic amendments to reclaim mine dumps and other types of wastelands has shown numerous benefits in terms of increased plant growth and yield, improved soil moisture retention, increased cation exchange capacity and better soil nutrient retention.

Solid waste generated in India may be classified under several principal generic categories such as crop residues, farm wastes, industrial wastes, forest products, municipal solid wastes, municipal sewage sludge, animal wastes, marine products, silvicultural energy farm products and aquatic biomass. Industrial solid wastes include wastes from mining, sugar, fermentation, pulp and paper, pharmaceutical industries and most significantly the hazardous and radioactive solid wastes. A considerable amount of solid waste is generated in the various stages of pulp and papermaking. The total annual paper production for 1999 in India was reported to be 3.795 Mt (million tons) that accounts for 1.2% of global production (FAO, 2001a). An integrated large mill having a turnover of 100 t/day discharges wastes of 50–60 t of lime sludge, 5–6 t of bamboo/wood dust, 3–4 t of fiber fines, in addition to about 60 t of coal ash (Bellamy et al., 1995). Handling and disposing of such materials is a continuous problem for the industry. The management of such a huge quantity of paper sludge is essential and requires proper planning for its utilization and disposal. Being rich in cellulose content, if dumped it may cause severe hazard to the environment.

Another waste of growing concern is the sugar industry waste. There are nearly about 300–500 small- and large-scale sugar industries functioning in India. In 2000 they

produced 18.94 Mt of raw sugar that gave India the unquestionable leading position in the world with 14.9% of the global production (FAO, 2001b,c). In the last decade (since 1991), the raw sugar production in India increased to 67% (FAO, 1998, 2001b,c). This reflects a scale of the problem concerning sugar industry waste management. On an average, 200 t of pressmud is produced per day by the sugar industry. Molasses, a by-product of the sugar industry has already earned commercial value and is extensively used for resource recovery through the fermentation route. Pressmud is rich in nitrogen, phosphorus and potassium and also has significant sugar content. Disposal of pressmud at landfill sites without any treatment and planning may cause an environmental hazard.

The mine waste generated from the mining industry poses serious environmental problems to the ecosystem. In India, 707,000 ha of area was used for mining and 1.677 Mt of manganese, 58.3 Mt of iron and 264.4 Mt of coal were produced in 1995 (Indian Bureau of Mines, 1995). Coal production shows particularly high dynamics. In 2000, India produced 310 Mt of coal that was used for generating about 66% of the national power production (World Coal Institute, 2000), with planned further fast growth. Coal demand is expected to double to 890 Mt/yr by 2010 (Gale, 1999); estimated coal consumption will reach 725 Mt/yr in 2011–2012 (Prasad et al., 2000). There is also a progressive worldwide increase in metalliferous mining in recent years underpinned by social, economic and technological demand (United Nations, 1991, 1992, 1998, 1999, 2000).

The mining industry turns large areas of land into barren dumps. In the typical Indian barren mine waste dump that consists of overburden and run-off mine spoil, which is full of stone and boulders, the only carbon source for microbial utilization is the plant biomass that is expected to accumulate over several growing seasons on the site. The large-scale opencast mining affects the quality of natural soil. The removal of organic surface soil during the mining process substantially reduces the *fertility* and water, as well as nutrient retention properties of the soil.

Industrial solid waste reclamation measures are therefore considered to be an integral part of industrial solid waste disposal, planning and management. Among the industrial solid wastes, reclamation of the mine waste from the mining industry requires innovative techniques that reduce costs and increase the chances of plant establishment and survival. Essentially the mine waste reclamation objectives are directed towards the long-term stability of the land surface which ensures that there is no surface erosion by water or wind, reduction of leaching throughputs, lessening the amounts of potentially toxic elements released into local water courses and to groundwater, development of a vegetated landscape or ecosystem in harmony with the surrounding environment and with some positive value in an aesthetic productivity or nature conservation context.

VI.7.2. Constraints in mine waste reclamation

The reasons that mine wastes present difficulties for plant growth is from a combination of their physical, chemical or biological properties. The absence of an organic fraction in surface layers adds to the prevention of plant growth. Organic matter, which crucially contributes to the soil structure, provides a reservoir of macronutrients and a resource for invertebrates and microorganisms.

The physical constraints of mine waste reclamation accounts for the unfavorable porosity, aeration, water infiltration and percolation properties, along with a high bulk density and absence of structural aggregates leading to water and wind erosion of unprotected disused land surfaces. The other growth limiting factors include mine land temperature and deteriorating groundwater level.

The chemical constraints involve the extremes of spoil pH, and a low concentration of essential plant macro and micronutrients, viz. nitrogen, phosphorus, potassium, calcium and magnesium. Nitrogen levels are invariably inadequate for plant growth, phosphorus levels are generally very low; and deficiencies of potassium, calcium and magnesium also may occur (Williamson et al., 1982). The high concentrations of heavy metals in some mine waste also have a deleterious effect on plant growth.

Biological constraints include the absence of beneficial microorganisms, which play an important role in restoring the physico-chemical and biological properties of spoil. The microorganisms contribute to the development of mine waste structure, synthesis of plant nutrients through the mediation of various biogeochemical cycles and amelioration of adverse chemical and physical limitations. The potential microsymbionts such as nitrogen fixers are associated with rhizosphere of plants. Moreover, mycorrhizal fungi are responsible for mobilization of nutrients, especially on nutritionally poor soils while phosphate solubilizers are responsible for the solubilization and mineralization of insoluble phosphates in soil. Therefore, to establish or to restore the biogeochemical cycles, it is essential to develop suitable strains of microflora as the mine waste is devoid of microorganisms. The mine waste cannot support the proliferation of microbes due to the poor nutritional and adverse physical conditions of spore such as extreme temperature and variable pH. Mine waste may be devoid of or have limited microbially mediated processes due to the abiotic properties of mine lands that include low moisture status, widely fluctuating temperature, soil physico-chemical factors such as extremes of pH and low levels of organic matter (Tate and Kerin, 1985).

The reclamation scheme that is adopted should be effective in ameliorating all the constraints with successful utilization of mine waste for developing a vegetative canopy on barren lands and thus restoring the mine waste productivity and fertility.

VI.7.3. Phytoreclamation: a holistic approach

Reclamation with chemical fertilizers is expensive and requires intensive management and annual fertilizer additions for several years.

In undisturbed ecosystems primary production, decomposition and nutrient cycling are the main processes for the stability of the ecosystem. Therefore, the rapid re-establishment of the primary producers on disturbed land should be the main aim of a reclamation program. Once the vegetation is established, the rate at which essential nutrients are released from dead plant residues and returned to the plant system, and the rate of stable organic matter accumulation on these disturbed systems will largely be a function of biological characteristics of the mine waste. The soil microbial biomass and plant residues both are sources of carbon, nitrogen, sulfur and phosphorus. Further, due to high metabolic and reproductive rates, the soil microorganisms also have the capability to rapidly

immobilize nutrients that would otherwise be lost through leaching. Soil microbes also exhibit great metabolic versatility that allows them to adapt to the low nutrient levels and adverse chemical and physical characteristics of many mine wastes (Wali, 1979; Ellewood et al., 1980). Since mine waste often lacks such key nutrients as nitrogen and phosphorus, it is essential to utilize symbiotic microorganisms (i.e. nitrogen-fixing bacteria and mycorrhizal fungi) for improving the nutrient status of plants used to colonize mine wastes.

The technology of phytoreclamation envisages spreading of a specially blended organic material containing high percentage of organic matter, usually solid wastes from industries and inorganic fertilizers like N, P and K on the surface of dumped overburdens. Instead of chemical organic fertilizers, biofertilizers like *Rhizobium*, *Azotobacter*, *Azospirillum*, phosphate solubilizers and mycorrhiza can be used, which when added to the spoil have a special advantage. They fix atmospheric nitrogen and mobilize essential macronutrients making it easily accessible to plants. This approach helps to achieve the fertility of the post mining land (barren dumps) in a short time, thus improving the water holding capacity of the spoil and enables creation of topsoil to sustain high quality vegetation.

Phytoreclamation can be made successful by identification of constraints and resolving them by careful selection of plant species, appropriate amendment and selective microorganisms as biofertilizers. Therefore, phytoreclamation seems to be an attractive and cost-effective alternative for revegetating barren mine waste.

VI.7.3.1. Use of organic waste as amendment for improvement of the nutrient status of spoil

Organic matter in the form of waste materials offers great advantage in redevelopment of drastically disturbed soils. Direct stimulation of plant growth on mine waste results from mineralization of plant nutrients contained in the organic matter. The level of organic matter in the soil is a result of the balance between biomass synthesis and mineralization. Stroo and Jencks (1982) found that recovery of microbial activity in mine spoil was directly related to organic matter and nitrogen accumulation. Immediately following amendment, the microbial respiration in the spoil increases and respiration rate declines to the low level as the readily degradable carbon sources are exhausted. This is followed by slow mineralization of the more biodegradation-resistant carbon substrates. An extended period of microbial activity and increased fertility and soil organic matter levels compared with unamended soil, results from the slow decomposition of the biodegradation-resistant plant components and the slow turnover of humified carbon compounds. The time of these reactions extend over several decades or longer. This explains the slow development of soil structure in reclaimed mine soils (Schaffer et al., 1980). Buffering capacity, chelation and cation exchange properties of a soil are of prime importance in determination of toxicant availability in mine land soils as well as in leachates from disposal sites. Organic amendments rules out these properties.

For over two decades, reclamation of various mine waste disposal sites and other disturbed lands has been investigated or successfully implemented using different waste materials as organic amendments, e.g. cal-sag – a sediment from navigable water ways and organic waste from the city (Vanluik and Harrison, 1982), reused industrial orange waste (Correia et al., 1995), paper mill sludge (Feagley et al., 1994; Bellamy et al., 1995),

sewage sludge (Parkinson et al., 1980; Matcalf, 1984; Kooper and Sabey, 1986; Pietz et al., 1989; Danker et al., 2003) or other organic waste such as composted dairy manure, poultry litter and biosolids (Sloan and Cawthon, 2003), also as a mixture with inorganic waste such as powerplant fly ash in order to utilize their water holding capacity and potential of both waste materials to supply all the essential nutrients for plant growth. The generally positive results of investigations of such mixtures with fly ash have been reported recently, e.g. composted mixtures of orange peels, municipal compost (Alva et al., 1999a,b), biosolids (Yuncong et al., 2001), dairy manure, poultry litter and biosolids (Sloan and Cawthon, 2003) and sewage sludge (Bhumbla et al., 2001); the latter two mixtures were applied to mine soils.

The organic matter was found also to have regulating effect on the soil temperature. It delays the fixation of mineral phosphoric acid and supplies organic decomposition products that aid the growth. Moreover, it is a source of slow and uniformly active nitrogen and consequently has a beneficial influence on the protein content of the plant. By virtue of these properties organic matter often creates the conditions necessary for the successful use of inorganic fertilizers.

Through cooperation of organic waste materials that improve the soil properties on the one hand, and biofertilizers, which supply plant nutrient on the other, adequate environmental conditions can be provided for the selected plant species on the mine land.

VI.7.3.2. Bioreclamation with use of biofertilizers

The importance of using specialized biofertilizer cultures to improve the nitrogen fixation, mycorrhizal fungi for mobilization of plant nutrients, phosphate solubilizers and formation of aggregates of sand grains by fungi, bacteria, actinomycetes and algae highlights the need for an active microbial community in the mine waste in addition to the organic amendments.

VI.7.3.2.1. Role of biofertilizers in reclamation

Biofertilizers, a term which refers to microorganisms which either fix atmospheric N_2 into plant-usable forms or enhance the solubility of soil nutrients, are becoming increasingly important as a key component of the integrated plant nutrient supply system.

Use of biofertilizers in mine waste reclamation has advantage over chemical fertilizer because of the poor physical structure of spoil. High porosity of spoil leads to leaching of chemical fertilizer to the groundwater while biofertilizer remains with the rhizosphere of the plant.

Biological nitrogen fixation (BNF) offers an economically attractive and ecologically sound route for augmenting N-supplies. Thus, *Rhizobium* for legumes, blue-green algae and *Azolla* for wetland rice, *Azotobacter* and *Azospirillum* for several crops can play significant roles in revegetation. Biofertilizers cannot meet the total nutrient needs and are in fact one of the inputs that can be used along with other fertilizers. The N-fixing

biofertilizers make a net addition to N supplies by fixing atmospheric N for the soil–plant system. The estimated contribution of different biofertilizers is as follows:

1 t *Rhizobium* = 100 t N (50 kg N-fixed/yr/crop at 500 g/ha dose)
1 t *Azotobacter* = 40 t N (20 kg N-fixed/yr/crop at 500 g/ha dose)
1 t *Azospirillum* = 40 t N (20 kg N-fixed/yr/crop at 500 g/ha dose)
1 t BGA = 2 ton N (20 kg N-fixed/yr/crop at 10 g/ha dose)

BNF with its ability to capture an inexhaustible source of N at low capital cost must play an increasingly important role in revegetation, spoil improvement and yield sustainability.

Phosphatic biofertilizers help in increasing the solubility/availability of phosphate that is already present in the soil in sparingly soluble forms. They in a way deplete the soil P reserves but considering the low utilization efficiency of phosphatic fertilizers, P-solubilizing biofertilizers can play an important role in improving the efficiency of P residues left in the soil.

VI.7.3.2.2. Biodynamic influence and contribution of biofertilizers in mine land reclamation

A profile of different biofertilizers are given in Table VI.7.1 (after Molsara et al., 1995). Biofertilizers are known to make a number of positive contributions:

- Supplement fertilizer supplies for meeting the nutrient needs of plants;
- Can add 20–200 kg N/ha (by fixation) under optimum conditions and solubilize/mobilize 30–50 kg P_2O_5/ha;
- Liberate growth promoting substances and vitamins and help to maintain soil fertility;
- Suppress the incidence of pathogens and control diseases;
- Increase yield by 10–50%, N-fixers reduce depletion of soil nutrients and provide sustainability to the ecosystem;
- Are cheaper than conventional nitrogenous and phosphatic fertilizers, pollution-free and are based on renewable energy sources;
- Improve soil physical properties, tilt and soil health in general, and act as biological conditioners of soil;
- Can easily be transported.

In addition to the above nitrogen fixers and phosphate solubilizers, mycorrhizal inoculation to plants can help in alleviating stress conditions on mine sites.

VI.7.3.2.3. Effect of vesicular arbuscular mycorrhizae (VAM) on bioreclamation

Principally VAM are broadly classified as ectomycorrhizae and endomycorrhizae. They are obligate symbionts and have not been isolated in pure cultures; the only method to maintain them is by inoculating the specific species of plants with spores of VAM. The classification of VAM is based on spore morphology and cellular structure. Most common VAM belong to the following genera (Verma, 1995):

Table VI.7.1. A profile of different biofertilizers (after Molsara et al., 1995).

A. Biofertilizers that fix nitrogen

Biofertilizer	Function/contribution	Limitation	Used for crops
Rhizobium (symbiotic)	Fixation of 50–100 kg N/ha 10–35% increase in yield	Fixation only with legumes Visible effect not reflected in traditional area	Pulse legumes like chickpea, redgram, pea, lentil black gram, etc. Oil seed legumes like soybean and groundnut; forage legumes like clover and lucern
	Leaves residual nitrogen	Needs optimum P and Mo	Tree legumes like *Leucaena*, *D. sissoo*, Acacia, Cassia
Azotobacter (non-symbiotic) and *Azospirillum* (associative)	Fixation of 20–25 kg N/ha 10–15% increase in yield Production of growth promoting substances	Demands high organic matter	Wheat, maize, cotton, sorghum, sugarcane, pearl millet, rice, vegetables, several other crops and tree species such as teak, etc.
Blue-green algae or cyanobacteria (phototropic)	Fixation of 20–30 kg N/ha 10–15% increase in yield Production of growth promoting substances	Effective only in submerged rice Demands bright sunlight	Flooded rice
Azolla (symbiotic)	Fixation of 30–100 kg N/ha Yield increase 10–20%	Survival difficult at high temperature Great demand for phosphorus	Only for flooded rice

(continued)

Table VI.7.1. (Continued)

B. Biofertilizers that solubilize phosphorus		
Microorganisms	Important genus	Important species
Bacteria	*Bacillus*	*B. megaterium* var. *phosphaticum*
		B. circulans
		B. subtilis
		B. polymyxa
	Pseudomonas	*P. striata*
		P. liquifaciens
		P. putida
Fungi	*Aspergillus*	*A. awamori*
		A. fumigatus
		A. flavus
	Penicillium	*P. digitatum*
		P. lilacimum
Actinomycetes	*Streptomycetes*	

Genus	Example of species
Glomus	*G. fassiculatum, G. mosseae*
Gigaspora	*Gigaspora nigra*
Acaulospora	*A. scrobiculata*
Sclerocystis	*S. clavispora*
Endogone	*E. increseta*

The potential use of mycorrhizal fungi as biofertilizers, bioprotectors and their role in sustainable agriculture and soil fertility is fascinating. Mycorrhizae are universal symbionts and colonize the roots of over 90% of all plant species to the benefit of both plant and fungus. The hyphae of VAM penetrate the roots of host plants, form specialized structures within arbuscles and sometimes vesicles. Arbuscles are considered to be where transfer of nutrients (to the host) and carbon (to the fungus) takes place and vesicles to be organs of storage. Outside the root, hyphae form an extensive mycelium often extending several centimeters from the roots (Li et al., 1991). This serves as the primary organ for nutrient uptake and can also bear spores, which is a means of survival for these obligate symbionts (Fig. VI.7.1). VAM is recommended for use for forest trees, forage grasses, maize, millets, sorghum, barley and leguminous crops.

Well-known benefits of plant colonization by VAM include:

- Enhanced phosphorus nutrition by reducing fertilizer inputs (Harley and Smith, 1983);
- Enhanced uptake of potassium, sulfate, copper and zinc (Barea et al., 1991);
- Enhanced uptake of nitrate and ammonium from the soil (Barea et al., 1987, 1989);

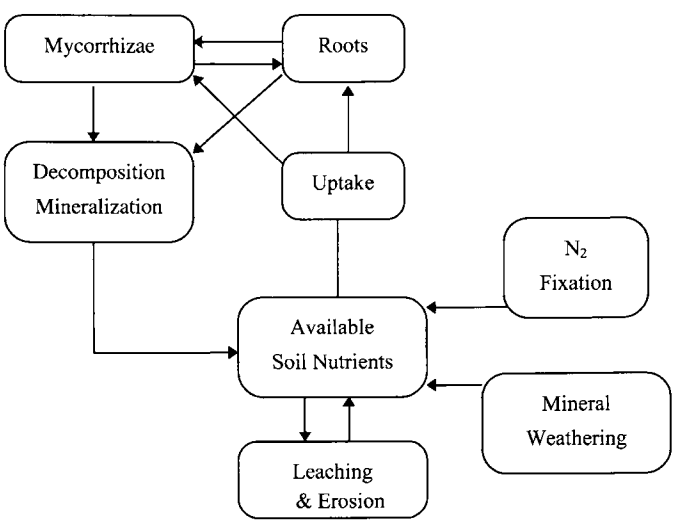


Figure VI.7.1. Role of VAM (after Li et al., 1991).

- Enhancing the nutrition of plants by developing profuse root system;
- Improving soil structure by binding soil particles and microaggregates by external mycelium (Miller and Jastrow, 1992);
- Biocontrol agent reducing the use of pesticides and enhancing resistance to root diseases;
- Reducing stunting on fumigated soil;
- Promoting more uniform crop, increases growth and yield;
- Helping for survival of plant in drought stressed conditions;
- Improving hardiness of transplanted stock.

The success of inoculation of biofertilizers in the field depends upon the production procedure used, product quality, application technique, presence of toxic agrochemicals and influence of soil environment.

VI.7.3.3. Bioreclamation of mine waste using biofertilizers

Realizing the problems of using chemical fertilizers for mine waste reclamation, attention has been diverted to an alternative source, i.e. biofertilizers. The role of biofertilizers in agriculture is well established (Desmukh, 1998; Sharma, 2002). There is a need to transfer these established technologies and practices in establishing forest plantations and reclaiming degraded lands. Potential benefits of microsymbionts such as mycorrhizal fungi responsible for phosphorus absorption, specially on nutritionally poor soils, nitrogen fixers (*Frankia*) associated with non-leguminous trees, micro-aerophillic nitrogen fixers (*Azospirillum*) associated with tropical grasses, free living nitrogen fixers (*Azotobacter*, *Beijerinckia* and *Derxia*, etc.) associated with rhizosphere of plants and phosphomicrobials responsible for solubilization and mobilization of phosphate in soil have not yet been fully exploited for wasteland development and forest production. At present evidence is still insufficient to justify the use of inoculants other than *Rhizobium* for legumes to increase the quality of soil and plants associated with forest.

The essential nature of mycorrhizae for the successful colonization of certain mine wastes was established by the landmark work of J.R. Schramm in the early 1960s. Since that time, research has been expanded to include vesicular–arbuscular (VA) and ericoid mycorrhizae and the development of techniques for inoculating host plants with fungi specifically adapted to coal mine wastes in the harsh conditions of extremes of temperature and low nitrogen. Other limiting factors comprise available phosphorus, and other nutrients such as zinc, copper and ammonium, water scarcity and extremes of pH values.

Schramm (1966) found that nearly all the successful colonizers of coal wastes in Pennsylvania were mycorrhizal. These included species of *Pinus*, *Betula*, *Populus* and *Salix*, and all of them were ectomycorrhizal.

Marx et al. (1984) used the concept of forming ectomycorrhizae on tree seedlings in nurseries with specific fungi ecologically adapted to the planting site, which was originally developed by Moser and further used by other researchers. Cited successful applications of this technique include improving field performance of *Pinus caribaea* inoculated with pure culture of *Suillus polorans*, and *Pinus radiata* inoculated with isolates of *Rhizopogon luteolus*, *Suillus granulatus*, *S. luteus* and *Cenococcum geophilum* in Australia. Marx et al. (1984) further refined the Moser's technique and reported good results in inoculating

bare-root nursery beds with *Pisolithus tinctorius*. Mycorrhizal seedlings of *P. caribaea* inoculated with *R. luteolus* were more robust, healthy and superior in height and dry matter production than the uninoculated seedlings. Investigations have also shown that inoculation of container grown oak seedlings with specific ectomycorrhizal fungi further improved seedlings survival and early growth in green house and field. Container grown black Oak (*Quercus velutina* Lam.) and pines seedlings colonized with *P. tinctorius* and Sawforth Oak inoculated with *Thelephora terrestris* survived and grew better than bare rooted stock on a reforestation site.

The adhesion of soil particles to roots in dry soil has been suggested as a mechanism to increase water conductivity (Coutts, 1982) and it may also function to enhance the movement of mobile ions such as nitrate. Hyphae of VA fungi may extend up to 0.8 m from the root surface (Rhodes and Gerdemann, 1975), but rhizomorphs of *Pisolithus* may extend 4 m into the soil (Schramm, 1966), a result that suggests ectomycorrhizae are better adapted to long distance transport than VA mycorrhizae.

Ten-year-old untreated coal tips in Scotland were successfully colonized by both grasses and dicotyledonous plants that all but one species (which was non-mycorrhizal) were infected with VA fungi (Daft and Nicolson, 1974).

The harsh procedures used to remove bitumen from sand mined in northern Alberta resulted in mine tailings that are completely devoid of mycorrhizal inoculum (Parkinson, 1979). Zak and Parkinson (1982) found that less than 1% of slender wheat-grass roots grown in untreated sand were infected after one growing season, whereas tailings amended with peat from a forested site resulted in 23% infection.

Lambert and Cole (1979) found the significant effect of pH and a kind of mine waste on VA mycorrhizal yield, when they studied five different vegetated mine wastes and a forest soil as inoculum for white clover in the greenhouse with the spoil adjusted to either pH 4.5 or 6.5. Although VA mycorrhizal infection rates were similar among the inoculation treatments, yield response varied four times at pH 4.5 and fivefold at pH 6.5 with different inocula.

Some mine wastes may contain high levels of potentially toxic metals. On the basis of pot experiments with adding copper and zinc to pots containing a clay loam soil and seeding with clover inoculated with either an isolate of *Glomus mosseae* from metal contaminated soil or an isolate from an agricultural soil, Gildon and Tinker (1981) have shown that VA mycorrhizal symbionts can become adapted to metal contaminated soils. They concluded that endophyte tolerance was important, implying that the mycorrhizal symbionts must be considered as a component of whole plant tolerance to potentially toxic metals.

In field crops and horticultural plants, growth stimulatory influence of VAM-fungi inoculants is well known. Effectiveness of these inoculants has not been clearly demonstrated in forest species except in *Liriodendron tulipifera*, *Agathus australis* and *Araucaria* species. VAM fungi infected plants, when grown in nutrient deficient soils, often produce greater dry weight than not infected plants. Significant enhancement in growth and dry weight of seedlings (*Fraxinus americina*) inoculated with *Glomus epigaeum* has been found even at low levels of root colonization. VAM fungi inoculation of *Glomus etunicatum* can successfully be introduced for producing seedling of *Leucaena leaucocephala* under low fertility levels. Growth and nutrient uptake by *Sesbania grandiflora* was improved when sterile soil was inoculated with *Glomus fassiculatum* and to lesser extent by *G. mosseae*. Due to VAM fungi inoculation, significant enhancement in

growth and survival of several other forest species, e.g. of cuttings of *Salix dasyalados* and *S. daphnoides* or flowering dog wood (*Cornus florida* L.) seedlings.

Growing information has been available concerning selection of *Rhizobium* strains and leguminous plants adopted for planting on mine wastes. The comparative efficiency of different legume species in building up nitrogen contents and increasing growth in a companion grass on mine wastes has been investigated. Introduction of free-living nitrogen fixing bacteria in the rhizosphere of revegetated perennial grass species on strip-mined land has been advocated. Many leguminous and non-leguminous plant species have been tried on coal and dolomite mine overburdens and bauxite mined out areas in Madhya Pradesh in India. The best performance was observed in the case of *Eucalyptus tereticornis* on coal mine overburdens. However, leguminous plants such as *Dalbergia sissoo*, *Albizzia procera*, *A. lebbek*, *Acacia auriculiformis* and *Acacia meliferia* are reported doing better then many non-leguminous plants (Dadhwal et al., 1995; Singh et al., 1995; Nikhil, 1999). At opencast mining sites, the nitrogen fixing trees (NFT) adapt to heavily disturbed soil system and at the same time grow faster to produce heavy foliage to cover the exposed sites.

Biofertilizers being a low cost technology may be advantageously used in wasteland development. Higher monetary return can be achieved with low expenditure as the inoculation cost comes to about Rs. 15–30/ha (Rs. 50 ≈US $1) by use of various inoculants marketed in India. In less productive soils where the plants are under stress in early growth period, application of 10–20 kg chemical nitrogen per hectare is required for initial growth and establishment of seedlings. *Rhizobia* can fix up to 80–100 kg nitrogen per hectare, equivalent to 90 kg of urea at just 40% of its cost. Findings from several field experiments revealed that less than a kilogram of high quality rhizobial inoculant, properly placed with legume seeds can replace more than 100 kg of nitrogenous fertilizers per hectare. Economically, the cost of application of *Rhizobium* culture comes out to be Rs. 0.30 per plant whereas equivalent dose of urea application is to cost about Rs. 2 per plant. *Azotobacter* culture inoculation can add 30–40 kg nitrogen per hectare per year. Several studies have demonstrated that the biofertilizer use (*Rhizobium*, *Azotobacter*, VA mycorrhizae) may provide a valuable and practical tool for achieving the desired end point of reclamation practices on mine wastes.

Here, an over decade's long experience with large-scale implementation in India of mine waste bioreclamation using the integrated biotechnological approach (IBA) has been discussed.

VI.7.4. Case studies: bioreclamation of the manganese and coal mine wastelands

National Environmental Engineering Research Institute (NEERI), Nagpur in collaboration with Manganese Ore India Limited (MOIL) and Coal India Limited (CIL) developed a reclamation strategy, which is environmentally compatible, economically viable and well suited to Indian conditions.

MOIL has six mines in Maharashtra state and four mines in Madhya Pradesh state and produces about 500,000 t of manganese ore per annum. Of the total ore production in the country, about 40% has been contributed by MOIL. The spoil generated in the mines is heaped at dumping ground that covers an area of 386 ha.

Western Coalfields Limited (WCL) is one of the eight subsidiary company of CIL contributing to about 11% of national coal production. WCL has mining operations spread over the states of Maharashtra and Madhya Pradesh. Of the 87 producing coal mines under WCL, 31 are opencast and 56 are underground with the total coal production of about 29.01 Mt and the overburden generation of about 59.39 Mm^3 (million cubic meters). The reclamation and revegetation project using IBA has been going on presently at five manganese ore mines, viz. Gumgaon, Chikia, Dongribuzurg, Tirodi and Mansar under MOIL and four coal mines Padmapur, Durgapur, Sasti and Umrer under WCL. Location of the reclamation sites under MOIL and WCL is depicted in Figure VI.7.2. Type of mining and areas under spoil dumps included into revegetation project are given in Table VI.7.2.

Below, the basic steps of the revegetation project, which started in early 1990s, have been briefly presented and discussed.

VI.7.4.1. Experimental plan

A detailed survey was carried out for spoil dump topography for landscaping at five mining areas under MOIL and four mining areas under WCL, which were under experiment. Spoil samples collected from the relevant sites were characterized with respect to the physico-chemical properties and microbiological characteristics. Barren manganese and coal mine waste dumps are shown in Figures VI.7.3 and VI.7.4, respectively. An approach plan was designed by NEERI for carrying out the reclamation work at different sites under MOIL and WCL (Fig. VI.7.5).

Physico-chemical properties of the dumped waste are presented in Tables VI.7.3 and VI.7.4. The manganese and coal mine wastes was a coarse material of pH values close to neutral or moderately alkaline; it contained low level of soluble salts indicated by conductivity of the water extract 1:10 in the range of 0.41–1.10 mS/cm. Organic matter content of spoil was very low, in the range of 0.08–0.13%. Similarly the nutrient status of both spoils in terms of NPK was poor. Both manganese mine waste and coal mine waste were deficient in nitrogen, which was in the range of 0.0004–0.0009%. The water holding capacity of the spoil was low and ranged from 7.6 to 8.0%.

The coal mine waste was characterized by the presence of heavy metals in the concentration sequence Mn > Zn > Pb > Cu > Cr. The manganese mine waste had high content of Mn (1275–2162 mg/kg) that was up to an order of magnitude higher than in coal mine waste whereas Cu > Ni > Pb were present in trace amounts. The higher bulk density and lower water holding capacity compared to soil, poor nutrient status, low organic carbon and texture of spoil were hostile for sustaining revegetation on the dumps. Hence, use of an organic amendment was essential to improve the physico-chemical and nutritive status of spoil. Ready availability, rich manurial value, non-toxic nature and low cost were the determinative factors for selection of an organic amendment. Keeping these factors in view, pressmud (a waste from sugar industry) and effluent treatment plant (ETP) sludge from pulp and paper industry were selected as ameliorants for manganese and coal mine waste dump reclamation, respectively (Tables VI.7.5 and VI.7.6). The pH of these ameliorants was moderately alkaline, around 8.0–8.2.



Figure VI.7.2. Location of mine sites selected for reclamation under MOIL and WCL.

VI.7.4.2. Laboratory studies

VI.7.4.2.1. Selection of the bedding material

The first step in the study comprised screening of the most appropriate blend of spoil and amendments in terms of their effect on the plant growth. In pot experiments conducted in three replicates, five different mixtures (in the proportions of ingredients by weight) were screened:

Table VI.7.2. Type of mining and areas under waste dumps included into revegetation project.

State/location of mines	Type of mining/type of waste	Area under waste dump (ha)
Manganese Ore India Limited		
Maharashtra state		
Chikia	UG	38.73
Dongribuzurg	OC	50.15
Gumgaon	UG	6.38
Mansar	OC	17.80
Madhya Pradesh		
Tirodi	OC	131.91
Total under project		244.97
Total under MOIL		386.40
Western Coalfields Limited		
Maharashtra state		
Durgapur	OB	29
Padmapur	OB	Nd
Sasti	OB	Nd
Umrer	OB	Nd

Type of manganese mine: UG, Underground; OC, Opencast.
Type of coal mine waste: OB, Overburden.
Nd, not defined.



Figure VI.7.3. Barren manganese mine waste dump.



Figure VI.7.4. Barren coal mine waste dump.

- T1 – mine waste only;
- T2 – 4 parts of mine waste + 1 part of topsoil;
- T3 – 4 parts of mine waste + 1 part of topsoil + pressmud/ETP sludge ≈ 25 t/ha;
- T4 – 4 parts of mine waste + 1 part of topsoil + pressmud/ETP sludge ≈ 50 t/ha;
- T5 – 4 parts of mine waste + 1 part of topsoil + pressmud/ETP sludge ≈ 100 t/ha.

The pots were planted with *Tectona grandis* (teak), *D. sissoo* (shishum), *Gmelina arborea* (shiwan) and *A. auriculiformis* (acacia) saplings of approximately the same recorded height 0.2 m. At the end of 3 months, the height of the saplings was measured. T5 treatment appeared to be the most responsive mixture: the teak and shiwan plant height increased sevenfold; the heights of shishum and acacia plant were 10-fold higher than the initial height (Fig. VI.7.6). Hence, T5 treatment was selected for further field trials.

VI.7.4.2.2. Screening of suitable plant species for plantation on mine waste dump

The growth response of plants depends upon the productivity of rhizosphere, physiological nature of plant species and climate. The presence of specific pollutants in the rhizosphere also play important role in growth performance of plants on such unfriendly area. Therefore, laboratory studies were carried out to screen and ascertain the suitability of different plant species to be grown in manganese mine waste dump and mined out area using previously selected T5 combination of bedding material (by weight) that consisted of 4 parts of mine waste + 1 part of topsoil + pressmud/ETP sludge ≈ 100 t/ha. The plant species screened for plantation at MOIL included:

Teak (*T. grandis*)
Shishum (*D. sissoo*)
Shiwan (*G. arborea*)
Neem (*Azadirachta indica*)

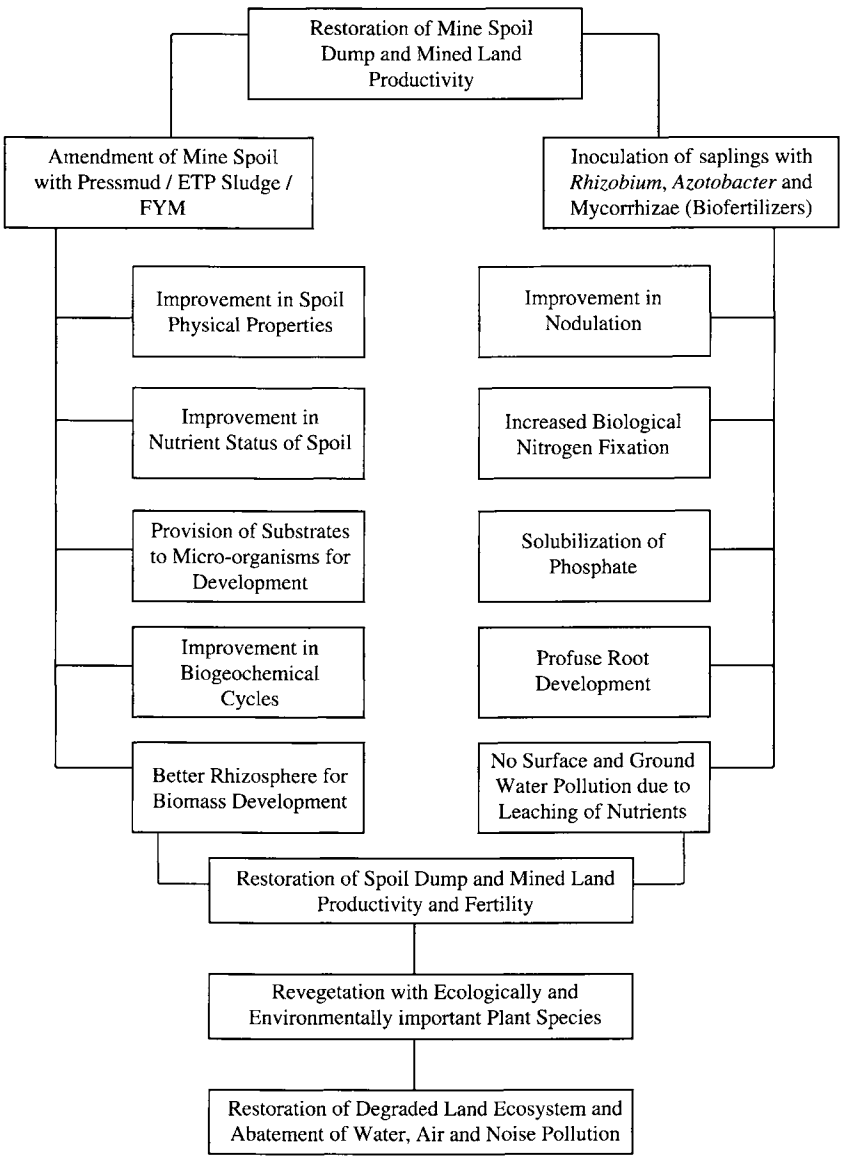


Figure VI.7.5. IBA developed for bioreclamation of mine waste dumps.

Karanj (*Pongamia pinnata*)
Australian babul (*A. auriculiformis*)
Cassia (*Cassia seamea*)
Subabul (*L. leucophala*)
Awala (*Emblica officinalis*)
Bamboo (*Dendrocalamus stirctus*)

Table VI.7.3. Physico-chemical properties of manganese mine waste.

Parameters	Range in mine waste
Textural classification (% wt)	
Stones and gravels	40–60
Sand	24–32
Silt	10–16
Clay	4–7
Chemical	
pH	7.0–7.5
Electric conductivity, ECe (mS/cm)	0.113–0.140
Heavy metals (mg/kg)	
Total Pb	10.2–20.0
Available Pb	0.002–0.004
Total Cu	25.0–55.0
Available Cu	0.002–0.004
Total Ni	25.5–38.5
Available Ni	0.003–0.010
Total Mn	1275–2162
Available Mn	1.30–6.30
Nutrients (% wt)	
Nitrogen, N	0.004–0.009
Phosphorus, P	0.005–0.007
Potassium, K	0.011–0.018

The plant species for plantation at WCL included:

Eucalyptus (*Eucalyptus hybhda*)
Neem (*A. indica*)
Teak (*T. grandis*)
Shiwan (*G. arborea*)
Shishum (*D. sissoo*)
Cassia (*C. semea*)
Gulmohar (*Delonix regia*)
Australian babul (*A. auriculiformis*)
Custard apple (*Annona squamosa*)
Peeple (*Ficus religiosa*)
Banyan (*Ficus bangalances*)
Awala (*E. officinalis*)
Tamarindus (*Tamahndus indica*)

VI.7.4.2.3. Isolation and identification of nitrogen fixing bacteria and VAM fungi

Although organic carbon is a major constituent of the nutrient supply, the other macronutrients, viz. nitrogen, phosphorus and potassium are also equally required. As the

Table VI.7.4. Physico-chemical properties of coal mine waste.

Parameters	Range in mine waste
Physical	
Bulk density (g/cm^3)	1.860–1.930
Maximum water holding capacity, WHC (%)	7.60–8.00
Porosity (%)	20.10–21.30
Chemical	
pH	7.80–8.10
Electric conductivity, ECe (mS/cm)	0.82–1.10
Organic carbon (%)	0.08–0.13
Water extractable ions 1:10 (meq/l)	
Na	1.30–1.70
K	0.08–0.09
Ca + Mg	6.80–7.50
HCO_3	4.10–4.40
Cl	4.40–5.20
Heavy metals (total), mg/kg	
Chromium	12.8–13.3
Copper	42.0–46.4
Lead	72.0–76.0
Manganese	210.0–214.0
Zinc	80.0–86.0
Nutrients (mg/100 g)	
Nitrogen, N	
Total	6.50–7.60
Available	0.70–0.80
Phosphorus, P	
Total	9.60–10.5
Available	0.40–0.50
Potassium, K	
Total	0.28–0.34
Available	0.09–0.12

plants are unable to uptake atmospheric nitrogen, a biocompatible approach was adopted by the use of nitrogen fixing bacteria to trap atmospheric nitrogen and make it readily accessible to plants. The use of endomycorrhizal fungi also has many fold advantages. Hence, VAM species were isolated, identified and used for bioreclamation studies of manganese mine waste dumps in combination with nitrogen fixing bacterial strains of *Rhizobium* and *Azotobacter*.

Two site-specific biofertilizer strains were isolated and identified. *Bradyrhizobium japonicum* strain BRS1, a slow grower strain was isolated from a healthy nodule of *D. sissoo*. The inoculation effect of BRS1 resulted in profuse root development and nodule formation in *D. sissoo* which is depicted in Figure VI.7.7.

Table VI.7.5. Characteristics of pressmud from sugar industry.

Parameters	Range in pressmud
Chemical	
pH	7.40–7.60
Organic carbon (%)	39.8–44.7
Heavy metals (mg/kg)	
Total Mn	1480.20–1970.50
Total Zn	237.50–285.40
Total Cu	112.40–131.70
Nutrients (% wt)	
Nitrogen, N	1.12–1.85
Phosphorus, P	4.72–6.25
Potassium, K	1.75–2.45

The *Azotobacter chroococum* strain TA1 was isolated from rhizospheric soil samples in the vicinity of roots of *T. grandis* growing nearby the mine site. The effect of TA1 inoculation on roots of bamboo plant is shown in Figure VI.7.8.

Spores of VAM fungi were extracted from the rhizospheric soil samples collected from vegetated areas nearby the barren sites by using 20 g soil and Wet Sieving and Decanting technique (Gerdman and Nicolson, 1963). The spores were identified, which belonged to *G. fasciculatum* (Fig. VI.7.9) and *Gigaspora gigantia* (Fig. VI.7.10).

To assess the metal tolerance of the isolates, the minimum inhibitory concentrations (MIC) of site-specific biofertilizer strains of BRS1 and TA1 for common heavy metal contaminants Cu, Fe, Mn and Zn were determined. The MIC determination was done on HM minimal media of Cole and Elkan (1973). The MIC of Mn, Zn, Cu and Fe for BRS1 were 410, 400, 120 and 70 μg/g. The MIC values for TA1 were somewhat lower and accounted for 360, 210, 65 and 55 μg/g, respectively.

VI.7.4.2.4. Inoculation of saplings with biofertilizers BRS1 and TA1 and VAM spores of VAMB1 and VAMB2

Root inoculation method was adapted to inoculate the saplings of plants with biofertilizer strains. An adhesive solution was prepared by dissolving 50 g of gum acacia and 100 g of sucrose per liter of water. To this, 500 ml of broth cultures of BRS1 and TA1 (liter value = 10^8 CFU/ml) were added separately to make slurry. Roots of leguminous plant saplings were dipped in BRS1 slurry while roots of non-leguminous plant saplings were dipped in TA1 slurry for 20 min and transplanted immediately into the pits. 10 g of mixed inoculum of *Glomus* and *Gigaspora* species (30 spores/g) was suspended in water and pipetted onto ordinary filter paper. Filter paper was rapped around the roots of saplings at the time of plantation into the pits.

Table VI.7.6. Characteristics of ETP sludge from paper mill.

Parameters	ETP sludge
Physical	
Bulk density (g/cc)	0.28–0.31
Maximum WHC (%)	170.4–174.0
Porosity (%)	60.10–62.08
Chemical	
pH	8.00–8.20
Electric conductivity, ECe (mS/cm)	1.40–1.60
Organic carbon (%)	39.6–42.2
Water extractable ions 1:10 (meq/l)	
Na	8.60–9.80
K	0.40–0.60
Ca	3.60–4.40
Mg	1.40–1.80
HCO_3	5.40–6.30
Cl	8.60–9.30
Heavy metals (total), mg/kg	
Chromium	12.6–34.2
Copper	44.8–47.6
Lead	65.0–79.2
Manganese	640.0–653.0
Zinc	253.0–302.0
Nutrients (mg/100 g)	
Nitrogen, N	
Total	106–110
Available	5.60–6.10
Phosphorus, P	
Total	390–410
Available	4.00–4.40
Potassium, K	
Total	1.67–1.72
Available	1.09–1.14

VI.7.4.3. Field studies

Based on the laboratory studies the technology was transferred for field trial at manganese and coal mine dumps.

In total, 222 ha of mine dumps at Gumgaon, Chikia, Dongribuzurg, Tirodi and Mansar under MOIL (72 ha) and Padmapur, Durgapur, Sasti and Umrer under WCL (150 ha) have been planted since early 1990s. For planting at top surface and on slopes of mine dumps, pitting technique was adapted and 2500 pits were dug per hectare. Pits at mine sites on

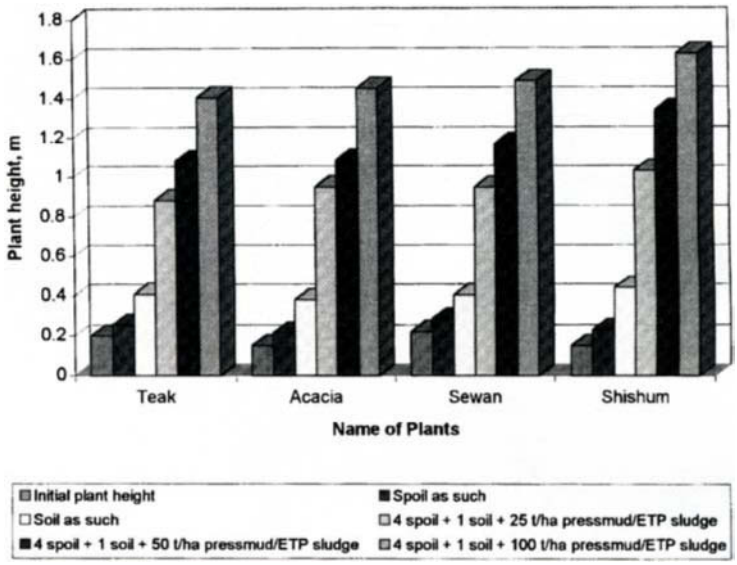


Figure VI.7.6. Effect of different combinations of bedding material on plant growth (after 3 months).



Figure VI.7.7. Profuse root development and nodule formation in the experimental shishum (*D. sissoo*) plant inoculated by *B. japonicum* strain BRS1 as compared to control.

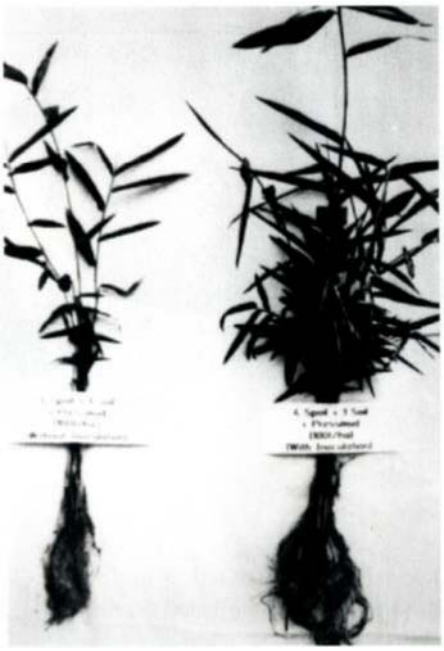


Figure VI.7.8. Profuse root development in the experimental bamboo (*D. stirctus*) plant inoculated by *A. chroococum* strain TA1 as compared to control.

slope were of 0.6 m × 0.6 m × 0.6 m and at top level of 1 m × 1 m × 1 m in dimension, respectively. Each pit was filled with a previously selected T5 combination of bedding material (by weight) that consisted of 4 parts of mine waste + 1 part of topsoil + pressmud/ETP sludge ≈ 100 t/ha. Nearly 565,000 of various tree species of ecological



Figure VI.7.9. Single mature spore of *G. fasciculatum.*

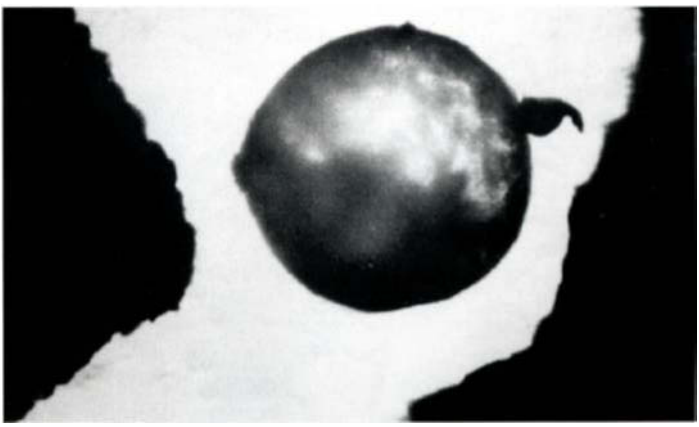


Figure VI.7.10. Single mature spore of *G. gigantia.*

and economical importance have been planted at these sites. The plants were irrigated regularly for 6 months until they were established on mine sites.

VI.7.4.3.1. Impact of amendment, biofertilizer and VAM spore inoculation on rhizospheric microbial population and physico-chemical characteristics of spoil

Five samples of bedding material per hectare were collected randomly from top 0.3 m from the pits planted with different tree species and analyzed in triplicate. The microbial population was enumerated in terms of colony forming units per gram of spoil (CFU/g) by using serial dilution and spread plate methods. Population of different microbes was studied following standard procedures for soil microbial estimations (Black et al., 1965; Page et al., 1982). Counts of aerobic heterotrophic bacteria, actinomycetes, fungi, nitrogen fixing strains of *Rhizobium* and *Azotobacter* were made by the spread plate method on nutrient agar, Kenknight and Munaier's agar, Rose Bengal Chloramphenicol agar, Yeast extract mannitol agar with Congo red and Jensen's agar, respectively. The VAM spores were enumerated by wet sieving and decanting technique (Gerdman and Nicolson, 1963). Changes in physico-chemical properties of coal mine waste were carried out according to standard methods of Black et al. (1965). The carbon mineralization studies were carried out according to Stotzky's method (1960). Nitrogen mineralization rate was monitored in leaching columns of 0.05 m diameter and 0.4 m length for 20 weeks. The columns were leached using 0.01 M calcium solution followed by addition of a nutrient solution (without N) containing 0.0025 M K_2SO_4, 0.002 M $MgSO_4 \cdot 7H_2O$, 0.002 M $(CaK)_2(SO_4)_3$ and 0.005 M calcium phytate. Leachates were analyzed for NH_4-N and NO_3-N.

After 24 months of amendment and reclamation, the bacterial population reached to a count of 10^8 CFU/g (Fig. VI.7.11A). Similar trend was also observed in the case of fungal and actinomycete population, which stabilized and reached to 10^6 and 10^5 CFU/g of spoil sample, respectively (Fig. VI.7.11B,C). The manganese and coal mine waste initially were completely devoid of nitrogen fixers but on inoculation of saplings with biofertilizer

strains of BRS1 and TA1, the *Rhizobium* count remarkably reached to 8.9×10^7 CFU/g (Fig. VI.7.11D) whereas *Azotobacter* count stabilized in the range of 2.2×10^7–6.3×10^7 CFU/g (Fig. VI.7.11E).

The VAM spores, which were initially absent in the mine wastes, after 24 months reached the count up to 41 spores/g (Fig. VI.7.11F).

Amendment of mine waste with pressmud/ETP sludge $\approx$ 100 t/ha decreased the bulk density to 1.33 g/cm^3 and increased the water holding capacity of the mine waste sevenfold and porosity threefold (Table VI.7.7). Changes in chemical characteristics of the coal mine waste due to amendment showed that the ECe (Electric conductivity) of amended spoil extract increased and was 1.4–2.5 times higher than the initial ECe of spoil. Sludge amendment resulted in the improvement of calcium, magnesium and potassium contents, which were useful for plant growth. The organic matter content of the amended spoil varied from 2.0 to 7.4% as against the 0.08–0.13% organic matter in unamended mine waste. The increased organic content complexes the heavy metals and decreases its availability in spoils. The available nitrogen increased for two orders of magnitude. Similar increase in available phosphate and potassium was observed. The increase in available NPK shows improved spoils productivity thus promoting luxuriant plant growth.

The CO_2 evolution indicated the steady growth of the microbial population showing a linear trend. Microbial population brings about mineralization of carbon, nitrogenous compound present in the pressmud/ETP sludge. Results indicated that 19.6% carbon was mineralized after 20 weeks of incubation in T5 treatment whereas nitrogen mineralization was 18.3%, respectively (Figs. VI.7.12 and VI.7.13). The increase in nitrogen and carbon mineralization rate is an index of enhanced metabolic activity of rhizospheric microbial population.

VI.7.4.3.2. Growth performance and survival rate of plants at manganese and coal mine waste dumps

The IBA technology has resulted in successful reclamation of mine waste dumps and creation of lush green belt on the barren mine sites. Revegetated manganese and coal mine waste dumps are shown in Figs. VI.7.14 and VI.7.15. The IBA has resulted in over 85% survival of plant species and four- to fivefold increase in plant growth as opposed to around 20% survival of stunted plants without IBA (Figs. VI.7.16 and VI.7.17).

There was a six- to tenfold improvement in biomass after application of IBA (Fig. VI.7.18). Without IBA, the same process might have taken 100–300 years. Through NEERI's efforts, 150 ha of mine dumps in coal mines, and 72 ha of manganese spoil dumps have been successfully reclaimed.

VI.7.4.4. Socio-economic impact of IBA

A landmark in the reclamation program carried out by NEERI was the development of sericulture project at Gumgaon manganese mine site. On the foothill of the mine waste dump at Gumgaon about 0.3 m depth productive soil profile was prepared using mine waste, 15% topsoil and pressmud. Inoculum of mycorrhizal fungi was introduced to make the rhizosphere more productive. 40,000 mulberry- shoots were planted on dump as a diversified activity inline with the ecodevelopment and environmental protection.

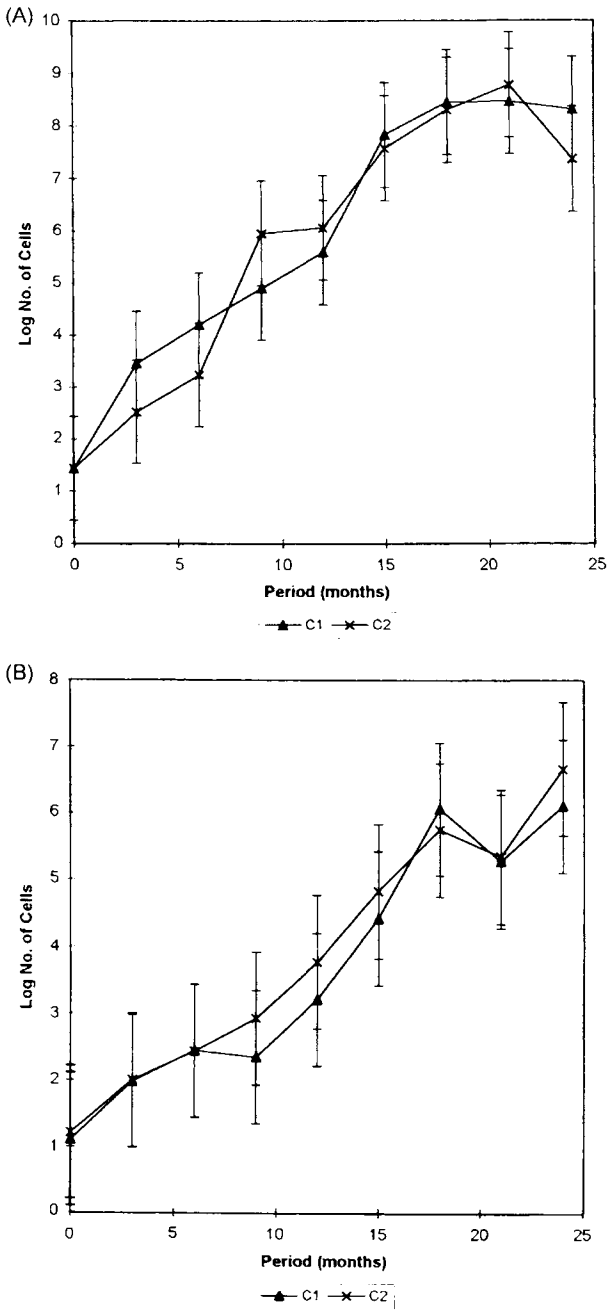


Figure VI.7.11. A–F. Variation in rhizospheric microbial population at different time intervals in 2 years' period. C1 – Pits filled with 75% spoil, 13% topsoil and 12% pressmud/ETP sludge and tree species inoculated with *B. japonicum* BRS1 and *G. fasciculatum* VAMB1; C2 – Pits filled with 75% spoil, 12% topsoil and 12% pressmud/ETP sludge and tree species inoculated with *A. chroococum* TA1 and *G. fasciculatum* VAMB1 and *G. gigantia* VAMB2. A – Variation in bacterial population; B – Variation in fungal population; C – Variation in actinomycetes population; D – Variation in rhizobial population; E – Variation in *Azotobacter* population; F – Variation in VAM population.

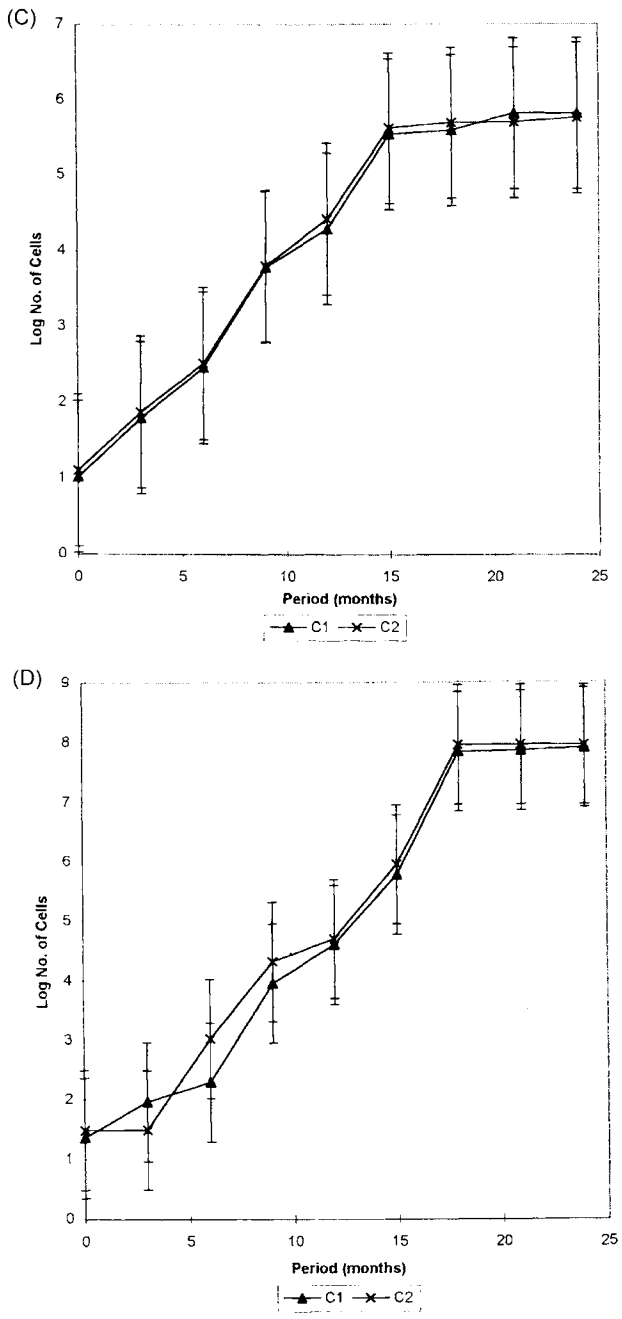
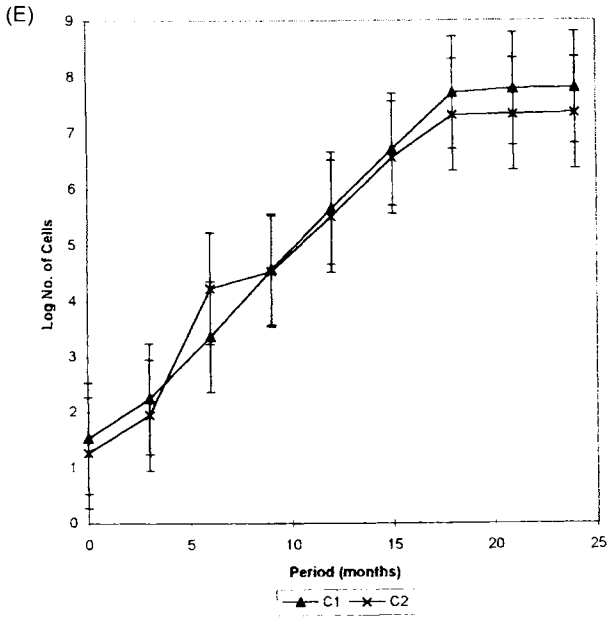


Figure VI.7.11. (Continued)



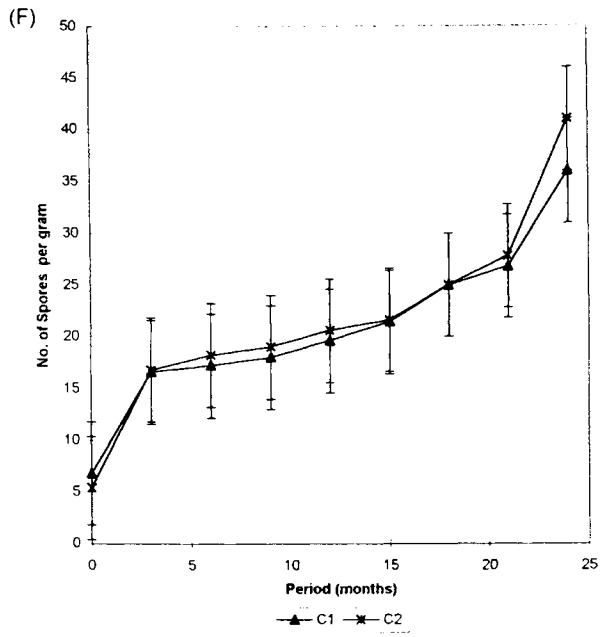


Figure VI.7.11. (Continued)

Table VI.7.7. Yearly changes in physico-chemical properties of coal mine waste due to blending with ETP sludge.

Parameters	1st year	2nd year	3rd year
Physical			
Bulk density (g/cm^3)	1.61–1.76	1.42–1.68	1.26–1.35
Maximum WHC (%)	26.0–31.8	39.2–45.2	52.2–55.3
Porosity (%)	43.1–45.9	50.10–55.82	59.96–62.25
Textural classification (% wt)			
Coarse sand	45–60	42–58	40–50
Fine sand	20–32	22–29	18–28
Silt	14–20	13–19	11–18
Clay	8–12	10–15	20–26
Chemical			
pH	6.0–7.6	5.8–8.0	5.6 –8.13
ECe (mS/cm)	1.14–2.74	0.654–1.73	0.285–1.09
Organic carbon (%)	2.0–4.10	2.14–5.20	2.27–7.40
Water extractable ions 1:10 (meq/l)			
Na	2.2–9.4	2.1–5.6	1.2 –3.18
K	0.12–0.72	0.09–0.68	0.02–0.39
Ca	3.36–10.9	2.92–4.8	0.90–3.3
Mg	2.02–10.9	1.06–5.9	0.65–3.7
HCO_3	2.0–8.0	1.8–6.4	0.78–4.1
Cl	6.2–13.6	4.3–9.3	1.27–5.7
Heavy metals (total), mg/kg			
Chromium	16.5–22.0	10.2–18.1	7.2–12.9
Copper	36.3–40.7	27.8–32.2	10.3–21.8
Lead	68.8–65.3	34.6–42.8	26.4–31.1
Manganese	41.0–436.3	161.3–319.8	162.9–305.5
Zinc	162.2–187.8	102.3–155.5	98.6–132.3
Nutrients (mg/100 g)			
Nitrogen, N			
Total	216.0–437.3	226.6–556.1	240.0–794.2
Available	23.2–45.8	27.1–62.5	31.6–81.9
Phosphorus, P			
Total	32.7–34.6	43.26–45.32	54.3–56.4
Available	4.8–5.22	5.9–6.1	6.8–7.0
Potassium, K			
Total	75.3–82.5	96.1–105.0	125.2–136.3
Available	7.6–9.0	9.8–11.8	12.9–14.7

Subsequently additional area was developed and 120,000 mulberry plants were planted covering an area of over 6 ha. Rearing of silkworm on mulberry leaves was done and cocoons were obtained which were later sold to Khadi Gram Udyog. This activity besides giving boost to the sericulture was promoted with socio-economic objective and to create

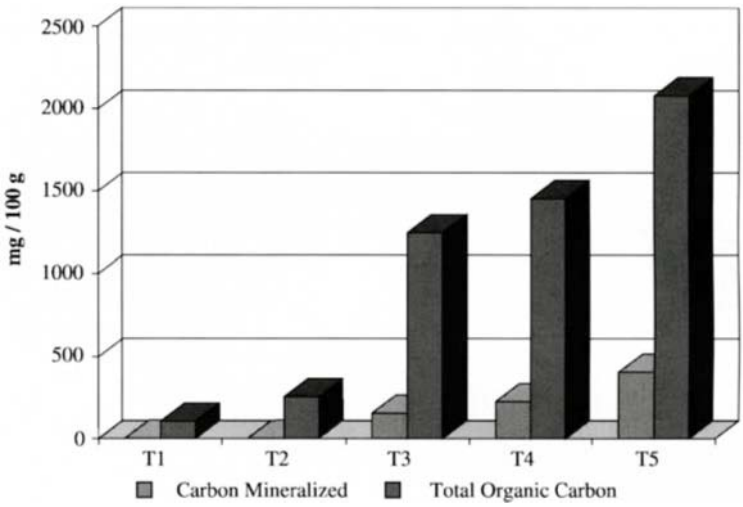


Figure VI.7.12. Carbon mineralization rates at different combinations of bedding material (T1–T5 treatment options).

positive awareness among a large section of people around the mining area. The commercialization of mulberry plantation and silkworm rearing has been started by MOIL since the early 1990s. During 1991–1995, annual yield of cocoons ranged from 37 to over 115 kg, and mulberry shoots up to 9 t.

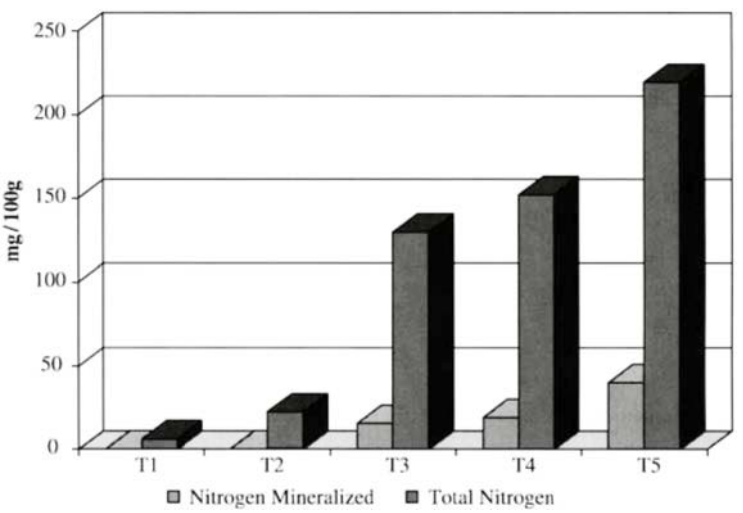


Figure VI.7.13. Nitrogen mineralization rates at different combinations of bedding material (T1–T5 treatment options).



Figure VI.7.14. Revegetated manganese mine waste dumps using IBA.

VI.7.4.5. Cost-benefit analysis of the integrated biotechnological approach

The economical feasibility of the application of IBA in the bioreclamation of mine waste dumping sites and land disturbed due to mining activity, is illustrated below in the cost-benefit analysis for bioremediation of 10 ha mining site in India:

Dump area for bioremediation	10 ha
Total cost[a] including pitting, planting and maintenance for 3 years	Rs. 600,000 (≈ US $12,000)
Benefits (4–20 years)	Rs. 1,600,000–5,900,000 (≈ US $32,000–118,000)
Payback period	2.5 years

[a]In Rupees; US $1 ≈ 50 Rs.

VI.7.5. Concluding remarks

The final goal of a reclamation program is establishment of a self-sustaining vegetative cover that requires a minimum of maintenance. Successful establishment of vegetation is dependent on climatic and edaphic factors, and chemical, physical and biological characteristics of the mine wastes to be reclaimed.

There are problems of survival and growth of plants on the mine waste dumps due to poor physical properties, low nutrient status and absence of microflora.

The NEERI, Nagpur in collaboration with MOIL and CIL developed a reclamation strategy that is environmentally compatible, economically viable and well suited to



Figure VI.7.15. Revegetated coal mine waste dumps using IBA as compared with non-reclaimed foreground devoid of vegetation.

Indian conditions. Under a massive afforestation program carried out since early 1990s at selected manganese and coal mine waste dumps in Maharashtra and Madhya Pradesh states, over 220 ha of wasteland had been successfully reclaimed by using a systematic and scientific approach. An IBA was adopted for sustainable revegetation, and a biocompatible technology comprising biofertilizers + VAM and industrial waste materials as organic amendments to ameliorate mine waste was used.

The IBA helped in successful reclamation of the barren dumps, which resulted in 90–95% plant survival rate; 6–10-fold increase in biomass production; establishment of biogeochemical cycles and microflora resembling that observed in good productive soil in just 18 months. This was the most important achievement for re-establishment of a sustainable rhizosphere. The IBA helped in reclaiming the mine waste dumps and wastelands within 3–4 years without the use of chemicals and inorganic fertilizers. The IBA promoted resource conservation through waste utilization, helped in fast recovery and restoration of fertility and productivity of the degraded ecosystem and provided carbon dioxide sinks, built fertile topsoil; generated fuel, fiber, food, fodder and fruits and other economical benefits in terms of production of timber and industrial wood and raw material for cottage industry.

IBA also provided several ecological benefits in terms of oxygen production, soil erosion control, groundwater recharge and generation of carbon dioxide sinks. The IBA thus ensures clean and healthy environment by abating air, water and land pollution.

Using IBA, the joint venture of industry and the research institute has successfully turned barren landscape of MOIL and CIL's mines into lush forests of high economical and ecological value. Presented illustrative case studies summarize over decade's experience and contribution towards installation of the country's first model example of scientific reclamation program through IBA.

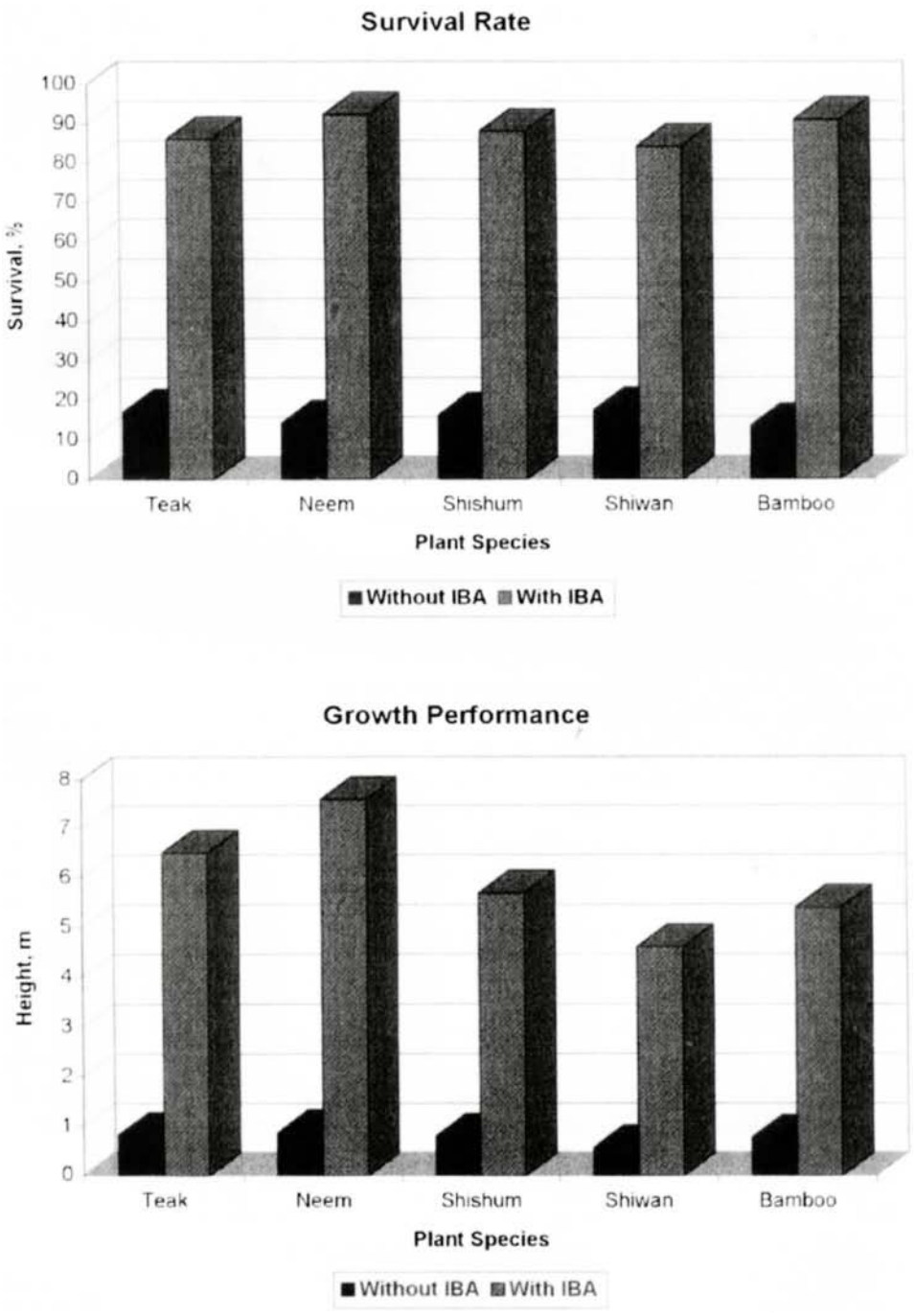


Figure VI.7.16. Survival rate and growth performance of different plant species on manganese waste dump.

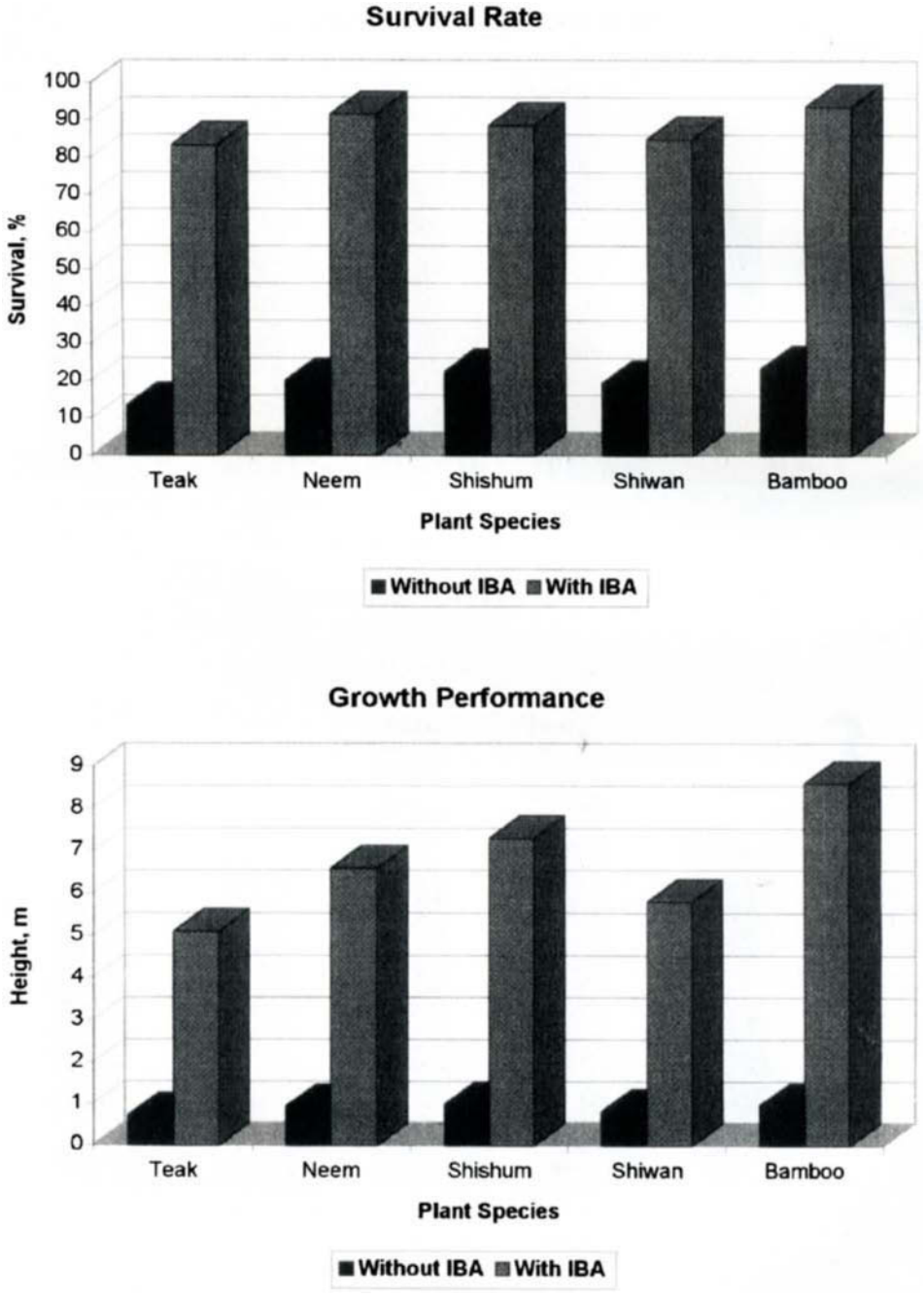


Figure VI.7.17. Survival rate and growth performance of different plant species on coal mine waste dump.

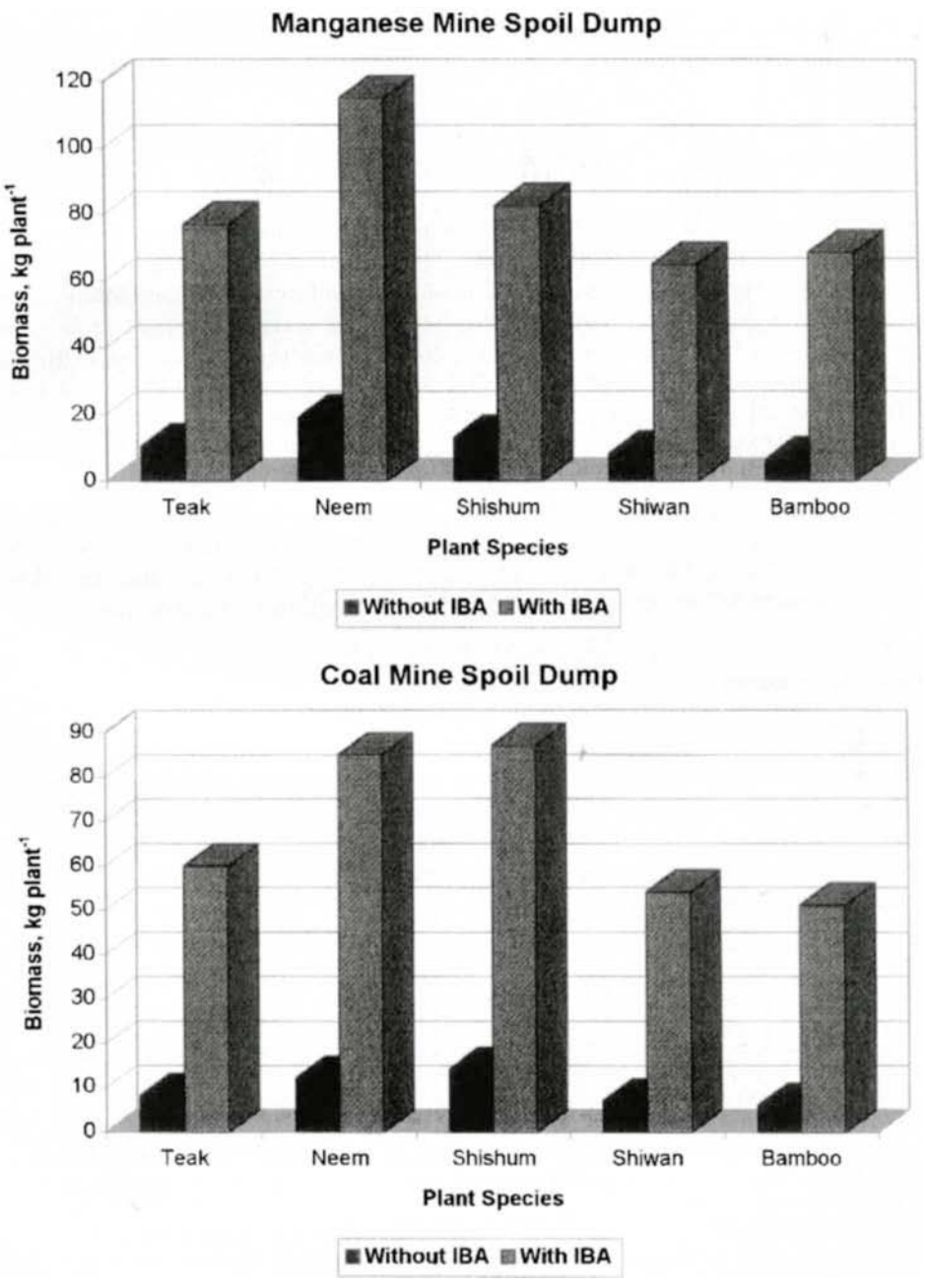


Figure VI.7.18. Biomass production of different plant species on manganese and coal mine waste dumps.

This study has shown that an IBA involving use of organic amendments, biofertilizers and VAM is the most appropriate solution for bioreclamation and development of mine waste dumps.

Immemorial note

Dr A.S. Juwarkar, born on March 6, 1951, Maharashtra, India (July 11th, 1996) was a scientist of national and international repute. He had an outstanding academic record throughout his career. As a scientist and head of the Land Environment and Management (LEM) Division of NEERI, Nagpur, India, he pursued several important projects on bioreclamation and treatment of wastewater through high rate transpiration system. He had several national and international papers to his credit and guided several PhD students.

Dr A.S. Juwarkar significantly contributed in starting and developing a successful long-term program of bioreclamation of mine waste dumps using IBA that fetched him the Best Scientist Award from NEERI. Now, several years after his passing away, luxuriant vegetation in the first dumps that were reclaimed under his supervision, and in the wastelands that have been greened using his experience, makes us proud to continue his work.

We, the staff of NEERI bow to the chief architect of LEM Division and are making a sincere effort to follow the footprints left by the great visionary, Dr A.S. Juwarkar.

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VI.8

Bulk use of power plant fly ash in deep mines and at the surface for contaminant and fire control

Irena Twardowska

VI.8.1. Introduction

Despite a number of beneficial properties and stepped up use in a wide array of field-proven applications, coal combustion waste (CCW) cannot be just renamed a raw material to solve the environmental problems posed by its generation and disposal. CCW is considered a waste as soon as it enters the waste stream and is disposed of or temporarily stored and not utilized in an environmentally safe way. As has been shown in Chapter III.7, CCW is not an inert material and may create a serious threat to the environment, in particular to ground water resources, up to a hazardous level in a long-range period. Therefore, CCW management must fulfill the criteria of environmental safety. Having in mind its diverse characteristics, both positive and negative, sound management of CCW should go beyond safe storage and disposal and take into account the possibility of reducing its volume through bulk use. The current practices show that this goal is not easy to achieve in the countries that are large CCW generators (Table VI.8.1). Up to now, the optimistic examples of thorough utilization used to back up the idea of CCW being renamed a by-product are relevant solely for the smallest CCW generators (e.g. the Netherlands or Denmark), where a very limited CCW production ($\leq$1 Mt) does not exceed the market demand. In the USA, which holds the second position after China in coal production and coal-based power generation in the world, CCW generation was estimated to increase from about 80 Mt in 1990 to over 100 Mt in 1999 (Butalia and Wolfe, 1999; Adriano and Weber, 2001). In 1992, 74.4 Mt of CCW was reported by American Coal Ash Association (ACAA, after Tyson, 1994) to be generated in the form of coal ash, i.e. fly ash (FA) (59.6% wt.) and bottom ash (BA) (17.1%), boiler slag (5.0%), and FGD solids (18.3%). ACAA survey data for 1996 showed increase of CCW generation to 92.5 Mt, i.e. for almost 20% (Stewart, 1999). The rate of its utilization, though, has not changed much, and during this decade accounted roughly for 25% of the amount produced. The traditional markets comprise predominantly cement/concrete and in lesser amounts production of other construction materials (e.g. blocks, bricks, tiles, lightweight aggregates), structural fill, road base and sub-base, blasting grit and roofing granules, as well as miscellaneous minor applications such as filler in asphalt, anti-skid material, grouting, toxic waste stabilization and solidification, fillers in plastics and paints, wallboard manufacture, zeolite production, etc. These markets, though, cannot assure

Table VI.8.1. Examples of annual coal combustion waste generation and use in selected countries – large FA generators, Mt (%).

CCW management	USA							India	Poland	UK	Japan
	1990[a]	1992[b]	1996[c]					1998[d]	1998[e]	1989–1998[f]	1989[g]
Products, markets	Total	Total	FA	BA	BS	FGDS	Total	Total	Total	Total	Total
Generation, Mt (% of total)	78.75	74.4	53.88 (58.3)	14.58 (15.8)	2.33 (2.5)	21.65 (23.4)	92.45 (100)	75.0	17.76	12.54–13.00	3.925
Utilization, Mt (% of generation)	19.28 (24.5)	18.4 (24.8)	14.74 (27.3)	4.42 (30.3)	2.18 (93.3)	1.50 (6.9)	22.84 (24.7)	1.5–4 (2–5)[c]	11.39 (64.1)	6.12 (48.8)	1.920 (49.0)
Cement/concrete	7.25 (9.2)	7.2 (9.7)	7.28[h] (13.5)	0.69[h] (4.73)	0.00[h] (0.00)	0.06[h] (0.28)	8.04[h] (8.70)	x	–	0.73 (5.8)	1.421 (36.2)
Building materials, blocks	–	–	–	–	–	–	–	xx	–	3.92 (31.3)	0.173 (4.4)
Flowable fill/ structural fill	3.78 (4.8)	2.4 (3.2)	2.25 (4.17)	0.65 (4.46)	0.04 (1.72)	0.06 (0.28)	3.00 (3.24)	–	7.29 (41.0)	1.10 (8.8)	–
Road base/ sub-base	1.84 (2.4)	2.2 (3.00)	0.68 (1.26)	0.66 (4.53)	0.00 (0.00)	0.11 (0.51)	1.44 (1.56)	–	–	–	0.134[i] (3.4)
Blasting grit/ roofing granule	1.67 (2.1)	1.9 (2.6)	0.00 (0.00)	0.15 (1.03)	1.97 (84.6)	0.00 (0.00)	2.13 (2.30)	–	–	–	0.058 (1.5)
Other markets listed below:	4.74 (6.0)	4.7 (6.3)	4.52 (8.39)	2.28 (15.6)	0.16 (6.87)	1.27 (5.87)	8.23 (8.91)	–	4.10 (23.1)	0.37 (3.0)	0.077 (2.0)
Asphalt filler	0.131 (0.17)	–	0.15 (0.27)	0.03 (0.20)	0.05 (2.14)	0.00 (0.00)	0.22 (0.24)	–	–	–	[i]
Snow, ice control	1.56 (1.98)	–	0.00 (0.00)	0.61 (4.18)	0.10 (4.29)	0.00 (0.00)	0.71 (0.77)	–	–	–	–
Grouting	0.31 (0.39)	–	[h]	[h]	[h]	[h]	[h]	–	–	0.25 (2.0)	–

Mining application	0.054	–	0.69	0.06	0.00	0.03	0.77	x	4.10	–	–
	(0.07)		(1.28)	(0.41)	(0.00)	(0.14)	(0.83)		(23.1)		
Wallboard	0.036	–	0.01	0.00	0.00	0.79	0.81	–	–	–	–
	(0.05)		(0.02)	(0.00)	(0.00)	(3.65)	(0.88)				
Waste stabilization	–	–	1.75	0.23	0.00	0.05	2.04	–	–	–	–
solidification			(3.25)	(1.58)	(0.00)	(0.23)	(2.21)				
Miscellaneous[j]	2.647	–	1.91	1.34	0.01	0.40	3.66	–	–	0.12	0.077
	(3.36)		(3.54)	(9.19)	(0.43)	(1.85)	(3.96)			(1.0)	(2.0)
Agriculture	–	–	0.01	0.01	0.00	0.00	0.02	xx	0.00	0.00	0.058
and fisheries			(0.02)	(0.07)	(0.00)	(0.00)	(0.02)		(0.0)	(0.0)	(1.5)

FA = Fly ash; BA = Bottom ash; S = Boiler slag; FGDS = Flue gas desulfurization solids; xx – major amount; x – minor amount.

[a]ACAA data 1990, after Collins, 1992.

[b]ACAA data 1992, after Tyson, 1994; CCW use: FA 27%, BA 28%, S 75%, FGDS 2%.

[c]ACAA data 1996, after Stewart, 1999.

[d]Estimate, after Prasad et al., 2000 and Ray, 2000.

[e]Electricity and thermal energy generation: After Central Statistical Office, 1999 and State Environmental Protection Inspectorate, 1997; For full data on power generation in 1985–2001 see Table VI.8.2.

[f]National Power/Power Generation data 1989, after Clarke, 1994 and OECD Environmental Data, 1999.

[g]Japan Coal Ash Assn., 1989, after Clarke, 1994.

[h]Data for grouting are given together with cement/concrete.

[i]Data for road base and asphalt filler together.

[j]Miscellaneous = waste stabilization and solidification (if not given separately) and other low-volume applications such as fillers in plastics and paints, zeolite production, etc.

absorption of all, or at least of a more substantial proportion of the CCW generated (Collins, 1992; Clarke, 1994; Tyson, 1994; Butalia and Wolfe, 1999; Chugh and Sengupta, 1999; Stewart, 1999).

In India, at present coal and power production, around 75 Mt of CCW as coal ash is generated annually, and a further growth to 290 Mt by 2011–2012 is anticipated. The current coal ash utilization level is negligible and according to a rough estimation ranges between 2 and 3% (Prasad et al., 1999, 2000), and 6% (Ray, 2000). The major areas of bulk application are production of building materials (bricks, cement, tiles) and in agriculture as soil amendment and fertilizer. This last area seems to be particularly attractive to India as high-volume low-technology application, and potential sink for almost unlimited amounts of CCW, in particular when a visible growth of crop after application up to 600 t/ha was observed (Tripathi et al., 1997; Singh and Tripathi, 2000). In view of the mostly low lime content in Indian CCW (1–3% CaO) typical also for the majority of this waste in other countries, which displays low neutralizing capacity, along with 10-fold enrichment with heavy metals compared to burned coal, including mobile oxyanions of proven toxicity, and adverse weathering transformations of its properties due to devitrification (Twardowska and Szczepanska, 2002), large-area uncontrolled agricultural use may lead to irreversible soil contamination in the long-range period (Twardowska et al., 2003). These premises resulted in a ban on CCW use in agriculture in many countries, e.g. in the EU Member States, and also in Poland and limited use in other countries (e.g. in Japan) as environmentally problematic application. The safe utilization of CCW in agriculture, particularly for industrial dumping sites reclamation with use of technical species (Sloan and Cawton, 2001), e.g. aromatic plants growth (Kanungo, 2000) though seems sound and prospective, does not solve the problem of bulk utilization of FA.

These examples show that FA utilization is still far from being satisfactory in the developed countries, and almost none in the developing ones that use coal for power generation. The major limiting factors for higher extent of CCW utilization are saturation of traditional markets and availability of competing materials at lower processing, transportation and handling costs, apart from other reasons, such as possible prejudice of end users and regulators, as well as insufficient experience of professionals dealing with processing, distribution, advertising, contraction, regulations, etc.

The ways of improving the situation with CCW utilization that should bring about substantial progress include:

- A carefully elaborated legislative and regulatory mechanism based on the adequate system of charges, fees and penalties for CCW disposal and requirements with respect to the site construction that would induce the generators to seek the possibilities of CCW utilization in the environmentally safe way on the cost-benefit basis, through the supporting financially the CCW utilizing industries to assure their competitiveness in the traditional and new markets.
- Harmonization of CCW handling techniques with further use.
- Development of new potential markets for high-volume CCW use, which are at least equally technically sound, commercially proven and environmentally safe as traditional materials. An attractive field of high-volume CCW application is its use for specific purposes in deep coal mines or at the surface.

- Promotion and advertising actions, and demonstration projects supported also by governmental agencies showing particular beneficial qualities and advantages of different CCW applications.

In Poland, a remarkable growth of CCW use occurred, from 32.1% in 1985 to 73.4% in 2001, when 18.8 Mt of power plant wastes were generated, out of which 13.8 Mt of the annual production was utilized (Table VI.8.2) (Central Statistical Office 1994, 1997, 1999, 2001, 2002). This places Poland at the top of the countries that produce comparably high amounts of CCW with respect to the percentage of its use. This success should be owed mainly to the proper use of legislative and financial instruments. To a considerable extent, this high position of Poland in CCW utilization is also due to the extensive application of FA in deep mine workings. Since the second half of the 1980s, FA utilization underground has become increasingly popular in Poland. In the 1990s, the amount of FA utilized this way was growing particularly fast. In the area of the Upper Silesia Coal Basin (USCB), where 4.8 Mt of CCW (29.6% of the total) were generated in 1996, 4.5 Mt, i.e. 93.7% of this waste was utilized (State Environmental Protection Inspectorate, 1997). The rate of CCW use in the USCB comprised 48.2% of the total quantity utilized in Poland in 1996. According to the data of 1994 concerning the structure of CCW utilization in the region, 85.0% of the total amount generated was used underground. The rest was utilized for conventional applications, mainly for production of cement and building materials (11.7%), and the remainder in road construction and as structural fills (State Environmental Protection Inspectorate, 1995). New administrative division of the country in 1999 and formation of Silesia land in new borders that comprise the USCB, but also new areas, makes comparison with the latest data somewhat complicated. In 2001, electricity and thermal energy production in Silesia land resulted in generation of 5.6 Mt of CCW, of that 4.8 Mt, i.e. 84.4% was used (State Environmental Protection Inspectorate, 2002). Up to the end of 1994, 65 coal mines of the USCB utilized at least 17.4 Mt of CCW. By the end of 1996, this amount increased to 24.2 Mt; by the end of 1999, it accounted for about 34 Mt and continues to grow in time with the same intensity limited by the availability of CCW. Up to now, no other country can boast of comparable achievements in this field including the USA where for mining reclamation a negligible amount of 0.06 Mt in 1990 was reported to be used (Collins, 1992). In 1996, over 10 times more, i.e. 0.77 Mt (0.83% of total) was applied in the mining in the USA that is still a very low amount (Stewart, 1999).

Technically and technologically, power plant FA use underground has become a routine process in Poland during the last decade and it does not create problems. This field of application has been proven to be technically sound and commercially effective. The prerequisite of CCW use as a beneficial by-product, besides technical and commercial efficiency, is environmental safety. Considering the predominance of FA in CCW (from 72 to $>80\%$ of total CCW excluding FGD solids), and its lower utilization rate compared to BA and boiler slag, this chapter is focused on the environmental aspects of FA use in deep mine workings and on the surface. According to Polish statistics, FA handling techniques have a profound influence on its utilization. The lowest utilization rate shows coal ash transported hydraulically (slightly over 53%) which is due to its form and weight that makes it extremely inconvenient for further use, while dry FA is utilized almost thoroughly (92–93% in 1998–2001) (Table VI.8.2). "Pure" FA is the most abundant

Table VI.8.2. Generation and use of coal combustion waste (CCW) in Poland, 1985–2001 (after Central Statistical Office, 1994, 1997, 1999, 2001, 2002).

Year	Generated					Used						Stored				
	Mt					Mt	% of generated					Mt				
	CAM	FA	S	FGD-S	∑CCW	∑CCW	CAM	FA	S	FGD-S	∑CCW	CAM	FA	S	FGD-S	∑CCW
1985	–	–	–	–	27.3	8.8	–	–	–	–	32.1	–	–	–	–	168.1
1990	–	–	–	–	26.6	11.3	–	–	–	–	42.5	–	–	–	–	260.9
1992	–	–	–	–	21.7	10.0	–	–	–	–	46.3	–	–	–	–	267.4
1993	–	–	–	–	21.5	10.3	–	–	–	–	48.0	–	–	–	–	275.8
1995	–	–	–	–	20.1	12.5	–	–	–	–	62.2	–	–	–	–	318.5
1996	–	–	–	–	20.6	13.2	–	–	–	–	64.3	–	–	–	–	325.3
1998	9.0	4.1	2.8	2.6	18.5	12.5	53.6	91.9	86.3	57.4	67.5	239.1	27.6	20.6	4.1	291.4
2000	9.1	4.6	2.5	3.1	19.3	14.3	53.2	93.3	86.0	97.7	73.9	244.3	46.4	18.3	2.1	311.1
2001	8.6	5.2	2.3	2.4	18.5	13.2	46.5	93.2	88.3	96.7	71.3	246.6	45.3	18.1	0.9	310.9
1998	Electricity and thermal energy production				17.8	11.4	–	–	–	–	64.1	–	–	–	–	248.9
2000					18.1	13.7	–	–	–	–	75.7	–	–	–	–	251.7
2001					18.8	13.8	–	–	–	–	73.4	–	–	–	–	312.3

CAM – coal ash (FA/S mixtures transported hydraulically); FA – fly ash (dry); S – slag; FGD-S – flue-gas desulfurization solids (lime methods); ∑CCW – total coal combustion waste.

waste in electric utilities, which do not use desulfurization of flue gases, and in the ones using wet desulfurization process that is predominant in the USA, Germany and in most of the other countries using desulfurization of flue gases. Typically it accounts for 70–80% of the ash generated by conventional coal-fired power plants. Considering the widespread application of wet desulfurization of flue gases in power plants, the environmental evaluation of this kind of reused material is of particular interest for the potential end-user.

Environmental aspects of FA utilization underground were evaluated here on the basis of a study carried out in 24 deep coal mines of the USCB in Poland, which used FA routinely in the last decade. Pure FA originated from two power plants (Rybnik and Laziska, which produce 1600 and 1520 MW, respectively). FA with products of dry FGD process (FA + D-FGDS) originated from the Rybnik and Opole power plants, and FA containing products of ABB-NID semi-dry desulfurization process (FA + SD-FGDS) came from the Laziska power plant. Various options of bulk FA utilization at the surface were also analysed.

The major purposes of FA use discussed here are based on the specific hydrogeological and hydrogeochemical properties of this material, both adverse and positive, presented in detail in Chapter III.7. The basic premises of these applications and their limitations can be summarized as follows:

- All the low-ratio water mixtures of FA after solidification show excellent sealing properties against air penetration. Their penetration resistance ($R = 1000–19,000$ kPa) is 1–2 orders of magnitude higher than that of natural cohesive soils such as boulder clay ($R = 190$ kPa).
- FA has a high water retention capacity exceeding 50% wt.
- Hydraulic conductivity of pure FA at the level of $k \geq 10^{-8}$ m/s does not fulfill the criteria of impermeability both for horizontal water flow and for a vertical infiltration. This material can be classified as a very weakly insulating one similar to silt loam or sandy clay loam and cannot be used as a sole protective barrier against water infiltration.
- Due to high leachability and the concentration of macro-components and trace elements being an order of magnitude higher than in natural soils, among them toxic oxyanions as As, Mo, Se, Cr^{6+} and insufficient buffering capacity of low-alkaline FA, this material can be a source of long-term aquatic and terrestrial environment contamination at all three stages of leaching, i.e. wash-out (I), dissolution (II) and delayed release (III) stages.
- The best hydrogeological and hydrogeochemical parameters are displayed by high-alkaline FA, in particular FA + D-FGDS containing products of dry flue gas desulfurization lime process. These show the lowest hydraulic conductivity, up to impermeability to horizontal flow ($k = 10^{-8}–10^{-9}$ m/s), lack of tendency to acidification and hence of the massive trace elements release in the delayed release (III) stage, the shortest solidification time, the best sealing properties against air penetration and the highest water retention capacity.
- Low-water mixtures with FA containing products of semi-dry desulfurization process (FA + SD-FGDS) besides being improved in basic properties compared to pure FA such as air penetration resistance or lack of the tendency to acidification and hence of the delayed release (III) stage, display adverse features caused by the presence of

chemically instable sulfites, in particular a long period for solidification and certain thixotropic properties, which reduce reuse of this material at the surface in a wet climate or underground in wet workings.

The bulk use of FA underground and at the surface is thus focused on the utilization of its properties as an excellent sealing material against air penetration that has no competitor in this respect among the natural alternative materials, and its high water retention capacity. This way, FA utilization for these purposes would not just reduce the amount of disposed CCW waste, but would improve environmental quality and safety in the areas of CCW utilization. At the same time, environmental requirements dictate the need of taking into consideration and suppression of the adverse parameters of FA, such as low barrier properties with respect to water infiltration and high leachability of macro-components and problematic trace elements.

VI.8.2. Fly ash application underground

VI.8.2.1. Purposes of FA application

The main direct purposes of FA application in deep coal mines are liquidation of useless drifts, peat shafts and sealing of mined out and abandoned workings, backfilling (stowing) of mine workings and stopping construction for fire prevention and control, methane control and reduction of greenhouse effects caused by methane release to the atmosphere, simplification of a ventilation system, and reduction of surface deformations due to subsidence, as well as a component of binding material. Sealing properties of FA against air penetration create wide demand for CCW in deep mines as irreplaceable and infallible raw material, easily available and manageable. In mine workings CCW, predominantly FA, and in lesser amounts (up to 10%) also BA, are being used in the form of a dense mixture with mine water, or less frequently with flotation slurry from coal preparation process. The worst quality highly saline or/and of elevated radioactivity mine waters are used for mine water:FA mixtures are prepared for two reasons:

- To use the high water retention and binding capacity of FA for adequate reduction of contaminant loads discharged with mine waters to the surface receiving waters;
- To protect high quality ground water resources.

In addition to the major purposes, utilization of FA underground eliminates to a great extent a burden caused by a surface disposal of this airborne and highly leachable waste. While generated quantities of FA increase, the availability of appropriate disposal areas decreases and the costs of new disposal areas rise significantly. Nowadays, requirements for siting and managing disposal sites have become very stringent. No less important is eliminating the threat of the so-called secondary "low emission" of dust from the pond surface, as well as of an impact on the ground and surface waters in the vicinity of the disposal site.

Besides benefits, this material used underground may also cause adverse side effects, resulting from high leachability of constituents from its matrix. The extent of these side

effects largely depends upon geological, hydrogeological, and hydrological conditions in the site of FA use, as well as upon the material properties.

VI.8.2.2. Methods of FA utilization underground

In Polish practice, FA is loaded in a dry state directly from electrostatic precipitators into railway or road tankers through a hermetic connection, and transported to the unloading station at a mine. Again, through the hermetic connection, with use of compressed air, it passes to a feeder, where it is mixed with mine water in the required proportion and pumped to a retention tank. From the tank, the dense (low-water) FA mixture is transported underground gravitationally by pipelines to an outlet, behind the barrier (stopper) in the backfilled working (Fig. VI.8.1). The mine water:FA ratio is determined by the transportability of the mixture, the distance of the outlet from the retention tank at the surface, and the time of the mixture solidifying. The most frequent mine water:FA ratio is 1:1, up to 0.8:1 by weight. The deposited mixture undergoes gradual dewatering. An excess of water joins the mine drainage system and is pumped to the surface. Partially or thoroughly, the residual water is directed back to the circuit of mine water. The excess water from FA mixture is discharged to the surface recipients (rivers) either directly, or through the mine water-collecting pipeline. The amount of water and discharged loads of contaminants prescribed by the permit depend on the mine water and dissolved constituent load balance and the dilution capacity of the recipient. Besides compulsory environmental impact assessment (EIA) to be submitted by the FA utilizing company to the Environmental Protection Department to obtain a permit for its utilization underground for each mine, mine workings and kind of FA, an extensive study on the environmental evaluation of FA use in deep mines in different hydrogeological conditions was conducted in 1993–1996. As was already mentioned above, the assessment comprised FA originating from the three power plants (Rybnik, Laziska and Opole), being used in 24 coal mines of the USCB.

VI.8.3. Environmental evaluation of fly ash use in deep mine workings

VI.8.3.1. Criteria of the environmental impact assessment

Utilization of the large quantities of CCW in the underground mine workings in the form of dense FA:mine water (or FA:slurry) mixture creates entirely an new environmental issue. For its evaluation, adequate criteria should be applied, regarding the general regulations, acts and methods of EIA, as well as FA properties and its environmental behavior in the new array of applications under specific conditions. Transformation in time, mechanism and dynamics of release, and immobilization of contaminants from FA mixtures and their migration (depending upon the interaction with the disposal environment) are factors to be considered. In brief, the criteria of the EIA of FA may be formulated as following:

- The basic parameters for evaluation of the environmental effect of power plant waste deposition underground should be the load of contaminants in mine water used for the mixture preparation and the mobilizable contaminant load in FA per mass unit.

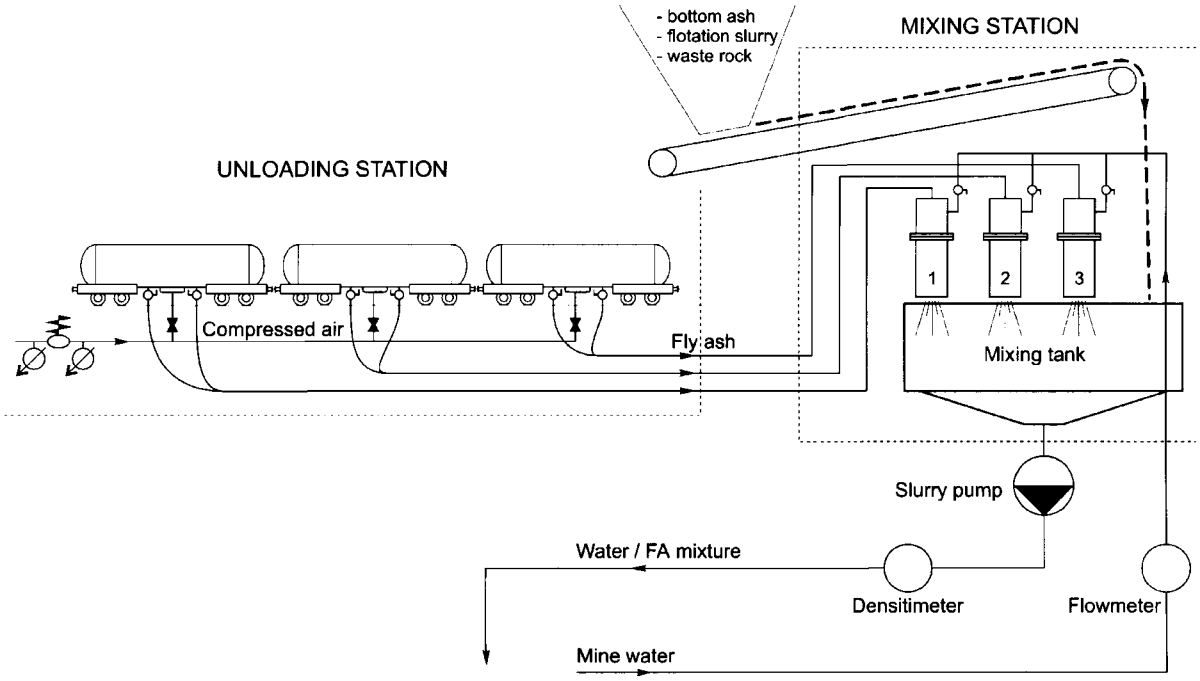


Figure VI.8.1. Scheme of installation for dense water:FA mixtures preparation and use in deep mine workings (after UTEX Ltd, Poland).

- The basic criterion should be the balance of actual input and output pollutant loads in the dense FA:mine water (slurry) mixture, with regard to the quality requirements of the recipient.

A concentration-based approach does not display clearly either the amount of contaminant released, or retained in the fly-ash matrix. The load-based criteria assure obtaining objective data on either adverse or beneficial environmental effects of CCW used in mine workings in the form of dense FA:mine water mixture. These criteria permit separate evaluation of the amount of pollutants introduced to the system by mine water and released or retained by FA. The positive or adverse environmental impact is thus evaluated as negative or positive load balance in outflow from the mixture compared to the load introduced to the mixture with mine water.

Environmental evaluation of FA use underground should also comprise: (i) assessing pollution potential of FA vs. transformations of waste properties with time; (ii) long-term prognosis of contaminant loads release/retention balance from mine water:FA mixture, in compliance with its disposal environment; (iii) characterization of hydrogeological and hydrogeochemical conditions in working or abandoned mines with regard to protection requirements of major groundwater basins (MGWBs); (iv) radioactivity level in mine workings resulting from utilization of CCW; (v) prognosis of post-closure hydrogeological and hydrogeochemical conditions in the mine where FA was used. An integral part of the EIA of FA utilization in deep mines should be environmental monitoring within the eventual impact radius.

On the grounds of the above criteria and procedure, extensive testing and research to characterize CCW for developing the guidelines of its environmentally safe use underground, for each particular case of application in the form of a dense mixture with mine water (or slurry), have been carried out. The environmental evaluation was a basis for obtaining a permit for FA utilization in each seam of each particular mine and revealed a variety of different issues in seemingly similar cases.

Characteristics of FA properties, elemental composition and leaching behavior, as well as hydrogeological characteristics of FA:mine water mixtures have been discussed in Chapter III.7.

VI.8.3.2. Ground water protection requirements

In the area of FA utilization underground, the critical protection areas (CPAs) of the MGBW should be considered and protected against contamination from this source. FA utilization at any rate may not pose a threat to the usable ground water resources. Kleczkowski (1990) defined usable ground water horizons (UGWH) and MGWB on the basis of the qualitative and quantitative criteria. Groundwater basins defined as MGWB are the fragments of UGWH of better hydrogeological conditions. With respect to qualitative criteria, two basic classes of water have been distinguished: (I) to be used for drinking water supply; (II) not considered to be used for drinking water supply. Waters belonging to Class I comprises four sub-classes (a, b, c, d) depending upon the need for water preparation: Ia – very good, no need for preparation; Ib – good, no need for preparation; Ic – concentrations of pollutant(s) slightly above the maximum permissible level MCL, easy to treat; Id – MCL considerably exceeded, preparation required.

The following criteria have been used for defining MGWBs in the Carboniferous strata: (i) potential capacity of water intake $>70\ m^3/h$; (ii) potential capacity of group water intakes $>10{,}000\ m^3/h$; (iii) water quality fulfills I class criteria. With respect to the Carboniferous MGBW, these criteria are applied both to well and mine water intakes. Carboniferous MGWBs are used mainly as mine intakes, to lesser extent as wells. In the areas of water shortage, for selection of Quaternary MGWB and UGWHs, individual quantitative criteria, which are lower than the basic ones, are being used. With respect to MGWB, the potential capacity of a well should be $>40\ m^3/h$, and a group intake should be above $2000\ m^3/d$. The potential capacity of a single well for UGWH should be no less than $5\ m^3/h$. The quality of water should fulfill the criteria of classes Ia–d.

That either UGWHs or MGWBs are not jeopardized by FA utilization is to be confirmed by the EIA.

VI.8.3.3. Characteristics of mine waters

Mine waters are a component of a dense FA:water mixture and therefore exert a considerable effect on its properties, environmental behavior and pollution potential. Optimization of the environmental effect of FA use underground requires thus adequate mine water management.

Waters occurring in the Carboniferous strata in the USCB represent different chemical composition and total dissolved solids (TDSs) ranging over wide limits from 0.1 to 230 g/l. It reflects hydrogeological zonality in the stratigraphic column typical for sedimentation basins, which is characterized by the general trend of downward increase of mineralization independent from the age of the stratigraphic column (Różkowski and Przewlocki, 1987; Różkowski, 1995). In the profile of the Upper Carboniferous in the USCB, explored by mine workings up to a depth of about 1200 m, three vertical hydrochemical zones can be distinguished: (I) infiltration, (II) mixed and (III) connate waters. In the upper zone of the active water exchange, young infiltration waters of a low salinity occur. The middle zone is of a transitional character and contains mixed infiltration and connate waters of a slow recharge rate and TDS from several to <30 g/l. The lower zone contains stagnating connate brines of TDS up to 370 g/l. The hydrogeochemical anomalies, which result from geological and anthropogenic factors, disturb this general regularity. Of the geological factors, the major ones are an occurrence of a sealing horizon formed of Tertiary clay sediments insulating the Carboniferous strata from the percolation of the atmospheric precipitation, observed decreasing permeability of Carboniferous sandstone with the depth and an occurrence of halite deposits in the Tertiary sediments. Another major group of factors modifying chemical composition and mineralization of mine waters is mining activity, which evokes mainly mixing waters from different zones due to long-term drainage, infiltration of contaminated waters from the surface as well as sulfide oxidation in the Carboniferous rocks. Waters of the upper zone in the depth range 1–500 m are of HCO_3–SO_4–Ca–Mg or SO_4–Cl–Ca–Mg type, TDS ranging from <1 to about 25 g/l. Mixed waters represent generally SO_4–Cl–Na type. The roof of the lowest zone of connate waters, which is represented by brines of Cl–Na or Cl–Na–Ca type, generally occurs at a depth of 400–500 m. Mine water is generally slightly alkaline ($pH \leq 7.8$), more rarely slightly acidic ($pH \geq 6.4$) or acidic ($pH < 4$). Examples of elemental composition and load balance of typical saline mine waters of

the USCB are presented in Tables VI.8.3 and VI.8.4 as input. Water inflow to mines of the USCB ranges from 0.5 to 7.4 m^3/min. The mines were classified by Wilk (1965) as the ones of high (>5 m^3/min), moderate (from >2 to ≤ 5 m^3/min) and low water inflow (≤ 2.0 m^3/min).

Of the trace elements, mine waters frequently contain high concentrations of Ba (up to 100 mg/l). Other elements occur in concentrations below 1 mg/l, in the range from 0.1 to 0.001 mg/l or in concentrations below the detectable level (e.g. Mo, V). The concentrations of trace elements in mine waters are governed by stability constraints and at the actual pH range are generally low. Nevertheless, the concentrations of metals in saline mine waters often exceed MCL for drinking water (in particular Mn, Pb, Ni, Cd) and in general are elevated compared to low-TDS Quaternary ground waters (Tables VI.8.3 and VI.8.4). In some seams saline mine waters display elevated or high natural radioactivity levels, up to 390 kBq/m^3 (Lebecka and Tomza, 1989).

Discharge of saline mine waters to the low-flow surface receiving waters in the USCB area results in the off-class deterioration of their quality and therefore the reduction of discharged contaminant loads becomes critical for the mine economy.

VI.8.4. Environmental effects of dense mine water:FA mixture use in dry mine workings

VI.8.4.1. General trends

Utilization of FA in mine workings in the form of dense mine water:FA mixtures, besides other effects beneficial for the environment, i.e. reduction of surface deformation (subsidence), fire prevention and methane control, simplification of a ventilation system and liquidation of old mine workings (goafs), results in a significant reduction of mine water discharge to the surface receiving waters and of loads of the majority of contaminants contained in the saline mine waters used for the preparation of pure FA: mine water mixtures.

Environmental evaluation of FA containing desulfurization products from dry and semi-dry process based on the load balance of contaminants retained in mine water: FA + FGDS mixture and released in the outflow of the excess water showed, similarly to pure FA, a generally positive effect of utilizing this material in deep mines in the form of a mixture with mine waters (Twardowska, 1999b).

The output concentrations of the majority of contaminants are higher in leachate than in the input mine water as a result of the release from pure FA or FA + FGDS. The output loads of these contaminants in leachate (Cl, Na, TDS, trace metals) are though considerably lower than the respective input loads in mine water used for preparation of mixtures with FA, mainly due to the permanent binding of water in the solidifying mixture that accounts from 50% up to 65% wt. related to the FA mass, along with a respective load of dissolved constituents. In some cases, also reduction of concentrations of some constituents in the excess outflow occurs, due to precipitation or sorption. This way utilization of CCW underground has a positive effect on the water quality of surface receiving waters. The leachate composition and the contaminant balance (reduced and released loads) for pure FA and FA + FGDS deposition underground may vary considerably depending upon

Table VI.8.3. Concentrations and load balance of dissolved constituents in the input mine water and output leachate from mine water:low alkaline FA mixture 0.8:1 wt., and contents of leachable constituents in solidified material. Pure low alkaline fly ash (LA-FA) from the Rybnik power plant.

Parameters, constituents	Mine water – Borynia mine		Leachate from water – fly ash mixture 1:1		Leached (+) or bound (−) loads	Solidified mixture – leachable load
	Input 0.8 m^3/t		Output 0.458 m^3/t (46%)			
Parameters	C_{in}, mg/l	L_{in}, g/t	C_{out}, mg/l	L_{out}, g/t	$\Delta L = L_{in} - L_{out}$, g/t	$\sum L_{1-3}$, g/t
μS/cm	36,000	–	30,000	–	–	–
pH	7.45	–	7.43	–	–	10.96–9.04
Alkalinity, meq/L	**2.60**	**2.08**	**0.6**	**0.22**	**− 1.86**	25.0
Hardness, meq/L	115.20	92.16	129.06	47.32	**− 44.84**	73.15
Hardness $CaCO_3$	5765	4612	6459	2368	**− 2244**	3661
Hardness Ca	69.97	55.97	128.34	47.06	**− 8.92**	72.78
Hardness Mg	**45.23**	**36.19**	**0.72**	**0.26**	**− 35.92**	0.37
Macro-constituents						
Ca	1402.28	1121.83	2572.00	943.07	**− 178.76**	1458.4
Mg	**550.0**	**440.0**	**8.70**	**3.19**	**− 436.81**	4.55
Na	**9285.2**	**7428.2**	**6292.9**	**2307.1**	**− 5122.56**	3664.4
K	165.92	132.73	213.4	78.25	**− 54.49**	585.8
NH_4^+- N	0.19	0.152	1.4	0.513	0.36	4.85
NO_3^- - N	0.713	0.567	1.406	0.515	**− 0.055**	0.09
Cl^-	**18,656**	**14,295**	**14,100**	**5170**	**− 9754.8**	7843.2
SO_4^{2-}	8.64	6.91	1441.96	528.72	521.81	639.7
HCO_3^-	**158.6**	**126.91**	**36.61**	**13.42**	**− 113.49**	366.10
CO_3^{2-}	0.0	0.0	0.0	0.0	0.0	390.06
OH^-	0.0	0.0	0.0	0.0	0.0	102.05
PO_4^{3-}	**0.064**	**0.051**	**0.035**	**0.013**	**− 0.038**	0.51
TDS	**30,220**	**24,176**	**24,682**	**9050**	**− 15,126**	15,390
COD	1008.8	807.1	1132.8	415.4	−391.7	1711.5

Trace elements						
Al	<0.060	<0.048	<0.060	<0.022	ND	ND
Ba	**92.23**	**73.79**	**0.396**	**0.145**	**−73.64**	ND
Cd	**0.11**	**0.088**	**0.06**	**0.022**	**− 0.066**	<0.075
Co	**0.14**	**0.112**	**0.11**	**0.040**	**− 0.072**	0.05
Cr_t	0.02	0.016	0.25	0.092	0.076	0.65
Cr(VI)	0.004	0.003	0.01	0.0033	0.0003	0.33
Cu	**0.19**	**0.152**	**0.07**	**0.026**	**− 0.126**	0.10
Fe	**0.23**	**0.184**	**0.10**	**0.034**	**− 0.15**	<0.075
Mn	**0.63**	**0.504**	**0.05**	**0.018**	**− 0.486**	<0.075
Mo	<0.025	<0.020	0.523	0.239	0.239	ND
Ni	0.09	0.072	0.13	0.048	**−0.024**	0.19
Pb	0.17	0.136	0.18	0.066	**− 0.070**	<0.075
V	<0.01	<0.008	<0.01	<0.004	ND	ND
Zn	**0.11**	**0.088**	**0.09**	**0.033**	**−0.055**	<0.075

ND – not determined; Constituents showing the reduction of concentrations and/or loads in leachate compared to the input mine water are bold.

Table VI.8.4. Concentrations and load balance of dissolved constituents in the input mine water and output leachate from mine water:high alkaline mixture 1:1 wt., and contents of leachable constituents in the solidified material. Pure high alkaline fly ash (HA-FA) from the Laziska power plant.

Parameters, constituents	Mine water – Moszczenica mine		Leachate from water – fly ash mixture 1:1		Leached (+) or bound (−) loads	Solidified mixture – leachable load
	Input, 1.0 m^3/t		Output, 0.42 m^3/t (42%)			
Parameters	C_{in}, mg/l	L_{in}, g/t	C_{out}, mg/l	L_{out}, g/t	$\Delta L = L_{in} - L_{out}$, g/t	$\sum L_{1-3}$, g/t
$\mu S/cm^{-1}$	46,300	–	49,200	–	–	–
pH	7.60	–	12.27	–	–	7.71–7.67
Alkalinity, meq/l	1.55	1.55	11.00	4.62	3.07	10.25
Hardness, meq/l	127.90	127.90	192.12	80.69	**− 47.21**	116.06
Hardness $CaCO_3$	6401	6401	9614	4038	**− 2363**	5809
Hardness Ca	84.50	84.50	191.70	80.51	**− 3.99**	94.60
Hardness Mg	**43.40**	**43.40**	**0.42**	**0.18**	**− 43.22**	21.46
Macro-constituents						
Ca	1694.2	1694.2	3841.5	1613.43	**− 80.77**	1896.2
Mg	**528**	**528**	**5.12**	**2.15**	**− 525.85**	260.95
Na	9950.4	9950.4	10,339.8	4342.72	**− 5607.68**	6614
K	216.4	216.4	501.2	210.50	**− 5.90**	662.45
NH_4^+- N	**10.08**	**10.08**	**7.00**	**2.94**	**− 7.14**	9.97
NO_3^-- N	**0.218**	**0.218**	**0.062**	**0.026**	**− 0.192**	0.33
Cl	20,380	20,380	23,620	9920.4	**− 10,459.6**	15,300
SO_4^{2-}	**7.82**	**7.82**	**7.41**	**3.11**	**− 4.71**	1040.93
HCO_3	94.58	94.58	0.00	0.00	**− 94.58**	625.42
CO_3^{2-}	0.00	0.00	30.01	12.60	12.60	0.00
OH^-	0.00	0.00	170.01	71.82	71.82	0.00
PO_4^{3-}	**0.342**	**0.342**	**0.036**	**0.015**	**− 0.327**	0.32
TDS	37,445	37,445	39,556	16,613.5	**− 20,831.5**	27,500
COD	889.2	889.2	925.6	388.75	**− 500.45**	3267

Trace elements						
Al	0.243	0.243	ND	ND	ND	ND
Ba	125.2	125.2	ND	ND	ND	ND
Cd	0.05	0.05	0.06	0.025	− **0.025**	1.10
Co	0.21	0.21	0.32	0.134	− **0.076**	0.15
Cr	0.03	0.03	0.29	0.122	0.092	1.00
Cr(VI)	0.001	0.001	0.173	0.073	0.072	1.00
Cu	0.06	0.06	0.08	0.034	− **0.026**	0.50
Fe	0.19	0.19	0.39	0.16	− **0.03**	1.40
Mn	0.11	0.11	0.13	0.055	− **0.055**	0.15
Mo	<0.025	<0.025	0.207	0.087	0.087	ND
Ni	**0.33**	**0.33**	**0.23**	**0.097**	− **0.233**	0.30
Pb	**0.35**	**0.35**	**0.33**	**0.14**	− **0.21**	0.50
V	<0.01	<0.01	ND	ND	ND	ND
Zn	0.03	0.03	0.16	0.067	0.037	0.40

ND – not determined; Constituents showing the reduction of concentrations and/or loads in leachate compared to the input mine water are bold.

the resultant effect of the interaction of two components – mine water and FA of different chemical composition (also upon the content and composition of FGDS). Concentrations of macro constituents and trace metals in the output solutions (leachate) compared to input (mine water) showed significant changes resulted both from the release of soluble constituents of FA and from the binding of dissolved constituents in mine water (Twardowska, 1999a,b). Examining leachate from the different low- and high-alkaline systems in deep mines and at the surface and the computer simulation of pore solution speciation with use of a geochemical computer models WATEQ4F (Ball and Nordstrom, 1991, 1994), MINTEQA2 (Allison et al., 1991) and PHREEQC (Parkhurst, 1995; Parkhurst and Appelo, 1999) proved that pH along with equilibrium constraints were the major factors controlling leachability of macro-constituents and trace elements.

VI.8.4.2. Effects of mine water:pure FA mixture utilization underground on contaminant loads discharged from mines

VI.8.4.2.1. Chemical composition of leachate from dense mine water:pure FA mixtures

The effect of FA characteristics, in particular of its alkalinity, on the leachate composition is exemplified in Tables VI.8.3 and VI.8.4. The typical changes compared to the input mine water common for both low- and high-alkaline FA:mine water systems consist of: (i) transformation of Ca–Mg hardness in the input mine water into almost entirely Ca hardness in leachate, while Mg appears to be thoroughly suppressed with Ca equilibria constraints; (ii) increase of K, which is a minor component of both input mine water and leachate; (iii) considerable increase of output COD for low-saline input water, and slight increase of COD at high COD and salinity of input mine water. Amphoteric trace elements and oxyanions distinctly increase in the leachate especially chromium, present mainly in a hexavalent form Cr(VI), and molybdenum. Pb displays considerable stability, while V appears to be resistant to mobilization. High enrichment of fluoride in the outflow was also observed.

In general, trace element concentrations in leachate follow leaching patterns caused by solubility/stability criteria, pH being the main controlling factor (Brookins, 1987; de Groot et al., 1989; van der Sloot et al., 1991, 1996, 1997). The ionic strength and chemical composition of the solution resulting from the interaction of mine water with FA exerts considerable effect on trace element release or binding and results in substantial diversity in leaching behavior of FA.

The differences in alteration of mine water chemical composition, which result from the contact with FA in low-alkaline and high-alkaline systems were found to be specific for these systems.

In low-alkalinity saline mine water systems (Table VI.8.3), the chemical composition of leachate is dictated by equilibrium with gypsum. The typical transformations of the output leachate from the mixture compared to the input mine water can be summarized as follows: (i) frequent pH stabilization at the moderate alkalinity level; (ii) decrease of carbonate contents in parallel with increase and stabilization of sulfate at the concentration dictated by the equilibrium with gypsum; (iii) frequent decrease of chloride and sodium concentrations due to complexation at Cl–Na type of input waters, which results in the adequate reduction of TDS; (iv) increase of nitrogen (N) compounds. Due to pH range

within the stability field of the majority of trace metals, weak metal release or reduction of Ba (due to precipitation of $BaSO_4$), Cd, Co, Cu, Fe, Mn and Zn occurs in the output leachate. Ni displays an increasing trend due the vast stability field in solution in a broad pH range and high content in FA.

In high-alkalinity FA:mine water systems (Table VI.8.4), chemical composition of leachate is governed by carbonate equilibria, which determine a pattern of the qualitative transformations of the input mine water. In general, the most characteristic trends in these systems are as follows: (i) increase of pH value, up to pH > 12; (ii) strong increase of alkalinity in parallel with carbonate hardness and decrease of sulfate hardness (iii) increase of chloride and Na concentrations due to release from FA matrix; the intensity of release is higher if Cl–Na salinity of the input mine water is low; (iv) increase of TDS as a result of increase of chlorides balanced by alkali ions and of carbonate hardness; (v) decrease of sulfate concentrations that adversely depends upon the SO_4 content in the input mine water and is deeper if the SO_4 concentrations in the input mine water are high; (vi) frequent distinct decrease of nitrogen compounds (ammonia and nitrate). Concentrations of trace metals in leachate strongly depend upon their stability field at elevated pH. Most of the metals in such systems with pure high alkaline FA show a general moderate increase. Trace metal concentrations in the leachate usually somewhat exceed the maximum permissible concentration level for drinking water (MCL).

The decrease of N compounds and sulfate contents in leachate from high alkaline FA:mine water mixtures or the reduction of Cl, Na and TDS in leachate from low alkaline FA:mine water mixtures is not an explicit rule and in some systems does not occur, which is due to the variety of chemical composition and physiochemical parameters of both FA and mine waters used for mixture preparation.

VI.8.4.2.2. Load balance

Generally, the leachate quality is worse than that of the input mine water. Nevertheless, the permanent binding of input water in high-TDS mine water:FA mixture up to 65% wt. results in a considerable reduction of the discharged loads of contaminants compared to those in the input mine water, including almost all trace metals (except Cr_t Cr(VI) and Mo), N compounds, major parameters and macro components like chloride, hardness, Na, K, TDS and COD, and in high alkaline systems or at high sulfate input water also sulfate (Tables VI.8.3 and VI.8.4, Fig. VI.8.2a,b). The most environmentally beneficial effect is the high reduction of discharged contaminant loads resulting from the preparation of FA mixtures of highly saline, acidic, high trace metal mine waters from the deep seams at the ratio assuring transportability at the minimum leachate, usually 1:1 or less. The adverse effect of pure FA use underground is an increase of pH value in excess outflow up to strongly alkaline pH $\geq$ 12 in the highly alkaline systems and mobilization of amphoteric metals like Cr and Ni. Oxyanions such as Mo show high mobility in a wide range of pH, both in neutral and alkaline systems. The released excessive loads, though, can be effectively minimized by the optimization of the mine water:FA ratio.

The application of a better quality, low-TDS mine water fit for any other purpose for preparation of dense mine water:FA mixtures should be avoided in order to protect usable ground-water resources and because of a strongly reduced or even completely lacking environmentally beneficial effect of contaminant binding. A comparison of the load

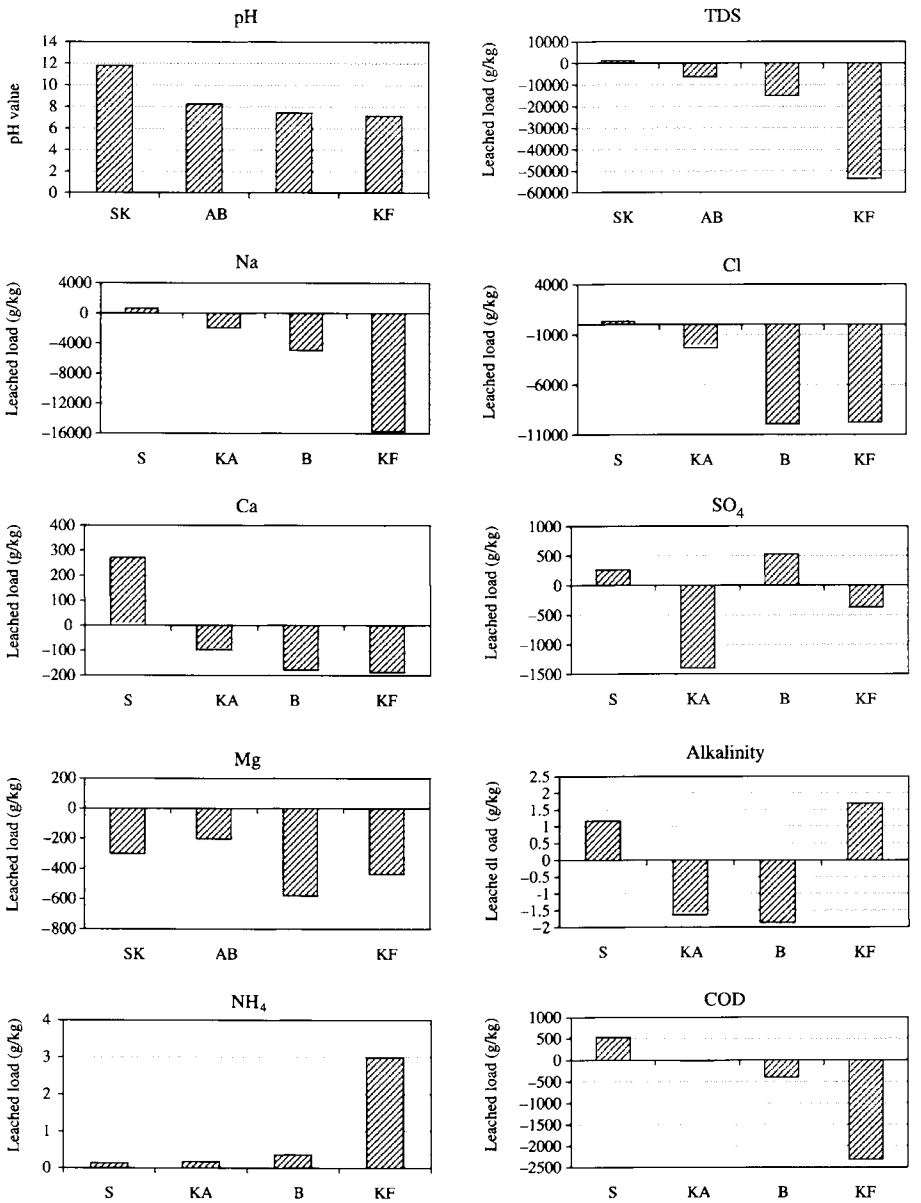


Figure VI.8.2. (a) Effect of mine water salinity in mixture with pure FA (1:1, wt.) on binding (−) or release (+) of macro-constituent loads. Material: Low alkaline FA from the Rybnik power plant. Mine water of increasing Cl–Na salinity in the TDS range from 2 to 100 g/l from different coal mines (USCB, Poland): Sosnica (S), Knurow-Aniolki (KA), Borynia (B) and Knurow-Foch (KF). TDS values: 2.7 g/l (S); 8.3 g/l (KA); 30.2 g/l (B); 93.7 g/l (KF). (b) Effect of mine water salinity in mixture with pure FA (1:1, wt.) on binding (−) or release (+) of trace element loads. Material: Low alkaline FA from the Rybnik power plant. Mine water of increasing Cl–Na salinity in the TDS range from 2 to 100 g/l from different coal mines (USCB, Poland): Sosnica (S), Knurow-Aniolki (KA), Borynia (B) and Knurow-Foch (KF). TDS values: 2.7 g/l (S); 8.3 g/l (KA); 30.2 g/l (B); 93.7 g/l (KF).

(b)

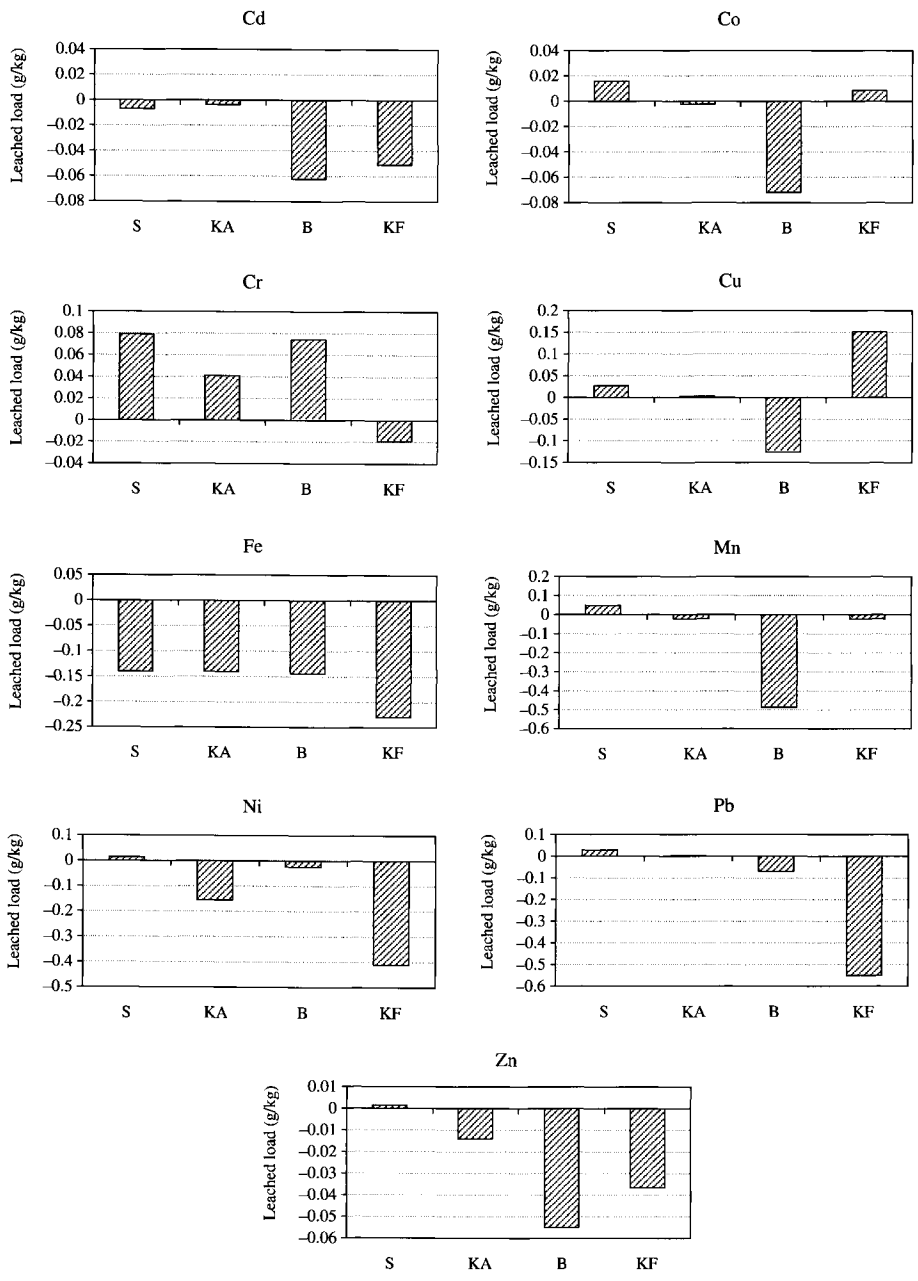


Figure VI.8.2. (Continued).

balance for a mixture of low- to high-TDS mine water (Fig. VI.8.2a,b) clearly shows the domination of release over binding of almost all measured macro-constituents and trace elements if low-TDS mine water (S in Figure VI.8.2a,b) is being used for a mixture preparation. If moderate to high-TDS saline mine water is used, the binding effect prevails with respect to the both macro- and trace constituents (KA, B, KF in Figure VI.8.2a,b). If no other water is available, the maximum technologically possible reduction of mine water:FA ratio would allow achieving a substantial decrease of the leachate volume. This also decreases the excessive loads of contaminants in leachate that are to be discharged to the water:FA mixture preparation circuit that can be separated from a general mine dewatering system if the released loads reduce the discharged water quality.

VI.8.4.2.3. Leachability of constituents from the solidified mixture

After binding of added mine water in a process of formation of calcium silicates and aluminosilicates, sulfate hydration and crystallization, loss of excess water, and solidification of mine water:FA mixture placed in dry mine workings, leachate terminates. The solidification of pure FA mixtures lasts 23–24 days. The further leaching of soluble constituents from FA mixture may occur either in wet mine workings or after flooding the mine in a post-closure period. In such conditions, the release of constituents will follow the leaching behavior pattern for monolith material, and will show low dynamics that is not addressed here.

To evaluate total load of the potentially leachable constituents in solidified dense FA mixtures, a standard leaching test of crushed material at liquid to solid ratio L:S = 2 according to EN 12457–1 (2002) in triplicate sequence was used. It displayed somewhat different leachability for low- and high-alkaline systems (Tables VI.8.3 and VI.8.4, Fig. VI.8.3a,b).

Low-alkaline solidified mixtures showed similar pH range as the outflow, but in some cases also increase of pH range of eluates up to values $11 < pH < 9$ (Table VI.8.3, Fig. VI.8.3a,b), while the pH range of eluates from the solidified high-alkaline mixture, opposite to the low-alkaline one, was definitely lower than that in dewatering stage, within slightly alkaline values (Table VI.8.4). The total leachable loads of TDS, Cl, Na and Ca-hardness in both systems were close to that retained in the material from mine water. High COD and high NH_4-N leachable loads originated from FA. The leachable load of sulfates in the low alkaline system was comparable to that released in the dewatering stage, while in the high alkaline system it was up to over three orders of magnitude higher than in the outflow. Most of the trace elements appeared to be stable in a solid phase at the actual pH range and unsusceptible to mobilization, similar to those in leachate at the dewatering stage of a mixture. The dynamics of constituent leaching from the monolithic solidified material will be naturally much lower.

The decreasing trend of pH values in both systems during sequential leaching signals the possibility of acidification of the material in course of a longer time if constant vertical infiltration through the FA mixture placed in mine workings occurs under the vadose zone conditions. Shifting from the highly alkaline to acidic pH values of pore solution in FA surface pond in the post-closure period with all the consequences of massive heavy metal mobilization have been already observed (Twardowska and Szczepanska, 2002) (see also Chapter III.7). The similar non-linear time-delayed trace

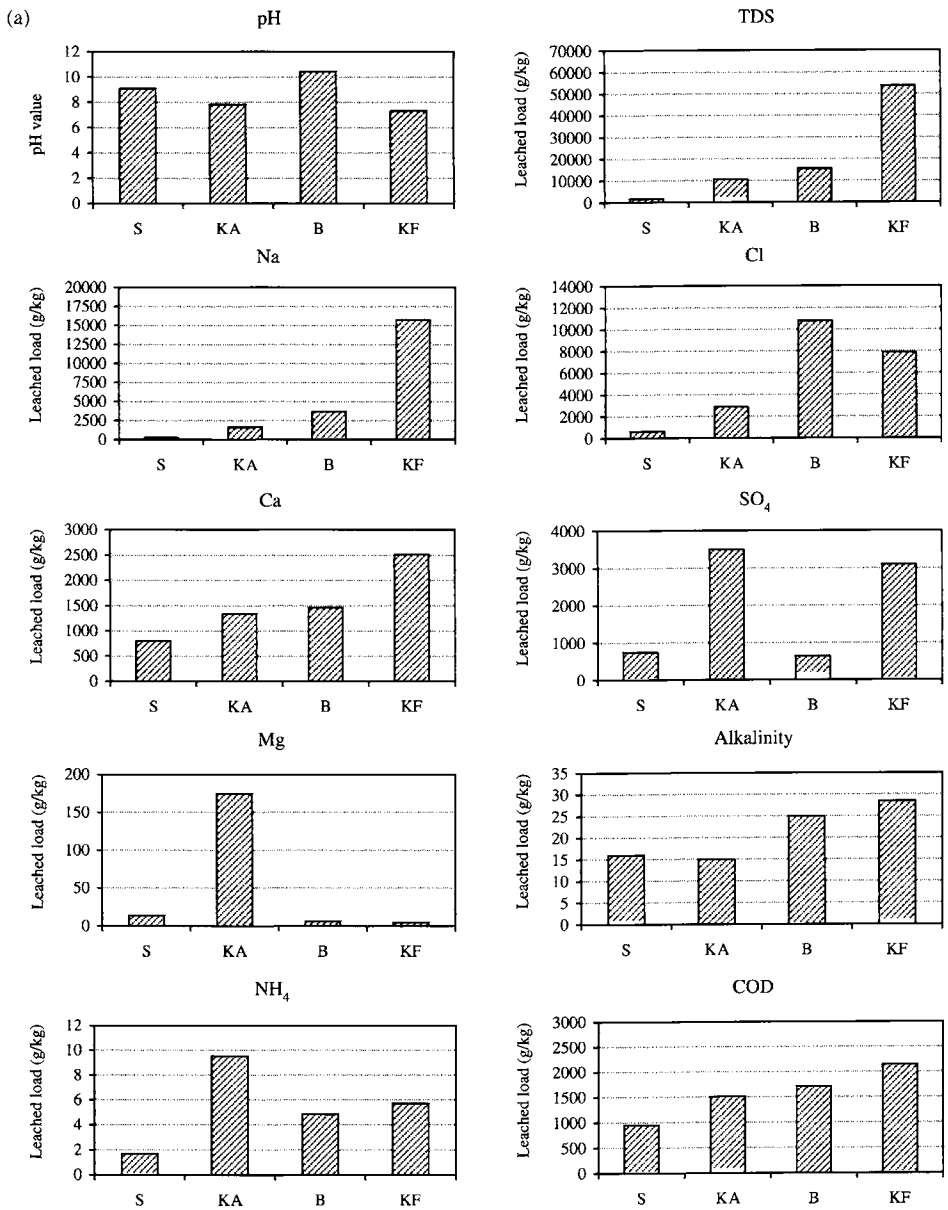


Figure VI.8.3. (a) Contents of leachable macro-constituents in solidified mixtures of pure low alkaline FA with mine water of increasing salinity of Cl–Na type (1:1, wt.). Material: Low alkaline FA from the Rybnik power plant. Mine water of Cl–Na salinity in the TDS range from 2 to 100 g/l from different coal mines (USCB, Poland): Sosnica (S), Knurow-Aniolki (KA), Borynia (B) and Knurow-Foch (KF). TDS values: 2.7 g/l (S); 8.3 g/l (KA); 30.2 g/l (B); 93.7 g/l (KF); (b) Contents of leachable trace elements in solidified mixtures of pure low alkaline FA with mine water of increasing salinity of Cl–Na type (1:1, wt.). Material: Low alkaline FA from the Rybnik power plant. Mine water of Cl–Na salinity in the TDS range from 2 to 100 g/l from different coal mines (USCB, Poland): Sosnica (S), Knurow-Aniolki (KA), Borynia (B) and Knurow-Foch (KF). TDS values: 2.7 g/l (S); 8.3 g/l (KA); 30.2 g/l (B); 93.7 g/l (KF).

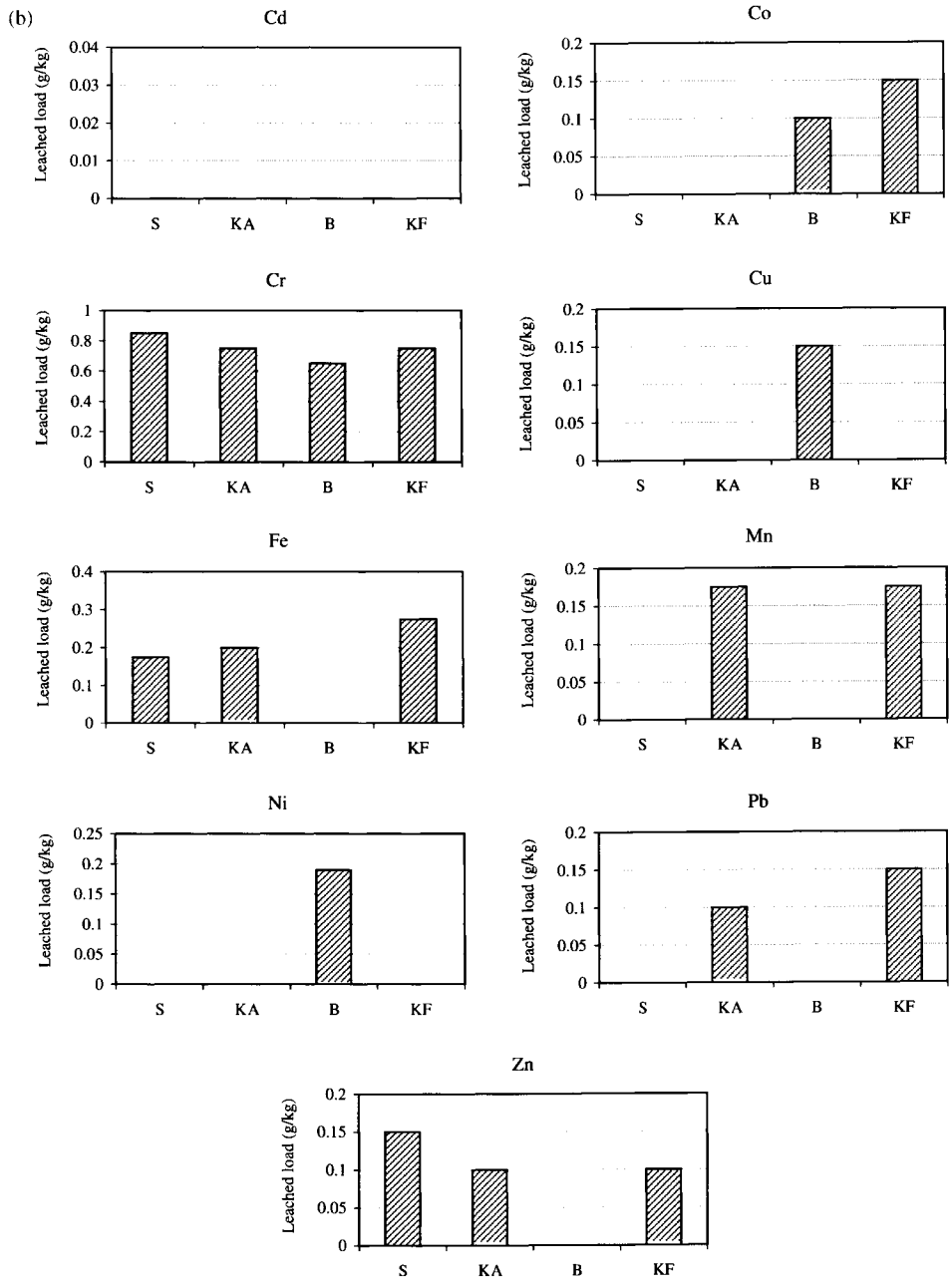


Figure VI.8.3. (Continued).

metal release might occur also in the FA layers underground provided that they are exposed to the vertical percolating of infiltration water directly from the surface or from the recoverable ground water resources. This suggests caution in placing FA mixtures in such infiltration zones if the reliable long-term predictive modeling of pH changes does not exclude the possibility of acidification.

VI.8.4.3. Effects of slurry:pure FA mixture utilization underground on contaminant loads discharged from mines

Instead of mine water for preparation of a transportable FA mixture, non-dewatered slurry from the flotation process in coal preparation plants can be used. The amount of slurry required for assuring the gravitational transportability of mixture is higher than for mine water, i.e. a ratio of slurry:FA of 2:1 by weight. This way of FA mixture preparation gives an opportunity of utilizing slurry underground and substantially reduces costs by resignation from filter press dewatering of slurry and its disposal at the dumping sites.

This method of preparing transportable FA mixtures is less popular than using mine water as it is more problematic and expensive. It needs a more precise electronically operated process of mixture preparation to keep exact parameters (density, flow rate) of mixture and slurry pumps must be used for slurry transport to the installation (Fig. VI.8.4).

The balance of contaminant retention and release using slurry for preparation of FA mixtures, similar to use of mine water, depends on the properties of FA and the liquid phase in the slurry. The leachate quality and load balance for such mixture with use of moderately alkaline and saline slurry and low alkaline FA from the Rybnik power plant were found to improve substantially compared to these in the input slurry due to the reduction of Cl and Na concentrations, TDS and Mg hardness, and low concentrations of trace metals ($<$MCL) resulting from the slightly or moderately alkaline pH values within their stability field in the solid phase (Twardowska, 1999a). In general, leachate quality from these mixtures was similar to those from adequate systems with mine water. Significant reduction of COD and a high increase of nitrogen compounds, mainly ammonia in leachate was specific for these systems, and usually did not occur in output from mine water:FA mixtures. Because of high input water retention in the mixture (from 57 to $>$70%), almost all the released loads of macro-constituent and trace metal loads in leachate were substantially lower than those in the input solution. Nevertheless, due to a moderate salinity of slurry water, the total load balance of contaminants was less favorable than for mixtures with brine mine water, as the highest load reduction occurred when waters of high salinity at low mine water:FA ratio were used.

Here, another system of acidic slurry (pH 3.78) from the Jastrzebie mine in a mixture at a ratio 0.7:0.3 with low-alkalinity FA has been analyzed with regard to environmental impact (Table VI.8.5). In this system, FA showed very good buffering properties, transforming pH of an output leachate into slightly alkaline one that remained as such after sequential extraction in triplicate of the solidified mixture. Similar to the alkaline system, reduction of Cl, Na, K and TDS concentrations in leachate compared to the input solution occurred. The differences in alteration of leachate characteristics compared to the alkaline slurry consisted in an increase of Mg-hardness and alkalinity, at practically stable SO_4 content in output. The adverse alteration comprises almost 10-fold increase of COD.

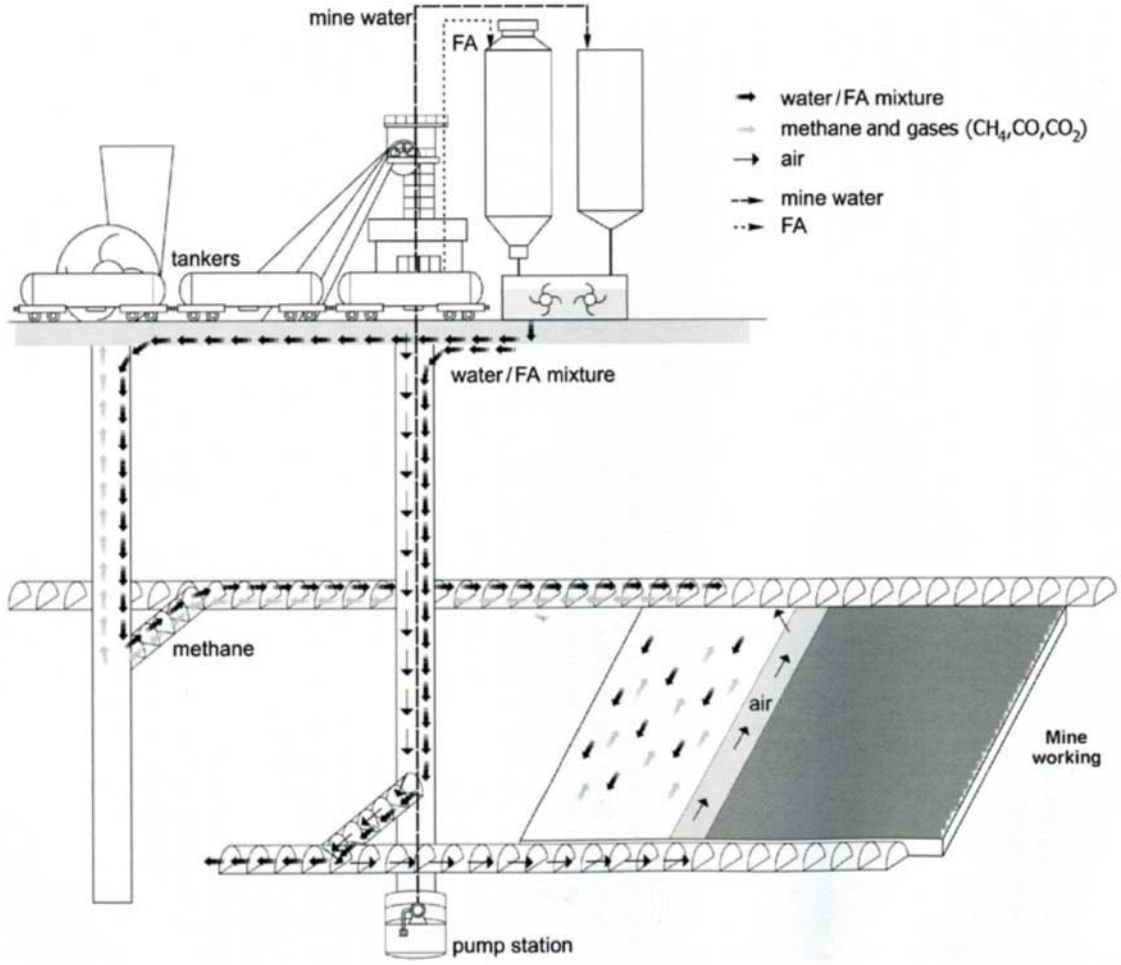


Figure VI.8.4. Scheme of installation for flotation slurry:FA mixture preparation to be utilized in deep mines (after UTEX Ltd., Poland).

Table VI.8.5. Concentrations and load balance of dissolved constituents in the input slurry water and output leachate from acidic flotation slurry:low alkaline FA mixture 2:1 wt., and contents of leachable constituents in solidified material. Pure low-alkaline FA from the Rybnik power plant.

Parameters, constituents	Slurry water – Jastrzebie mine		Leachate from slurry – fly ash mixture 2:1		Leached (+) or bound (−) loads	Solidified mixture – leachable load
	Input, 0.756 m^3/t		Output, 0.211 m^3/t (28%)			
	C_{in}, mg/l	L_{in}, g/t	C_{out}, mg/l	L_{out}, g/t	$\Delta L = L_{in} - L_{out}$, g/t	$\sum L_{1-3}$, g/t
μS/cm	10,500	–	10,000	–	–	–
pH	**3.78**	–	**7.84**	–	–	7.92–8.20
Alkalinity, meq/l	0.00	0.00	2.80	0.472	0.472	17.0
Acidity, meq/l	**7.70**	**6.05**	**0.00**	**0.00**	**− 6.05**	0.00
Hardness, meq/l	43.05	33.90	60.49	10.20	**− 23.702**	134.31
Hardness $CaCO_3$	2154	1696	3027	510	**− 1186**	6722
Hardness Ca	42.15	33.19	48.77	8.22	**− 24.97**	125.35
Hardness Mg	0.90	0.71	11.72	1.976	1.268	8.96
Macro-constituents						
Ca	844.88	665.36	977.54	164.8	−500.51	2512.2
Mg	11.0	8.663	142.5	**24.03**	15.367	109.0
Na	**1955.4**	**1539.9**	**1509.9**	**254.6**	**− 1285.2**	862.6
K	**82.96**	**65.33**	**39.87**	**6.386**	**− 58.608**	132.5
NH_4^+-N	10.32	8.127	14.65	2.47	**− 5.656**	8.57
NO_3^--N	**0.685**	**0.539**	**0.125**	**0.021**	**− 0.518**	0.105
Cl^-	**3922**	**3088.6**	**3498**	**589.88**	**− 2498.8**	2821.0
SO_4^{2-}	**1888.7**	**1487.4**	**1877.6**	**316.6**	**− 1170.76**	4360.8
HCO_3^-	–	–	170.85	28.80	28.81	1037.3
CO_3^{2-}	–	–	0.0	0.0	0.0	0.0
OH^-	–	–	0.0	0.0	0.0	0.0
PO_4^{3-}	0.026	0.0048	0.029	0.0049	−0.0155	0.76

(continued)

Table VI.8.5. (Continued)

Parameters, constituents	Slurry water – Jastrzebie mine		Leachate from slurry – fly ash mixture 2:1		Leached (+) or bound (−) loads	Solidified mixture – leachable load
	Input, 0.756 m^3/t		Output, 0.211 m^3/t (28%)			
	C_{in}, mg/l	L_{in}, g/t	C_{out}, mg/l	L_{out}, g/t	$\Delta L = L_{in} - L_{out}$, g/t	$\sum L_{1-3}$, g/t
TDS	**9242**	**7278.3**	**8354**	**1408.8**	**− 5869.53**	12,005
COD	166.4	130.96	1203.6	1373.2	71.92	11,718
Trace elements						
Al.	<0.060	0.047	0.643	0.108	0.0612	ND
Ba	0.238	0.187	0.312	0.053	**−0.135**	ND
Cd	**0.14**	**0.109**	**0.01**	**0.002**	**− 0.109**	0.10
Co	**0.16**	**0.125**	**0.06**	**0.010**	**− 0.1158**	0.175
Cr_t	0.02	0.015	0.04	0.007	**− 0.0089**	0.35
Cr(VI)	0.008	0.006	0.013	0.002	**− 0.0041**	0.145
Cu	**1.22**	**0.960**	**0.37**	**0.062**	**− 0.898**	0.10
Fe	**70.1**	**55.17**	**0.03**	**0.005**	**− 55.20**	0.01
Mn	**11.45**	**9.01**	**2.86**	**0.482**	**− 8.535**	<0.075
Ni	**0.29**	**0.227**	**0.12**	**0.020**	**−0.208**	0.30
Pb	**0.09**	**0.071**	**0.04**	**0.007**	**− 0.0641**	<0.075
V	<0.01	0.008	0.016	0.003	−0.0052	ND
Zn	**1.80**	**1.417**	**0.49**	**0.08**	**− 1.335**	0.125

ND – not determined; Constituents showing the reduction of concentrations and/or loads in leachate compared to the input slurry water are bold.

The favorable effect on leachate compared to the input solution was a dramatic reduction of high metal concentrations due to shifting pH values into their stability field, in particular Fe, Mn, Zn, Cu, Cd, Ni, Pb, and Co. Slight increase of amphoteric and oxyanionic metal concentrations, like Al, Cr, Cr(VI), Mo, V, all within MCL for drinking water, does not create any problems, as the output loads of these metals showed significant reduction. This example shows a particular beneficial effect of FA application in mines having problems with high-metal acidic waters, which is equally frequent in coalfields and metal ore mines in the world (e.g. in the USA, the UK, Australia, South Africa). In this most prospective field of FA application, the neutralizing and metal-reducing effect is due to the direct neutralization, but the most long-term effect consists in prevention and termination of acidity generation from the sulfite oxidation resulting from perfect sealing of a mined out or abandoned workings against air penetration.

VI.8.5. Environmental effects of mine water:fly ash mixture use in wet mine workings

In the case of application FA in the form of dense low-ratio mine water:FA mixture in dry mine workings insulated either from the infiltration zone of the recoverable ground water resources or from the inflow of saline waters from the upper seams, the leachate is limited entirely to the outflow of the excess water from the deposited mixture. Under the complicated hydrogeological conditions of mines, further leaching of FA mixtures by infiltration water either from the surface or from the upper seams may occur in wet seams and in the post-closure period due to water logging of dry seams.

The simulation of leaching behavior of high-alkaline FA:mine water mixture comprised the actual and potential cases of mine operating: (A) low-TDS mine water:FA mixture deposited in the infiltration area of recoverable ground water resources; (B) saline mine water:FA mixture deposited in the infiltration area of recoverable ground water resources; (C) saline mine water:FA mixture deposited in the area of roof inflow from static resources of saline mine water (Twardowska, 1999a). Flow-through leaching cycle comprised two phases (0 – dewatering and 1 – vertical in filtration under the vadose zone conditions, up to 2.5-fold cumulative pore water exchange rate). The phase I covered wash-out (I) and dissolution (II) stages. Both the results of simulation (Table VI.8.6) and the long-term practice of FA utilization in deep mines shows, that the most environmentally beneficial and safe option is utilization of FA mixtures with saline mine water in dry mine workings insulated from the recoverable ground water resources. Use of saline waters intensifies and accelerates solidification of FA layer, which is an additional advantage. Vertical infiltration of water through freshly deposited high-alkaline FA appeared to strongly enhance contaminant loads release from the mixture, roughly at an order of magnitude compared to the dewatering phase (0) and in concentrations exceeding MCL either in the both stages (e.g. for the case (A): pH, K, NH_4-N, COD, Cr(VI) and Mo) or in the wash-out (I) stage (for the case (A): Na, NO_2-N, SO_4, Cr_t). In the case (A) the released load origins from the FA matrix.

Utilization of FA mixtures with saline mine water in the feeding zone of recoverable ground water resources (case B) caused release in the infiltration phase of almost the total load of soluble constituents introduced into the mixture with saline water (Cl and Na),

Table VI.8.6. Concentration range of selected constituents in leachate and loads leached from the 2 m thick layers of water:FA mixture 1:2 wt. in simulated conditions of a vertical rain- or mine water infiltration in wet mine workings.

Parameters, constituents	(A)		(B)		(C)		MCL[a], mg/l	(A)		(B)		(C)	
	Concentrations							Loads					
Parameters	0	I	0	I	0	I[b]		0	I	0	I	0	I[b]
Water exchange rate	0.189	2.516	0.170	2.324	0.152	0.524		0.189	2.516	0.170	2.324	0.152	0.524
pH	7.62	8.25–**11.46**	**10.78**	**7.86–11.16**	7.66	7.90–8.16	6.5–8.5						
Alkalinity, meq/l	1.0	0.45–6.30	2.20	1.8–4.65	1.5	1.8–3.05		79.55	3608	160.00	2973	98.86	463,864
Hardness, meq/l	2.21	0.31–2.55	79.11	1.4–15.32	97.9	14.12–23.58		175.80	843.26	5753.4	11,169	6452	9336
Hardness $CaCO_3$	110.59	15.51–127.61	3959	70.06–766.68	4899	706.6–1180							
Macro-constituents, mg/l													
Na	362.35	313.8–15.3	**33,031**	**16,701–3615.4**	**32,021**	**29,403–33,177**	800	28,823	183,547	2,402,254	11,528,140	2,110,476	7,028,259
K	**167.65**	**199.2**–20.6	**542.03**	**653.8–104.5**	**532.59**	**403.6–456.4**	80	13,336	126,691	39,420	317,699	35,103	101,429
NH_4^+-N	**12.09**	**20.16**–1.01	**15.82**	**18.2**–1.08	**38.22**	**12.6–41.75**	10	961.71	6986	1150	5318	2519	ND
Cl	127.2	254.4–31.8	**35,340**	33,880–5745	**53,480**	**50,200–53,600**	1000	10,118	129,393	2,570,182	19,018,125	3,524,818	11,730,545
SO_4^{2-}	**864.5**	384.2–9.61	**864.54**	144.09–47.11	**1022**	**911.8**–125.11	500	68,767	220,096	62,876	145,962	67,345	174,268
TDS	1761	1508–288	90,133	52,756–9640	89,628	80,523–87,760		140,080	919,917	6,555,127	33,226,782	5,907,300	19,341,570
COD	128.2	**141.02**–76.92	**13,230**	**4615–1128**	**10,049**	**10,801–13,524**	125	10,198	138,409	962,199	3,672,283	662,349	2,524,420
Trace elements, mg/l													
Al	0.519	1.287–0.82	<0.06	0.204–1.073	<0.06	1.528–0.528	3	41.28	ND	<4.36	ND	<3.95	ND
Cd	<0.001	0.1–0.3	**0.45**	0.12–0.01	**0.44**	0.14–0.13	0.4	<0.08	4.19	6.54	52.23	10.54	33.02
CrVI	**0.436**	**0.492–0.15**	**0.401**	**0.283–0.149**	**0.194**	**0.193–0.309**	0.1	34.68	279.08	29.16	216.55	12.79	48.98
Cu	0.05	0.02–<0.001	0.11	0.08–0.01	0.11	0.14–0.10	0.5	3.98	9.75	8.00	42.25	7.25	25.93
Mo	**2.699**	**2.985–2.334**	**2.37**	**3.509–2.307**	**2.488**	**1.312**–0.122	1	214.69	ND	172.36	ND	163.98	ND
Ni	0.03	<0.001–0.01	**0.93**	**0.63**–0.04	**0.82**	**0.77–0.68**	0.5	2.39	4.71	67.64	263.73	54.05	172.27
Pb	0.04	0.23–<0.001	0.28	0.42–0.05	0.47	**0.66–0.60**	0.5	<0.79	38.83	20.36	174.93	30.98	122.11
Zn	<0.001	0.21–<0.001	<0.001	0.37–<0.001	<0.001	0.64–0.12		<0.08	47.46	<0.073	75.02	<0.066	52.68

FA – high alkaline FA from Laziska power plant. (A) Low TDS water:FA mixture, simulated rain water infiltration, flow rate 4.74 mm/d; (B) 50 g Cl/L-Na brine:FA mixture, simulated rain water infiltration, flow rate 4.74 mm/d; (C) 50 g Cl/L-Na brine:FA mixture, simulated brine roof inflow, flow rate 20 mm/d. Phase 0 – dewatering; Phase I – vertical infiltration under the vadose zone conditions; ND – not determined.

[a]Polish regulations for liquid waste discharged to waters and soils (Directive of the Minister of Environment, 2002).

[b]Solidification.

along with the loads of the macro-constituents and trace elements leached from the FA matrix in several times higher concentrations and amounts than in the case (A): Ca-hardness, COD, K, trace metals: Ni, Pb, Zn, Cd, Co, Cu, Mo, Mn, Fe. Despite a gradual release of these loads, the leachate displayed long-term deterioration. The positive effect of contaminant retention in the dewatering phase in both cases (A and B) was thus strongly reduced or annihilated in the infiltration phase. Therefore, due to adverse impact of soluble constituents release from the FA matrix on the infiltration water quality, any direct contact of FA mixtures with the feeding zone of recoverable ground water resources should be avoided. In particular, application there of FA mixtures prepared with use of saline mine water should be considered intolerable.

Utilization of FA mixtures in the zone of infiltration of saline waters from the static resources causes temporary increase of leached loads of contaminants prior to the cementation of the FA layer. If the released loads play a negligible role in the total soluble constituents' balance discharged to the receiving waters with the mine drainage, this temporary situation may be accepted as a low-impact one.

The presented results show a general adverse effect of mine water:FA exposure to vertical infiltration of water due to the contact with the recoverable ground water resources or with their feeding zone. Our long-term practice of FA utilization in underground mine workings shows that the most environmentally beneficial and safe option is utilization of FA mixtures with saline mine water in dry mine workings insulated from the recoverable ground water resources. In the light of our vast experience, the reports on the beneficial effect of FA on the ground water under the conditions of a permanent direct contact (Paul and Singh, 1995) should be treated as a particular case and cannot be generalized. Also other authors, in view of evidence of exhaustion of FA/coal ash alkalinity over extended time periods, point out the need of predicting the overall leaching behavior of CCW, in particular placed in environments where acid mine waters occur. For this purpose, the mine water leaching procedure (MWLP) was developed to sequentially leach particular CCW with the target mine's groundwater to evaluate leaching behavior of trace elements as alkalinity is exhausted (Ziemkiewicz et al., 2003a,b). Thus, in every case of the planned use of FA in mine workings, the long-term prognosis of the environmental effect of FA utilization in the actual hydrogeological conditions should be carried out to avoid unnecessary risk.

VI.8.6. Effect of FGD solids on the environmental behavior of dense mine water:FA + DGDS mixtures utilized underground

VI.8.6.1. General trends

The trends reflecting the environmental behavior of FA mixtures containing FGD solids from dry and semi-dry processes are similar to those for pure FA and displayed a generally positive environmental effect, predominantly due to retention of water in the mixture, and partly due to equilibria limitations, which cause permanent binding of a substantial part of the contaminant loads in the mixture. The resultant effect can be summarized as follows: the output concentrations of the majority of contaminants are higher in leachate than in the input mine water as a result of the release from FA + FGDS, while the output loads are

considerably lower due to high retention capacity of the material. The leachate composition and the contaminant balance for FA + FGDS deposition underground may vary considerably according to mine water and FA composition, to the great extent determined by the composition and content of FGDS. The characteristics of FGDS and FA + FGDS mixtures from dry and semi-dry processes are presented in Chapter III.7, while the effect on the aquatic environment of the use of FA containing FGD solids has been discussed in detail elsewhere (Twardowska, 1999b). Here, it will be summarized in brief.

VI.8.6.2. Effect of using FA + D-FGDS mixtures with mine water on the contaminant balance

The environmental behavior of low-ratio mine water mixtures with FA containing products of the dry desulfurization process (FA + D-FGDS) is highly determined by the content of unreacted CaO in these products, which assures the best hydrogeological and hydrogeochemical parameters: the lowest hydraulic conductivity, up to impermeability to the horizontal flow ($k = 10^{-8}-10^{-9}$ m/s), the best sealing properties against air penetration (penetration resistance $R = 13,000-19,000$ kPa, which is an order of magnitude higher than that of pure FA mixtures and 2 orders of magnitude higher than that of natural cohesive soils such as boulder clay $R = 190$ kPa), the shortest solidification time (mean 17 days), the highest water retention capacity (60–75%), lack of tendency to acidification and hence of the massive trace elements release in the delayed release (III) stage. The excess of CaO results in high pH and alkalinity of the leachate and thus is similar to the leachate composition and the load balance for the pure high-alkaline pH, in particular in the mixture-dewatering phase 0. Similar systematic behavior of high-alkaline material from the different power plants and processes dictated by pH values is illustrated in Figure VI.8.5 a,b.

The release of macro-constituents for this system is determined by carbonate equilibrium constraints. The general pattern of contaminant release displays low leachability of sulfates from FA and high Ca-carbonate hardness of leachate, lack of chloride complexation and frequent decrease of N compounds. The highest leachability of trace elements show Cr_t, mainly in the Cr(VI) form, and Mo. Most of the other trace elements occur in the leachate in elevated concentrations compared to the input mine water, though the load balance for both macro- and trace constituents shows high retention capacity of the mixture with high TDS water in the dewatering phase 0 (Figures VI.8.5 a,b, and V.8.6a,b – case B). The load balance of low-TDS water for almost all leached constituents including trace elements exhibits predominance of release over binding in the dewatering phase (Twardowska, 1999b). Leachability of macro-constituents and trace elements from ground solidified mixtures of FA + D-FGDS was found to be generally lower than that of pure high-alkaline FA (Fig. VI.8.5 a,b) and higher than from pure low-alkaline FA mixtures with mine water of moderate and high TDS. The binding of macro- and trace constituents in FA + D-FGDS mixtures with high-TDS mine waters in solidified mixture (1) appeared to be considerably higher than in the adequate mixture with low-alkaline pure FA (Fig. VI.8.6a,b – cases A and B). In actual conditions, due to significantly lower hydraulic conductivity and high cementation properties, much lower dynamics of constituents leaching from the solidified mixture is anticipated.

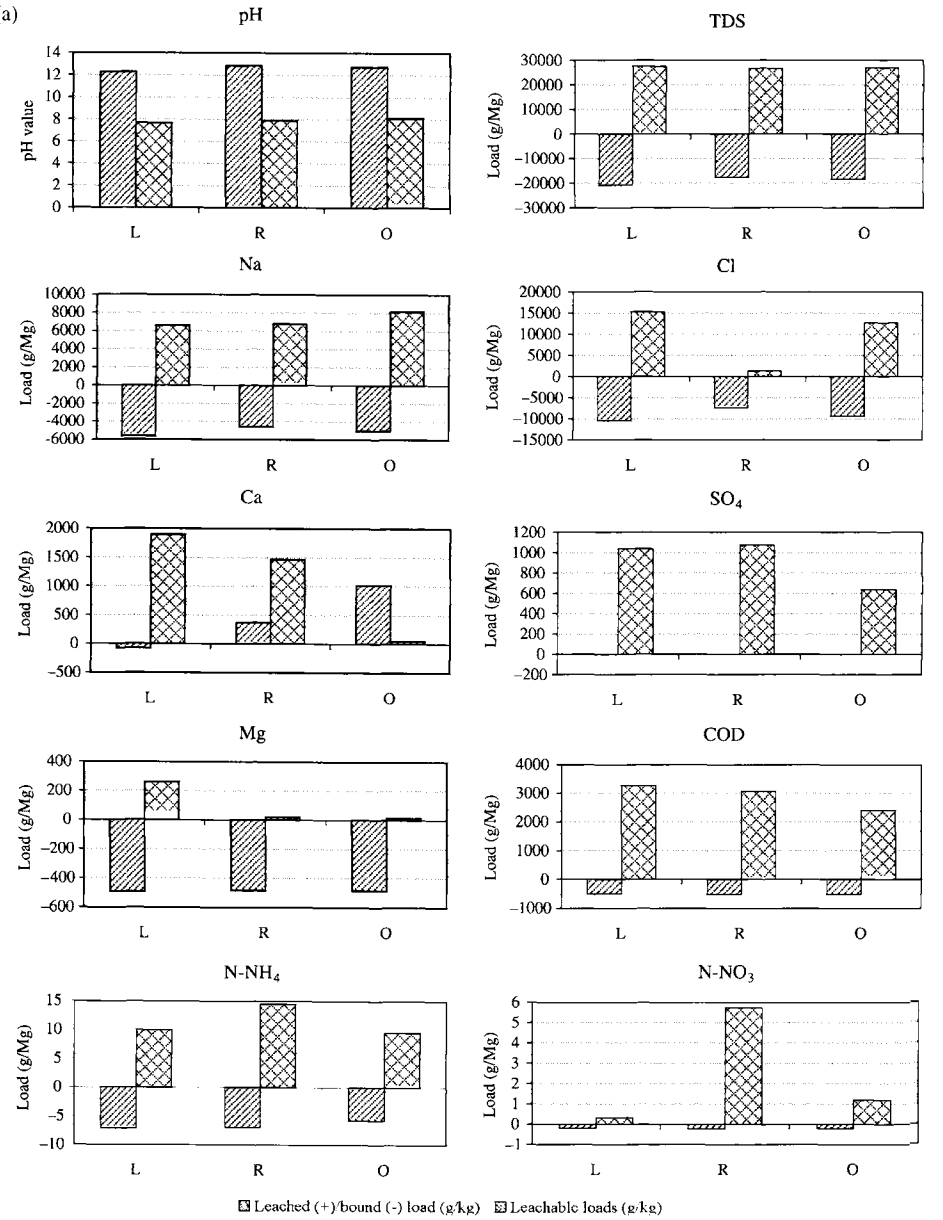


Figure VI.8.5. (a) Binding (−) and release (+) of macro-constituents from mine water mixtures with high alkaline pure FA or FA + D-FGDS (1:1 wt.) in the dewatering stage, and contents of leachable constituents in the solidified mixtures. Dense mixture components: Mine water from the Moszczenica mine of Cl–Na type, TDS 37.5 g/l; L – pure high alkaline FA from the Laziska power plant; R – FA + D-FGDS from the Rybnik power plant; O – FA + D-FGDS from the Opole power plant. (b) Binding (−) and release (+) of trace elements from mine water mixtures with high alkaline pure FA or FA + D-FGDS (1:1 wt.) in the dewatering stage, and contents of leachable trace elements in the solidified mixture. Dense mixture components: Mine water from the Moszczenica mine of Cl–Na type, TDS 37.5 g/l; L – pure HA-FA from the Laziska power plant; R – FA + D-FGDS from the Rybnik power plant; O – FA + D-FGDS from the Opole power plant.

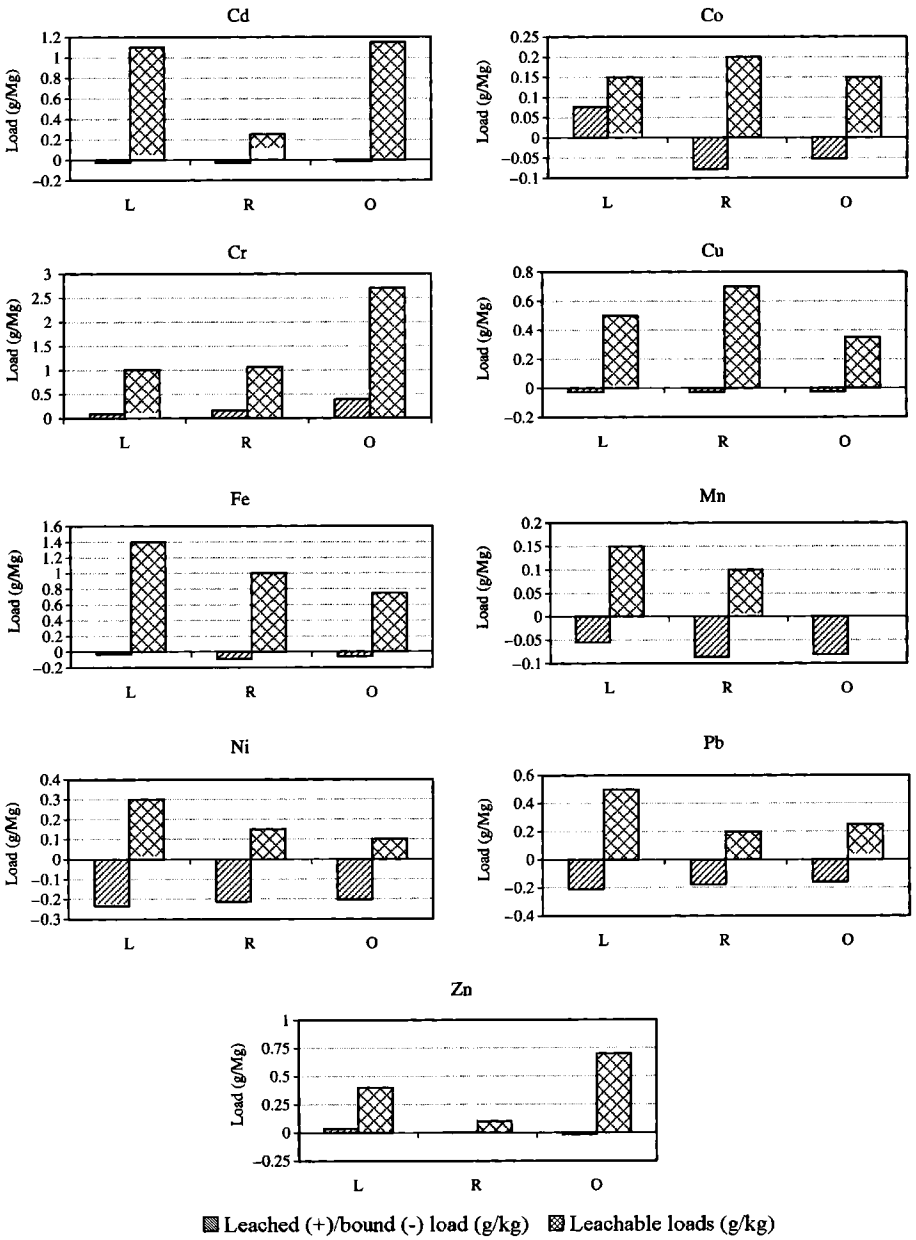


Figure VI.8.5. (Continued).

From the general pattern of constituent binding and release can be concluded that the most favorable load balance are mixtures of FA + D-FGDS with high-TDS mine water. Hence, to utilize thoroughly the binding capacity of FA + D-FGDS for reduction of contaminant loads discharged from mine drainage, mine waters of a high sulfate or

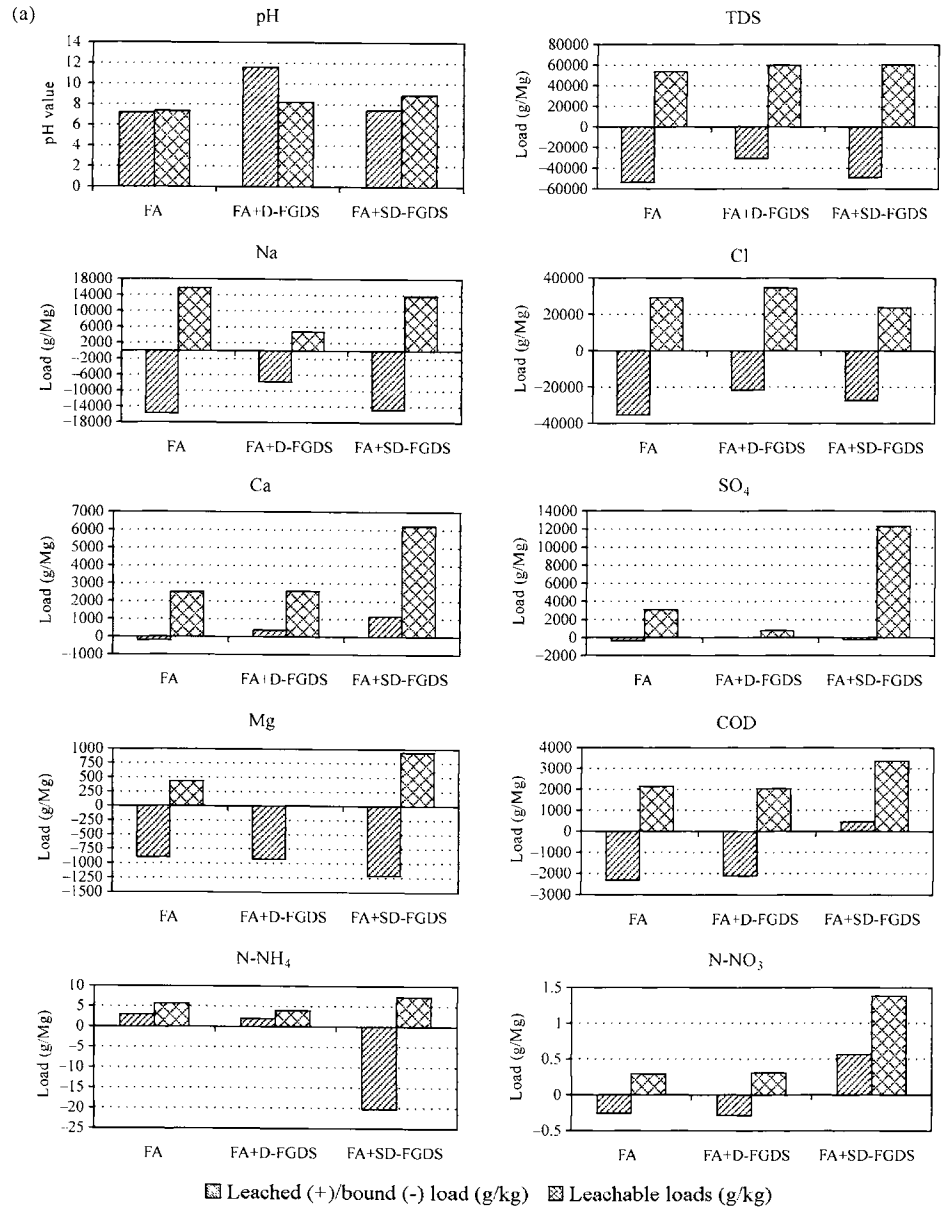


Figure VI.8.6. (a) Effect of content and kind of FGD solids from dry (D) and semi-dry (SD) process on binding (−) and release (+) of macro-constituents in the dewatering stage and contents of leachable constituents in solidified mixtures of FA + FGDS with mine water (1:1 wt.) utilized underground. Dense mixture 1:1 wt. components: Mine water from the Knurow mine of Cl–Na type, TDS ~ 100 g/l (94–96 g/l), pH 7.89–7.33; A – pure low alkaline FA from the Rybnik power plant; B – FA + D-FGDS from the Rybnik power plant; C – FA + SD-FGDS from the Laziska power plant, ABB-NID process. (b) Effect of content and kind of FGD solids from dry (D) and semi-dry (SD) process on binding (−) and release (+) of trace elements in the dewatering stage and contents of leachable trace elements in solidified mixtures of FA + FGDS with mine water (1:1 wt.) utilized underground. Dense mixture 1:1 wt. components: Mine water from the Knurow mine of Cl–Na type, TDS ~ 100 g/l (94–96 g/l), pH 7.89–7.33; A – pure low alkaline FA from the Rybnik power plant; B – FA + D-FGDS from the Rybnik power plant; C – FA + SD-FGDS from the Laziska power plant, ABB-NID process.

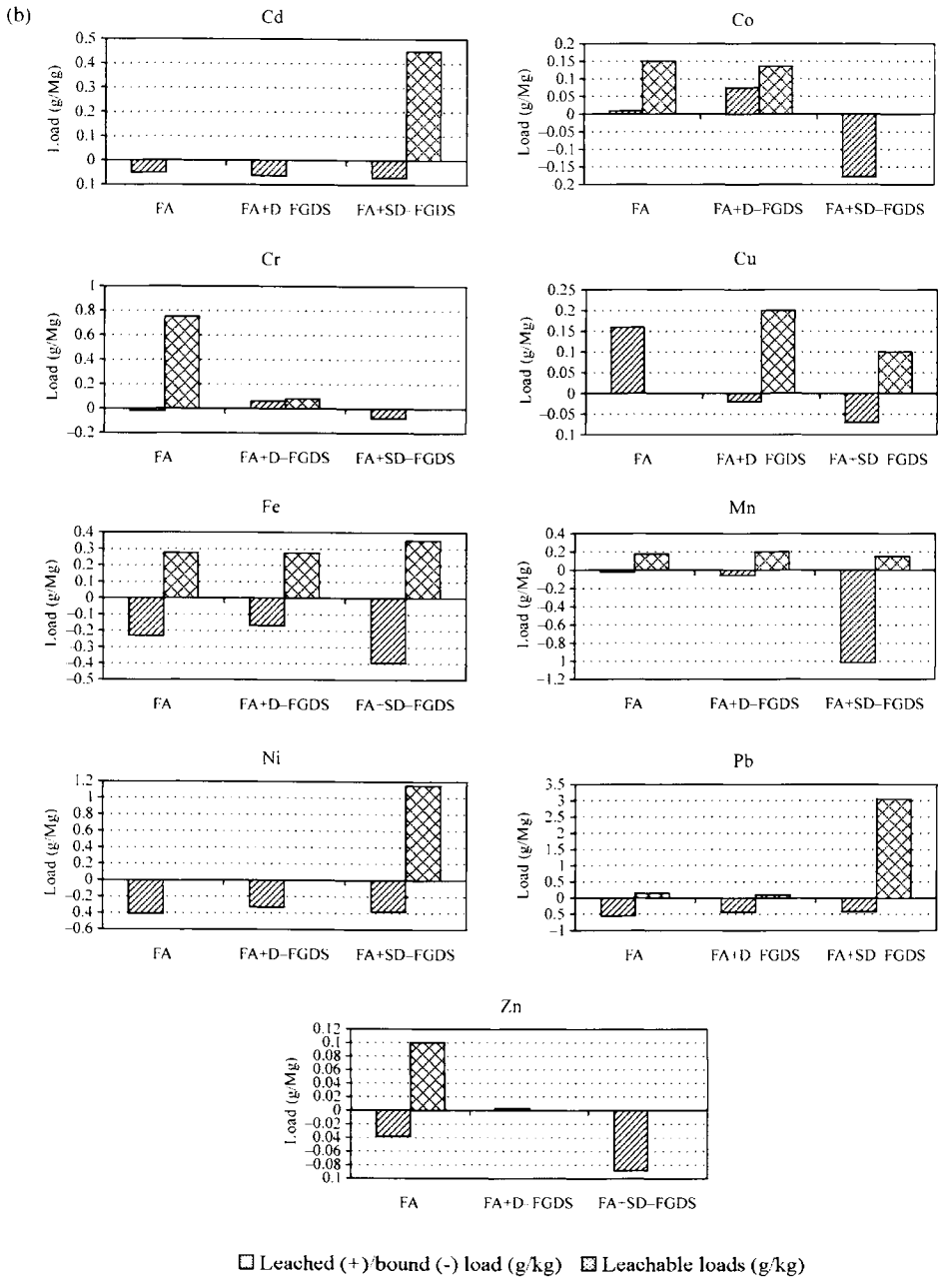


Figure VI.8.6. (Continued).

chloride salinity (TDS) should be used. In case of the deficiency of high-TDS waters, a closed circuit of mine water would be an optimum solution, provided it is technically sound and cost-effective. The leachability of dissolved solids, in particular sulfates, from the dewatered and solidified mixture despite the higher content in the matrix was similar to

or lower than leachability from the high-alkalinity pure FA. In the potential conditions of post-closure flooding the mine, the constituent release is anticipated to be low due to the cementation and lower hydraulic conductivity of the solidified mixture. In general, due to the leaching behavior and cementitious properties, the mine-water–FA + D-FGDS mixtures appear to be the most advantageous CCW product with respect to the long-term effect on the aquatic environment.

Because of the low-efficiency of the D-FGD processes, its use is limited to the treatment of low-sulfur flue gas emission or to the first stage of SO_2 reduction and it is being gradually replaced by less cost-effective and simple, but more efficient semi-dry and/or wet processes. Nevertheless, this method will be probably still applied in many countries as a transitional process that gives an opportunity of utilize excellent properties of FA with the products of dry FGD process as a sealing material in the most environmentally beneficial way.

VI.8.6.3. Effect on the contaminant balance of using FA + SD-FGDS mixtures with mine water

Lower retention capacity and high leachability of sulfates, formed by the oxidation of sulfides, resulted in a lower efficiency of the permanent binding of soluble constituents in the mixture of high FA + SD-FGDS solids compared to pure high alkaline FA, while the binding capacity of this material generally appeared to be similar to that of low alkaline pure FA (Fig. VI.8.6 – A, C). The semi-dry desulfurization process results in the neutralization of the end product, hence the pH value of the outflow from the FA + SD-FGDS mixture remains close to neutral in all phases of leaching. The systematic leaching behavior of this material is similar to that of low-alkalinity pure FA and is controlled by equilibrium with gypsum following the typical major transformations of the input water, i.e. decrease of alkalinity in parallel with increase of sulfate and hardness, which is transformed from the Ca–Mg-type into the Ca-type. The major specific property of this system was invariably low alkalinity, either in the stage of the dewatering, or after solidifying. The adverse transformations specific for this material containing unstable sulfides as FGD reaction products, is high leachability of sulfates and Ca from the solidified phase, along with a high COD due to sulfide oxidation. Nitrogen compounds do not show systematic behavior, with a generally prevailing trend to reduction in the output. Permanently neutral pH values lead to a stability in the matrix of the majority of trace elements, among them amphoteric metals like Cr. Increase in the output showed oxyanions Mo and V in conformity with the general pattern of leaching behavior, with maximum in pH range close to neutral (Figure VI.8.6a,b – case C) (Brookins, 1987; de Groot et al., 1989).

The general trend of transformation of chemical composition of mine water used for mixture preparation with FA + SD-FGDS consisted in increasing concentrations of all the macro constituents except Mg and carbonates. These constituents comprised both major (Cl, SO_4, Na, Ca) and minor ones (K). Nevertheless, the load balance displayed the reduction of loads of practically all macro- and trace constituents in outflow compared to the input mine water except Ca, COD and Mo. The long time of solidifying and the highest potential leachability of sulfates compared to all analyzed mixtures with FA, both pure and with end products from dry FGD process, is the disadvantage of this material. The leachability of trace

metals from the solidified mixtures of FA + SD-FGDS with low- and high-TDS mine water appeared to be similar, and for most of them within the range observed for other mine-water:FA systems. In comparison with these systems, Mo, Ni and generally low mobile Pb showed higher susceptibility to release, while Cr was distinctly less leachable.

In general, this material is applicable for use in dry mine workings. Occurrence of instable sulfides in the FA with a high SD-FGDS content results in the mentioned longer time of solidification and susceptibility to plastifying of solidified material in contact with water. Hence, this material should not be used in the wet mine workings.

VI.8.7. Dense mine water:FA mixtures as a sink of radioactivity in mine waters

As was shown in Chapter III.7, concentrations of radionuclides in CCW are distinctly elevated compared to the lithosphere and coal, from several times (^{40}K, ^{228}Ra), up to an order of magnitude (^{226}Ra). Nevertheless, this waste fulfills the criteria of unrestricted permit for their use in mine workings (total concentration of radionuclides < 10 kBq/kg) (PN-93/G-11010) as well as for the disposal at the surface and use for civil engineering works ($^{226}Ra < 350$ Bq/kg, and $^{228}Ra < 230$ Bq/kg) (GIG, 1994) and is not classified as a radioactive waste. At the same time, some saline waters occurring in different Carboniferous seams of the USCB display high level of radioactivity, up to 390 kBq/m^3. The annual radium load discharged with mine waters to the surface recipients is estimated to be about 150 GBq (Lebecka and Tomza, 1989).

According to the Polish Standards PN-88/Z-70071 (1988), waters with Ra concentrations over 0.7 kBq/m^3 are considered liquid radioactive waste. Mine water is considered radioactive if the Ra concentration exceeds 1 kBq/m^3. According to the Directive No 23/70 of the Government Attorney regarding Use of Nuclear Energy (1970), the discharge of radioactive waters to the open surface reservoirs is permitted provided that Ra concentration does not exceed 1.1 kBq/m^3, i.e. 10-fold MCL for drinking water, which accounts for $^{226}Ra = 0.11$ kBq/m^3. Such waters can be discharged to closed collecting sewers if the Ra concentration does not exceed MCL for drinking water by more than 100-fold, i.e. 11.1 kBq/m^3.

A considerable part of radioactive mine waters in the area of a positive radio-hydrogeological anomaly belongs to the Ra–Ba, low-sulfate type A. The rationale of the concept of using FA as a sink of radioactivity loads from high radioactive mine waters has been based on two major assumptions:

- FA, in particular with FGD solids, contain high concentrations of sulfate, hence have potentially high binding capacity for radium through co-precipitation with $BaSO_4$.
- FA has high water retention capacity (50–70%), hence may bind physically adequate radium loads along with high-radioactive waters also of a B type (low Ba, high-sulfate).

Practically, the radioactivity loads can be adequately reduced by use of high-radioactive waters for preparation of dense mine water:FA mixtures to be used routinely in mine workings for different purposes. From Ra–Ba waters radioactivity can be removed in parallel, both by chemical and physical binding. For Ra removal from Ra-waters of B type only physical binding can be applied.

The efficiency of Ra removal from mine water originating from three coal mines of the USCB, Poland, of radioactivity range $^{226}Ra = 2.171-103.208$ kBq/m^3 and $^{228}Ra = 1.48-67.76$ kBq/m^3 is exemplified in Table VI.8.7. For mine water:FA mixture preparation, pure FA from the Laziska power plant, and FA + D-FGDS from the Rybnik and Opole power plants were used, with sulfate content 0.74, 2.65 and 2.78% SO_4 wt., respectively. The results confirm excellent binding properties of FA for radionuclides, removed both chemically (co-precipitation with $BaSO_4$) and physically (water retention at the level from 60.0 to 85.75% wt. for water:FA ratio 1:1). In general, radioisotope residuum in outflow was similar, and independent from the input concentration. For FA + D-FGDS it was below MCL = 0.11 kBq/m^3 for drinking water, while in outflow from pure FA mixture the residual radioisotope concentration was somewhat higher, up to 2.5-fold MCL for ^{226}Ra. This reflects a little lower, but still very high binding capacity of pure FA for radioisotopes in high radioactive mine waters.

VI.8.8. Use of FA at the surface as a sealing agent

VI.8.8.1. Use of FA for preventive sealing of mining waste dumps

Besides an unquestionable environmentally beneficial use of FA underground, though not without certain limitations dictated by the hydrogeological conditions, there are other prospective fields of application of this material at the surface, aimed to use its sealing properties against air penetration, which are from 1 to 2 orders of magnitude higher than in natural cohesive soils. In this respect, FA has no competitors and thus should be strongly considered for the control of oxidation in the reactive material in order either to prevent, or to remediate the generation of pollutants or combustion processes. This area of application, though, creates serious side problems that result from the environmentally adverse properties of FA, in particular its fairly high permeability to vertical infiltration, high concentrations and leachability of contaminants, and possibility of their delayed release due to long-term transformations (see Chapter III.7). This sets the complicated task of optimization of FA use in a way that would permit to utilize in full its sealing properties and attenuate adverse impact, to achieve the most positive resultant effect.

One of these areas is use of FA for sealing mining waste dumps, e.g. coal mining waste that is the biggest amount of waste in Poland and creates environmental problems in coalfields worldwide due to susceptibility to self-ignition and long-term adverse environmental impact caused by sulfide oxidation and acidification of low-buffered waste with subsequent release of trace constituents from the material and the bedrock of the vadose zone lasting for decades. Due to the low consolidation properties of the considerable amount of Carboniferous rocks, self-ignition prevention requires application of expensive heavy compaction by vibratory rollers in thin layers. There is always a possible formation of local self-ignition centers at compaction failure or in older less heavily compacted dumps (see Chapter III.7). This has directed attention to seeking additional effective sealing means, of which FA was found the most promising. The development of methods of FA use as a sealing material was induced by a lack of self-ignition cases at the Przezchlebie coal mining waste dump where since 1969 coal mining waste from three coal mines with a minor amount of waste from six other mines together

Table VI.8.7. Reduction of the natural radioactivity of type A in mine waters with use of pure FA from the Laziska power plant and FA + D-FGDS (FA with products of desulfurization by dry method) from the Rybnik and Opole power plants.

Sample, treatment	Sampling date	Concentrations (kBq/m^3)		Reduction (%)	
		^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
Mine water from the Chwalowice mine cross-cut I E, levels 390 and 550 m	09.1994	103.208 ± 8.26	67.76 ± 13.57		
Mine water as above + pure FA from the Laziska power plant (1:1 wt.)		0.234 ± 0.024	0.23 ± 0.08	99.77	99.66
Mine water as above + FA + D-FGDS from the Rybnik power plant (1:1 wt.)		0.058 ± 0.012	<0.05	99.94	100
Mine water as above + FA + D-FGDS from the Opole power plant (1:1 wt.)		0.087 ± 0.013	0.17 ± 0.07	99.92	99.75
Mine water as above + FA + D-FGDS from the Rybnik power plant (1:1.9 wt.)		0.075 ± 0.013	<0.05	99.93	100
Mine water from the Jankowice mine – shaft VIII, level 565 m	09.1994	80.986 ± 6.48	23.10 ± 4.65		
Mine water as above + pure FA from the Laziska power plant (1:1 wt.)		0.0279 ± 0.027	0.09 ± 0.06	99.65	99.61
Mine water as above + FA + D-FGDS from the Rybnik power plant (1:1 wt.)		0.095 ± 0.014	<0.06	99.88	100
Mine water as above + FA + D-FGDS from the Opole power plant (1:1 wt.)		0.050 ± 0.011	<0.05	99.94	100
Mine water from the Moszczenica mine-cross – cut W, level 406 m	09.1994	2.171 ± 0.175	1.48 ± 0.30		
Mine water as above + pure FA from the Laziska power plant (1:1 wt.)		0.111 ± 0.015	<0.06	94.89	100
Mine water as above + FA + D-FGDS from the Rybnik power plant (1:1 wt.)		0.051 ± 0.011	<0.06	97.65	100
Mine water as above + FA + D-FGDS from the Opole power plant (1:1 wt.)		0.123 ± 0.016	0.17 ± 0.07	94.33	88.51
Mine water as above + FA + D-FGDS from the Opole power plant (1:1.1 wt.)		0.040 ± 0.006	<0.03	98.16	100

with dry FA were disposed. Since 1973, the FA from the Rybnik power plant was disposed at this dump in the increasing amounts, up to its domination with respect to coal mining waste in 1979, when its location at the dump terminated and the separate hydraulic disposal to the FA pond began. During the separate disposal, acidification of coal mining waste started to develop. Due to predominant disposal of coarse run-of-mine waste (70%) and rock properties, coal mining waste material can be classified as practically non-insulating ($k > 1 \times 10^{-1}$ m/d), partially very weakly insulating against vertical infiltration ($k = 1 \times 10^{-1} - 1 \times 10^{-3}$ m/d) and having low barrier properties against air penetration that has caused pyrite oxidation practically throughout the dump volume. Such parameters are typical for a majority of coal mining dumps of the region. The first developed and patented methods consist in the alternate placing of horizontal layers either of the dry FA (slightly wetted to prevent dusting) or dense water:FA mixture with coal mining waste during the dump construction. The FA layer thickness is dependent on the material available, but is generally considerably thinner than coal mining waste for fast solidification (up to 0.5 m), while water:FA ratio should assure the highest density technically possible to achieve at mixture preparation and spreading at the dump at the spot (Fig. VI.8.7) (Twardowska, 1988, 1990). The major idea was to use the buffering capacity of both materials, in particular of FA at the initial stage, and its sealing properties against air penetration in the long-term period to neutralize generated acid loads during the construction of the upper coal mining waste layer and thus to temporarily enhance buffering capacity of the freshly disposed coal mining waste, but primarily to intercept further acid loads generation in the coal mining waste layer underneath. In parallel, the sealing effect of FA cover is used for prevention of self-ignition. The maximum reduction of water used for FA placing was aimed to save the high water retention capacity of FA for eventual retardation of leachate and dissolved contaminants percolation during the construction of the dump section, until the final top of the dump with a sub-surface drainage system on the layer of a well hydraulically insulating material is constructed to attenuate further water infiltration through the dump. This condition is difficult to realize and thus the amount of water used should assure convenient uniform spreading of the FA cover on the top and its fast solidification with the minimum of an outflow, considering its adverse properties and possibility of further contaminant leaching from the lower coal mining waste layer. This method of "blanket"-like horizontal placing of FA mixture assures adequate continuous insulation of sulfide-bearing wastes from air penetration at low costs, and due to separation from insulated wastes, enables future use of insulated waste without unwanted admixture of FA for various applications, e.g. for engineering constructions or residual coal extraction.

Another method (Fig. VI.8.8) (GIG, 1994) consists of placing coal mining waste in layers 3.6–3.7 m thick on the dump slope with a plough dumping conveyor alternately with the dense FA:water mixture delivered by pipe to the slope, to sink in the coal mining waste and to form a cover layer 0.25–0.4 m thick in the half-height of the slope. Along the toe of the dump a bank ~ 1 m high is to be formed to fill the space between the dump toe and the bank with a FA:water mixture to get the FA layer 0.5 m thick, where coal mining waste is to be disposed to allow the FA to thoroughly mix with coal mining waste. After completion of this layer, a new bank is to be constructed and the procedure repeated. The leachate is to be collected for reuse in the circuit for FA mixture preparation. The major aim of the method is protection of the waste dump against self-ignition.

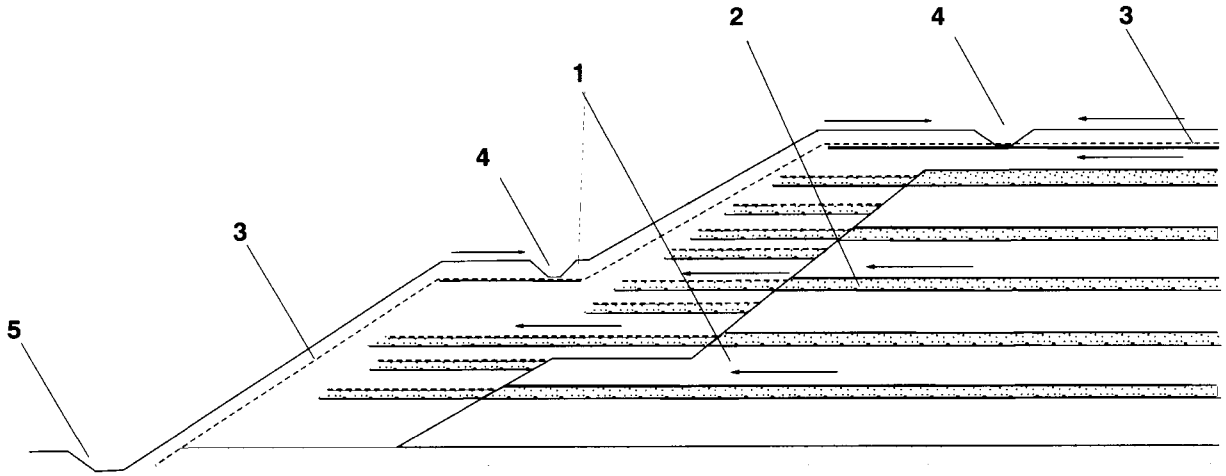


Figure VI.8.7. Construction of a coal mine waste dump with protective barriers in the form of blanket layers of dense water:FA mixtures.1 – coal mining waste; 2 – blanket layers of dense FA:water mixtures (≤0.5 m); 3 – subsurface drainage system; 4 – collecting drainage ditches on the top and terraces; 5 – toe drainage ditch.

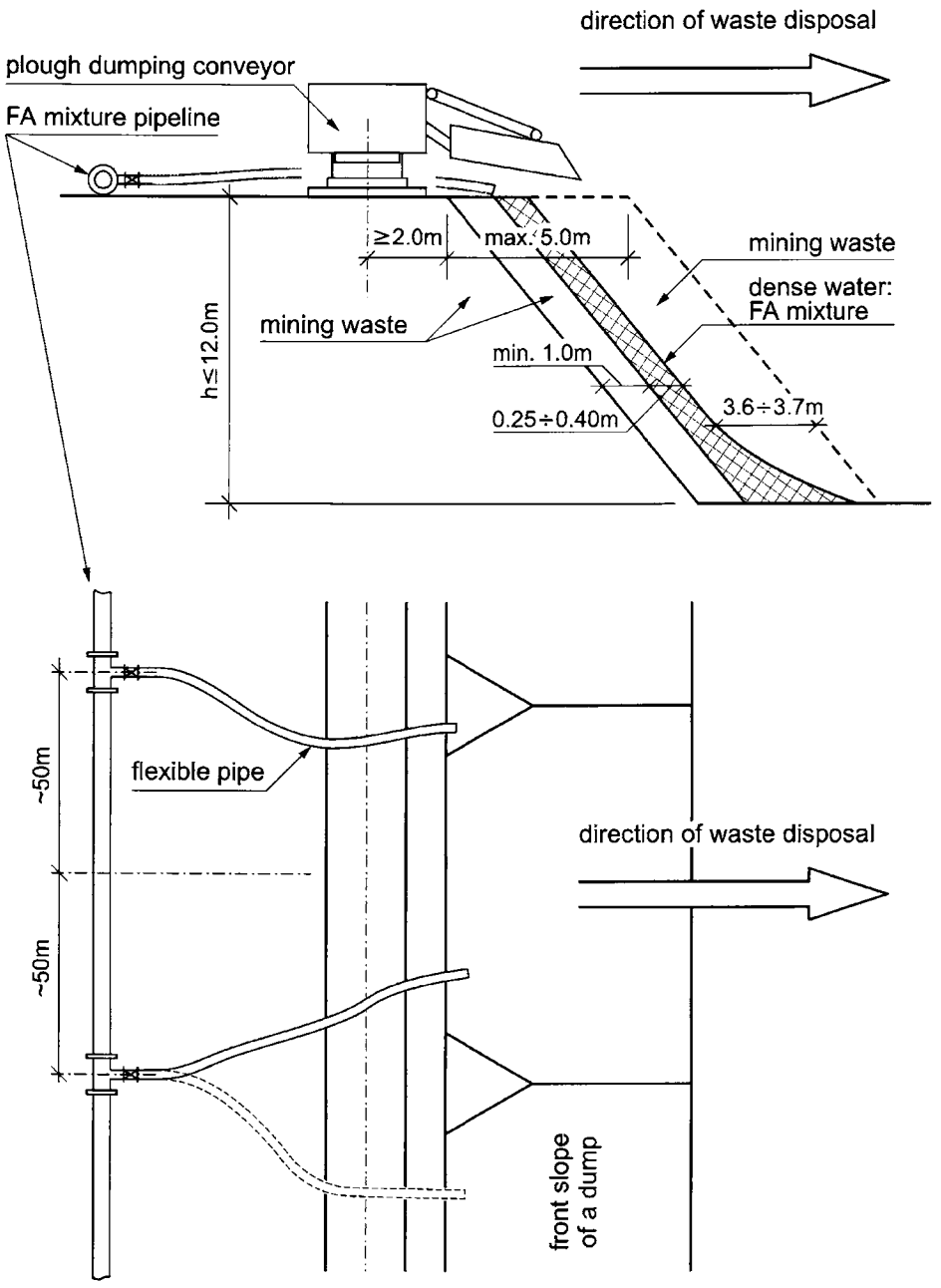


Figure VI.8.8. Construction of a coal mine waste dump sealed by dense water:FA mixtures placed at the front slope of a coal mining waste dump (after GIG, 1994).

This method was planned to be used at the Przezchlebie waste dump (INTECHKOP, 1994) to utilize the seasonal excess of FA generated in the Rybnik power plant. The project was not completed due to the lack of required amount of FA.

The modification of this method (Drąg, 1993) also considers thorough filling of the coal mining waste dump with the dense water:FA mixture delivered in two stages subsequently as water:FA mixtures of different density, 0.6:1 and 0.4:1 wt. at the top of the dump section separated with the banks to enable sinking the mixture into the lower coal mining waste layer and flowing down the working front slope of the dump. Besides self-ignition control, the method was claimed to prevent against the vertical infiltration and leaching of dissolved constituents from the dump.

This modification, which used partially FA + D-FGD from the Opole power plant in the limited scale in 5 ha of the total 180 ha was applied at the Maczki Bor central coal mining waste dump (USCB, Poland) where waste from several coal mines of the area has been disposed of. The dump has been sited in the mined out part of a sand quarry 10–30 m deep at the area of unprotected Quaternary aquifer of the usable groundwater horizon (UGWH) hydraulically connected with the Carboniferous aquifer. Despite an optimistic prognosis, a screening of the basic parameters in the swamp at the dump toe, as well as in the Quaternary and Carboniferous waters down-gradient of the dump sector sealed with dense water:FA mixture showed distinct adverse impact of the outflow and leachate from this sector, in particular alkalization of waters, enrichment of TDS, SO_4, Na, Cr, Zn, COD and transformation of water type into HCO_3–SO_4–Ca or HCO_3–SO_4–Na. This confirms high leachability and permeability of mixtures, and lack of barrier properties with respect to the vertical infiltration that should be strongly taken into account in case of using FA as a sealing agent for preventive purposes. In general, this method appeared to be unsuccessful and environmentally unfriendly. This case can be a good illustration of the importance of adequate technical solution to utilize beneficial and suppress adverse properties of dense FA mixtures used as insulating agent.

The simulation of contaminant leaching during 1.5-year exposure to the atmospheric conditions of 2 m layer of fresh-wrought coal mining waste sealed with a cover layer of pure low alkaline FA or FA + D-FGDS in the amount 10% wt. with respect to coal mining waste, in the form of dense water:FA mixture 0.6:1 illustrates the environmental behavior and interaction of these two kinds of wastes in the dump constructed according to the first of the presented methods (Twardowska, 1988) compared to the non-sealed (0) waste. This period of exposure comprised wash-out (I) and the transition the diffusion (II) stages (Fig. VI.8.9, Table VI.8.8). In the non-sealed layer, the leachate originated entirely from the precipitation. In the sealed layer, infiltration comprised also either the outflow of surplus water from the FA mixture, or the spare retention capacity, if added water is below the total retention capacity of FA. In the presented case, the sealing layer reduced the total amount of leachate from 19% (pure FA) to 27% (FA + D-FGDS). The major load of contaminants leached from the sealed layers came from the outflow, and was particularly high for the pure FA system that resulted in the unfavorable total load balance compared to unsealed layer for TDS, SO_4, Mg, COD, Cd, Cr, Mn, Ni, and Zn. For FA + D-FGDS system, where binding prevailed over release, the load balance was considerably lower for almost all leached constituents. The adverse property of both sealed systems was high release of Fl (in amounts from 1.7 g/t for pure FA to 8.74 g/t for

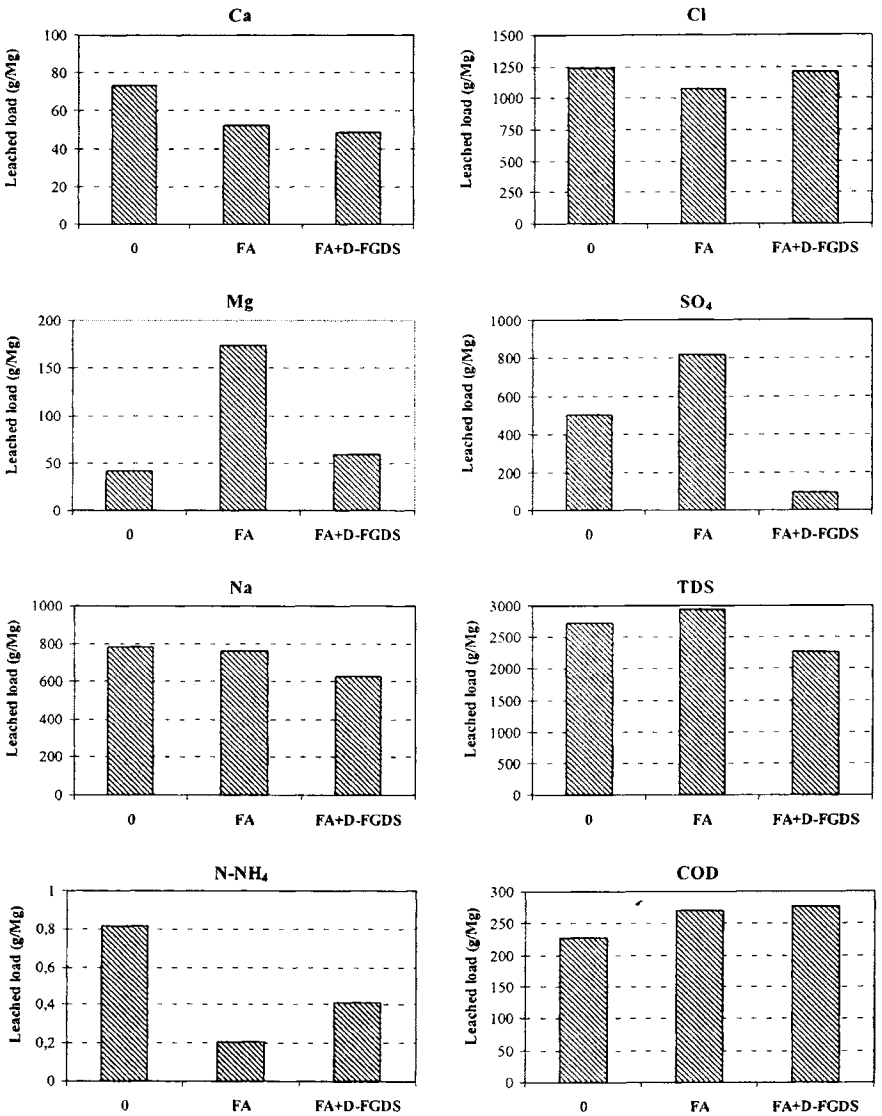


Figure VI.8.9. Environmental effect of contaminant release in the wash-out (I) stage from coal mining waste 2 m thick sealed surficially with the layer of dense water:FA and FA + D-FGDS mixtures 0.6:1 wt., compared to the unsealed coal mining waste dump; amount of FA = 10% wt. of coal mining waste. 0 – unsealed coal mining waste layer; FA – sealing layer of dense recirculation water:pure FA mixture; FA + D-FGDS – sealing layer of dense recirculation water:FA + D-FGDS mixture.

FA + D-FGDS compared to 0.37 g/t for unsealed waste) and Mo, and high COD that is typical for CCW. The further pattern of contaminant release, in particular in the Diffusion (II) stage shows high efficiency of the FA sealing cover in intercepting oxidation processes and pH correction, which is reflected in the several times lower,

Table VI.8.8. Concentration range of constituents in leachate from the 2 m thick layers of freshly disposed coal mining waste, surficially sealed with a layer of dense water:pure FA or FA + D-FGDS mixture 0.6:1 wt. compared to unsealed freshly disposed (and weathered) material in simulated conditions of 1 year's vertical rainwater infiltration (wash-out I and transition to diffusion II stages). *Sealing water:FA mixture*: FA: Low alkaline FA from the Rybnik power plant, 10% wt. of coal mining waste; Water: from closed circuit, TDS 3789 mg/l, Cl 1390 mg/l, SO_4 1039 mg/l; Mean daily precipitation 4.74 mm.

Parameters, constituents	Unsealed fresh/ (weathered) waste		Sealed with water: Pure FA: mixture		Sealed with water: FA + D-FGDS mixture[a]		MCL[b] mg/l
Parameters	I	I–II	I	I–II	I	I–II	
Water exchange rate, *R*	2.252	4.371–12.583	0.658	1.36–2.67	0.099	0.270–1.90	
Total leachate, *L/t*	56.67	110.00–316.67	68.18	140.91–456.82	6.684	18.182–127.807	
Conductivity, μS/cm	39,200	10,950–1220	38,200	8870–1201	62,500	58,400–8740	
pH	3.22	7.65–8.54 (7.96–8.0)[c]	6.94	8.35–8.38	7.48	7.46–8.09	6.5–8.5
Alkalinity, meq/l	0.00	2.1–5.5	0.40	6.0–5.95	0.85	0.8–2.35	
Hardness, meg/l	73.1	36.8–0.43	197.4	47.52–0.41	109.07	156.82–6.30	
Hardness Ca, meq/l	46.3	9.3–0.13	30.5	3.6–0.41	68.2	61.1–3.3	
Hardness Mg, meq/l	26.8	27.5–0.30	166.9	43.92–0.0	40.87	95.72–3.0	
Hardness $CaCO_3$, mg/l	3658	1842–21.52	9879	2378–20.52	5458	7848–315.3	
Macro-constituents, mg/l							
Ca	928.1	223.6–2.60	611.9	144.8–1.3	1367.8	1284.1–66.5	
Mg	326	334–3.69	2030	490–4.22	497	1164–36.4	
Na	**9321.2**	**2609–316.9**	**8778.8**	**2237.2–263.8**	**14,800**	**13,701–1502.9**	800
K	382.5	143.1–44.3	202.9	57.2–56.9	568.6	414.1–77.77	
NH_4^+-N	10.25	2.56–1.90	1.62	1.29–0.06	10.69	8.23–1.19	10
NO_3^--N	12.28	12.02–0.88	9.83	6.49–3.64	0.242	2.147–6.022	30
Cl^-	**16,320**	**3162**–65.28	**14,280**	**1428**–102	**29,316**	**27,348–2650**	1000
SO_4^{2-}	**4225.9**	**2881.8**–336.2 (**3280–1960**)[c]	**7396**	**4303.1**–299.2	**2085.2**	**1200.75**–86.45	500
HCO_3^-	0	128.14–311.19	24.40	358.8–356.9	51.86	48.81–143.39	
CO_3^{2-}	0	0–12	0	6–3	0	0	
PO_4^{3-}	0.038	0.052–0.05	0.22	0.198–0.092	0.024	0.020–0.016	3 (as P)
TDS	31,852	9360–1005	33,712	8876–984	55,076	49,368–4814	
COD	**3004.4**	**592.3**–25.7	**3519.4**	**412.0**–51.5	**10,922**	**6155.24–490.57**	125

Trace elements, mg/l							
Cd	0.1	0.06–0.1	0.21	0.17–0.1	0.15	0.14–0.03	0.4
Co	0.28	0.06–0.02	0.36	0.09–0.06	0.39	0.39–0.03	1
Cr_t	0.06	0.07–0.005	0.1	0.06–0.13	0.2	0.15–0.01	0.5
CrVI	0.006	0.008–0.003	0.006	0.003–0.011	0.04	0.034–0.004	0.1
Cu	0.08	0.07–0.01	0.12	0.25–0.04	0.12	0.03–0.01	0.5
Fe	0.22	0.09–3.57	0.22	0.13–40.2	0.25	0.39–0.05	10
Mn	0.78	0.03–0.11	2.2	0.35–0.19	0.36	0.21–0.15	
Ni	0.31	0.03–0.12	0.39	0.06–0.14	0.43	0.36–0.03	0.5
Pb	**1.89**	0.40–0.05	**1.32**	0.31–0.09	**0.98**	1.96–0.2	0.5
Zn	0.35	0.03–0.27	0.89	0.94–0.30	0.04	0.04–0.01	

[a]Simulated leaching cycle 0.5 years.
[b]Polish regulations for liquid waste discharged to waters and soils (Directive of the Minister of Environment, 2002).
[c]Data for weathered ~1 years old material.

decreasing concentrations of SO_4 while in unsealed material the increasing sulfate generation due to pyrite oxidation is observed (Table VI.8.8).

Therefore, the reduction of outflow of surplus water from the sealing mixture is crucial for assuring positive environmental effect at all stages of FA application to reactive waste as a sealing agent. This supports the preference for using dense FA mixtures alternately as a uniform cover in a minor amount with respect to sealed material, and for minimization of water in the mixture to reduce the outflow. High content of free lime in the FA + D-FGDS enhances contaminant binding. Limited and continuously decreasing availability of this material due to shifting to the more efficient semi-dry and wet desulfurization methods is a definite obstacle to its wider use. One of the options is adding free lime to FA, in the best case as a waste product.

The use of FA as a sealing agent was exemplified here in application for coal mining waste, though it can be applied to any mining waste containing sulfide, among them to acidic metal ore mining waste of much higher pollution potential. This creates a wide area of a beneficial utilization of this waste.

In each case of selecting the optimum material and parameters, detailed testing of the material adequate to the area of application is required. For interpretation of experimental data, several simple computer programs are of use as supporting tools, e.g. geochemical programs MINTEQA2 (Allison et al., 1991), WATEQ 4F (Ball and Nordstrom, 1991, 1994) for chemical speciation and evaluation of saturation parameters, or the most developed and sophisticated geochemical computer program PHREEQC (Parkhurst and Appelo, 1999; Charlton and Parkhurst, 2002), in particular the newest version PHREEQC Interactive v. 2.8.0.0 (2003). Besides speciation, the program PHREEQC can be used for reaction-path, one-dimensional advective transport of contaminants and inverse geochemical calculations, including calculations of isotope equilibrium constants for implementations in geochemical models (Thorstenson and Parkhurst, 2002). Relatively simple programs POLLUTE (Rowe et al., 1994) or KYSPILL v.2 (Anonymous, 1997; Serrano, 1997) allow prognosis of contaminant migration from waste disposal sites to ground waters, though every program has definite simplifications and limitations and should not replace the testing procedure fit to the case.

VI.8.8.2. Use of FA for fire control in mining areas in emergency cases

VI.8.8.2.1. Use of FA mixtures for fire control and attenuation of environmental pollution caused by fire in mining areas

Another very promising and not yet fully utilized area of FA application is fire control in coal mining areas. The scale of this problem is different, from the local fires in coal mining waste sites to the vast areas of coalfields set on fire. An example of the last case and its environmental and economic consequences is Jharia Coalfields in Bihar, India, where of 258 km^2 operated by Bharat Coking Coal, 17.32 km^2 i.e. 6.7% of the total operated area was set on fire according to CMPDIL (1986), while the current situation appears to be even worse. In terms of the total devastation of the territory, which resulted in the evacuation of population, thorough destruction of the structures and vegetation, severe damage and development of high salinity of soils, surface and ground water resources, as well as air pollution (PAHs, CO, CO_2, SO_2, H_2S, NO_x) in the much bigger area and scale than that set

on fire, this situation cannot be termed in other way than a disaster. The coking coal losses due to fires were estimated for 37 Mt, while total coal blocked by fires was evaluated at over 1.8 Bt (CMPDIL, 1988). The routine method of fire control is cutting off the sources of air. In the Jharia coalfield, five fires were reported to have been intercepted by placing three subsequent layers of seals (Malhotra, 2001). The primary seal consisted of placing a repeatedly compacted soil blanket in the fire area prepared by "fire digging" and vibrating to receive the seals with tyre-mounted equipment. The secondary seal comprised working out an overburden material and laying it in stages with repeated compaction, along with digging and compaction of developed cracks. The tertiary blanket was again formed of compacted soil.

The described procedure required moving and digging out enormous amounts of soil and overburden material of different, mostly fairly poor sealing properties, and repeated compaction of this material to enhance efficiency of sealing, all jobs in extremely difficult and dangerous conditions of active fire. Application of FA:water mixture as a sealing material of a proven, at least one order of magnitude higher penetration resistance than the natural cohesive soils, with no compaction required, would have achieved a better effect in fire control and attenuation of environmental damages caused by fire in a much simpler, safer, cost-effective and efficient way. FA is an abundant material in the area, thus its utilization as a best seal having no comparable alternatives is an inescapable conclusion and will allow use of a large amount of FA in the most beneficial way.

VI.8.8.2.2. Use of FA for endogenous fire control in coal mining waste dumps and interception of the environmental pollution caused by fire

Poor compaction properties of coal mining waste rock from the majority of Carboniferous seams of the USCB results in the elevated endogenous fire danger. It is particularly severe at the older high dumps constructed in thick (6–12 m) layers placed by a plough dumping conveyor and compacted at the top, while penetration of wind from a front side slope can easily occur. It results in sporadic, but extremely troublesome cases of self-ignition and environmental contamination of the same character as described above. The fire control at the closed sites or at the dumps under operation has been always a dangerous, time-consuming and expensive procedure that consisted of multiple re-compaction of an inflamed material in the fire centers, often under extreme emergency conditions.

Application of FA:water mixtures for fire interception at the Skalny coal mining waste dump in 1999 with use of combination of several simultaneously used technologies, which comprised absorption trenches, vertical hole injection, sealing inter-layers and spreading on the surface, along with partial sealing of slopes proved its high efficiency. It resulted in suppression of fire in 22 of 26 monitoring points registered as decrease of temperature and CO and other fire gases up to two orders of magnitude, which profoundly reduced air pollution within a large radius from the site (Golec and Mólka, 2000). Technological flowsheet of installation for fire control consisted of the stationary or mobile station for mixture preparation from dry FA being delivered in standard hermetic truck tankers and mine water in regulated optimum ratio. To enhance sealing properties, to the pure FA the waste lime may be added. From the mixing tank the ready mixture is pumped in steel pipes to the places of application. The general scheme of mixture preparation is similar to that used for any purpose, e.g. for utilization underground (Fig. VI.8.1), and can be applied also

for fire control in coal seams in mining areas. This case study exemplifies high efficiency and prospects of FA use as sealing material for fire control in emergency cases, as well as for fire prevention, along with the parallel environmental protection effects.

VI.8.9. Conclusions

As practice shows, FA, both pure and containing flue gas desulfurization solids (FGDS from dry and semi-dry processes), can be widely and beneficially used underground and at the surface for a variety of applications where its sealing properties against air penetration, water retention and contaminant binding properties, which outclass the adequate properties of natural available materials, are the most crucial parameters.

Besides the main direct purposes of FA application (in the form of dense mixtures with mine water) in deep coal mines for sealing mined out and abandoned workings, backfilling of mine workings and stopping construction for fire prevention and control, methane control and reduction of a greenhouse effects caused by methane release to the atmosphere, simplification of a ventilation system, and reduction of surface deformations due to subsidence, high water retention and binding capacity of FA causes adequate reduction of contaminant loads discharged with mine waters to the surface recipients.

The most environmentally beneficial and safe way of utilizing FA, pure or containing dry or semi-dry desulfurization products (FA + D-FGDS or FA + SD-FGDS) underground as a sealing material is its use in the form of dense mixtures with saline or/and acidic low-quality mine waters or flotation slurry in the mine workings insulated from the recoverable usable ground water resources. Utilizing slurry underground reduces costs by resignation from filter press dewatering of slurry and its disposal.

Using FA or FA + FGDS in such workings, at an optimally high TDS/acidic mine water:FA ratio, which assures transportability of mixture to the place of deposition at minimum leachate will cause considerable reduction of aquatic environmental contamination in the period of mining and after mine closure. A particularly beneficial effect of FA application on the reduction of trace metal load was found in its application in mines having problems with high-metal acidic waters, which are equally frequent in coalfields and metal ore mines in the world. The use of good quality low TDS-mine waters for preparation of mine water:FA mixtures and utilization of FA in the feeding zones of recoverable ground water resources should be restricted. The mine water:FA ratio should be optimized for each system individually on the basis of the most effective contaminant load balance and the requirements of the transportability of the mixture to the place of deposition. For dry or moderately flooded mines, the optimum solution is to utilize all pumped mine water for FA mixture preparation in a closed circuit that would effectively and thoroughly eliminate discharge of pollutants to the surface receiving waters. As a rule, the mines in the USCB of low mine water inflow are working in such a no-discharge system.

Use of FA + SD-FGDS in dry mine workings appeared to be the most rational approach, taking into consideration long solidification time and certain thixotropic properties of this material.

Dense FA, and in particular FA + FGDS mixtures, used underground have appeared to be also an effective sink of high radioactivity loads from mine waters of the Ra–Ba type that shows reduction in outflow to a concentrations below MCL for drinking water.

Besides the environmentally beneficial use of FA underground, a prospective field of application of this material at the surface is its use for sealing coal mining waste dumps to prevent self-ignition and long-term adverse environmental impact caused by sulfide oxidation and acidification of low-buffered waste with subsequent release of trace constituents from the material and the bedrock of the vadose zone lasting for decades. In this respect, FA has no competitors and thus should be strongly considered for the control of oxidation in the reactive material in order either to prevent, or to remediate the generation of pollutants or combustion processes. This area of application sets the complicated task of optimization of FA use in a way that would utilize in full its sealing properties and attenuate adverse impact of massive release of contaminants from FA mixture in the wash-out (I) stage, to achieve the most positive resultant effect. The reduction of outflow of surplus water from the sealing mixture was found crucial for assuring positive environmental effect at all stages of FA application to reactive waste as a sealing agent. Of different types of CCW, FA + D-FGDS was found to be the most efficient in contaminant binding due to its high content of free lime. Limited and continuously decreasing availability of this material due to shifting to the more efficient semi-dry and wet desulfurization methods is a definite obstacle in its wider use. One of the options is adding of free lime to FA, in the best case as a waste product.

FA as a sealing agent can be applied to any mining waste containing sulfide, among them to metal ore mining waste of much higher pollution potential. This creates a wide area of a beneficial utilization of this waste.

Another very promising but not yet fully utilized area of using excellent sealing properties of FA is fire interception in the coal mining areas and dumping sites. Positive results of fire suppression at the coal mining waste dump in the USCB, Poland, suggest its wide application for fire control in coalfields and dumping sites.

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VI.9
Agricultural utilization of coal combustion residues

Urszula Kukier and Malcolm E. Sumner

VI.9.1. Introduction

Coal-fired electric power plants generate enormous amounts of waste products whose physical and chemical properties vary depending on the coal composition and specific conditions of the process. Because these materials are potentially valuable soil amendments, knowledge of their characteristics and interactions with soils and plants is essential for maximizing their environmental sound use. A great diversity in coal combustion technologies and technical solutions to air pollution control results in a variety of waste products. This chapter will cover three types of coal combustion residues widely differing from each other in their physical and chemical properties.

VI.9.2. Characterization of coal combustion waste products

Coal combustion in traditional powder-fed boilers produces two types of residues: fly ash, which is a fine fraction dispersed in the flue gas, and bottom ash collected in the boiler. Fly ash is separated from flue gas by electrostatic precipitators or a variety of mechanical methods. Typical partitioning between fly and bottom ash in pulverized coal-fired boilers is 8:2 (Santhanam et al., 1979). Fly ash particles have a spherical shape typical of dust particles generated by thermal processes involving melting, evaporation and subsequent condensation of constituents. The majority of the particles have sizes < 100 μm. Silicon, Al, Fe, K and Ca followed by Na and Ti are major components of the fly ash matrix with their concentrations being variable depending primarily on coal composition and combustion conditions (Table VI.9.1). Fly ash consists of an amorphous aluminosilicate glass, crystalline mineral mullite ($3Al_2O_3{\cdot}2SiO_2$) and quartz (SiO_2) with minor amounts of hematite (Fe_2O_3) and magnetite (Fe_3O_4) (Mattigod et al., 1990) and variable amounts of trace elements, some of which are essential for plants and animals and others are potentially toxic (Table VI.9.1, see also Chapter III.7).

Because of the large quantities of by-product produced, a great body of literature exists on fly ash chemical, mineralogical and physical characterization, potential beneficial utilization strategies and adverse environmental effects.

Large emissions of sulfur dioxide (SO_2) from coal combustion is one of the major atmospheric pollutants. To minimize these emissions, fluidized bed combustion (FBC) and

Table VI.9.1. Concentration of elements in coal combustion by-products.

Element	Fly ash	FBC	FGD
g/kg			
Al	59–143	4.0–20	0.1–1.64
Si	10–318	–	0.5–0.8
Ca	6–177	240–460	228–243
S	0.40–0.64	72–140	166–186
Fe	27.9–289	0.8–16.0	0.14–1.3
Mg	11.5–60.8	5.0–12.0	0.2–2.7
K	5.6–34.7	0.5–8.0	0.1
P	0.4–8.0	0.4–0.5	<0.1–0.2
mg/kg			
B	10–770	95–170	75
Se	1.2–17.0	0.16–0.58	<1.0–5.2
As	2.3–312	<0.1–0.3	0.14–5.73
Mo	6.5–41	0.12–0.28	0.35–1.7
Ni	1.8–115	13–29	–
Zn	14–406	29–105	2.9
Cd	0.1–3.9	0.5	–
Cu	45–616	12–19	0.6–3.2
Pb	3.1–241	1.5–7.5	–

Furr et al., 1977, 1978; Mattigod et al., 1990; Sumner, 1993; Kukier and Sumner, 1994; Alcordo and Rechcigl, 1995.

wet scrubbing technologies have been developed (Alcordo and Rechcigl, 1995). In the former, a mixture of ground coal and limestone or dolomite is injected into the combustion chamber so that combustion is accompanied by simultaneous absorption of evolved SO_2. FBC residue is a mixture of coal ash, products of the desulfurization reaction and unreacted sorbent. Anhydrite ($CaSO_4$) being a product of the reaction is the dominant mineral followed by lime (CaO) and small amounts of portlandite ($Ca(OH)_2$) both originating from thermally transformed calcite ($CaCO_3$) used as sorbent. Typically, FBC residues have pH values > 12 and electrical conductivities of about 11 dS/m (Reichert and Norton, 1996). The significant content of lime makes this by-product a potential substitute for agricultural lime. The ash component is a carrier of trace elements whose content may vary (Table VI.9.1). Because combustion temperature in the FBC process (about 900°C) is much lower than that in a traditional boiler, volatile trace elements are likely to be retained in the FBC residues.

The wet scrubbing of SO_2 in flue gas is an alternative way of minimizing emissions. In this technology, SO_2 is removed by bubbling through a dolomitic or calcitic limestone slurry (Santhanam et al., 1979; Alcordo and Rechcigl, 1995). Gaseous SO_2 dissolves in the water and reacts with the sorbent. Traditional scrubbing technologies produce a mixture of various proportions of calcium sulfite ($CaSO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$) known as flue gas desulfurization (FGD) waste. Modern forced oxidation desulfurization technology based on the same principle goes a step further and by forced oxidation converts $CaSO_3$ to

gypsum. The proper adjustment of reaction parameters results in a wallboard quality gypsum with very minor amounts of unspent sorbent ($CaCO_3$). The quality of this FGD by-product is comparable to that of mined gypsum.

Concentrations of trace elements in FGD by-products depend on their contents in the coal, sorbent material and quality of the process make-up water (Table VI.9.1). Ash can significantly contribute to the total concentrations of trace elements in FGD residue. The ash becomes mixed with FGD by-product when a scrubber is used for the simultaneous removal of fly ash and SO_2 or when fly ash collected separately is mixed with FGD sludge. In the forced oxidation technologies both practices are to be avoided in order to maintain a quality of by-product gypsum.

VI.9.3. Fly ash

Various techniques including electron microscopy, diffractometry and chemical extraction have been employed to study the structure of fly ash spheres and the distribution of elements within fly ash particles. According to a generally accepted model, three different regions can be distinguished in the majority of fly ash particles. The particle core composed of amorphous aluminosilicate glass is surrounded by a network of mullite crystals covered by an external layer of deposits. This unique structure is a result of the melting of coal mineral admixtures, evaporation and subsequent condensation occurring during combustion. Phyllosilicates present in coal particles are melted in the furnace, and form spherical drops. Thermal transformation of these minerals leads to the formation of glass and mullite. Many other minerals and chemical compounds from coal volatilize in the combustion zone and condense on earlier solidified glassy particles as the flue gas cools down. The external layer of the fly ash particles has a composition different than the glassy core. Elements concentrated on the particle surfaces comprise the most environmentally relevant fraction because they are in contact with water and their release is controlled primarily by precipitation/dissolution processes. The glassy core and mullite have low solubilities even in relatively concentrated inorganic acids. Elements present in the aluminosilcate glass are protected from contact with water and their release to the environment is controlled by the rate of weathering of the material. Hansen and Fisher (1980) estimated that more than 70% of As, Se, Mo, Zn and Cd present is concentrated on the surfaces of fly ash particles. Over 70% of Na, K, Mg and Fe is associated with the aluminosilicate matrix while Mn, Cr, Cu, Co, Ba, Pb and Ni exhibit intermediate tendencies being approximately equally distributed between the aluminosilicate matrix and non-matrix material. Gladney et al. (1978) suggested that B is also a particle surface enriched element.

VI.9.3.1. Influence on plant elemental uptake and yield

Numerous experiments have been carried out in order to compare plant availability of macro- and micronutrients from fly ashes to that of fertilizers commonly used for correction of deficiencies. Potassium is more available to plants from KCl than from equivalent rates supplied as fly ash (Martens et al., 1970) while S availability was equivalent to that of gypsum ($CaSO_4 \cdot 2H_2O$). Fly ash applied at rates 1–2% by weight of

soil corrected S deficiency (Elseewi et al., 1978) and dramatically increased yields of alfalfa (*Medicago sativa* L.) and Bermuda grass (*Cynodon dactylon* L.). Doran and Martens (1972) used fly ash for correction of Mo deficiency in alfalfa grown on an acid soil and found it to be as effective as $Na_2MoO_4 \cdot 2H_2O$. As demonstrated by Schnappinger et al. (1975), Zn plant availability from an acid fly ash was approximately equal to that of $ZnSO_4 \cdot 7H_2O$. Alkaline fly ashes, although higher in Zn, decreased the yield of corn (*Zea mays* L.) partly due to Zn deficiency induced by high pH. Fly ashes containing 232 and 370 mg/kg of B increased yield of alfalfa grown on a B deficient soil over a three-year period (Plank and Martens, 1974) with availability from fly ash being comparable to $Na_2B_4O_7 \cdot 10H_2O$. Mulford and Martens (1971) obtained similar results. The B status of fly ash amended soils has been extensively studied because of the potential yield responses and risks of plant injury if applied in excessive rates. The yield response curve is steep under both conditions of deficiency and excess (Sale et al., 1996). The hot water soluble B (HWSB) is the most widely accepted estimate of the plant available B. Good agreement between HWSB in fly ash amended soils and B uptake by alfalfa (Plank and Martens, 1974) and corn (Kukier and Sumner, 1994) has been obtained (Fig. VI.9.1). In a greenhouse study, Kukier and Sumner (1994) were able to predict the levels of HWSB in soil amended with a wide variety of fly ashes from an assay of the fly ash using the procedure developed for soils. The pH of solution obtained from fly ash boiling should be adjusted to the soil pH before amendment with fly ash. This method can be adapted for field conditions where it could be useful for estimation of safe application rates. In the case of very alkaline fly ash, correction for the change in soil pH would be necessary. Leaching and weathering of fly ash under natural conditions prior to a soil application effectively reduces B toxicity (Aitken and Bell, 1985; Kukier and Sumner, 1994). An alternative solution is to apply the material well in advance (few months) of planting to allow sufficient time for B leaching.

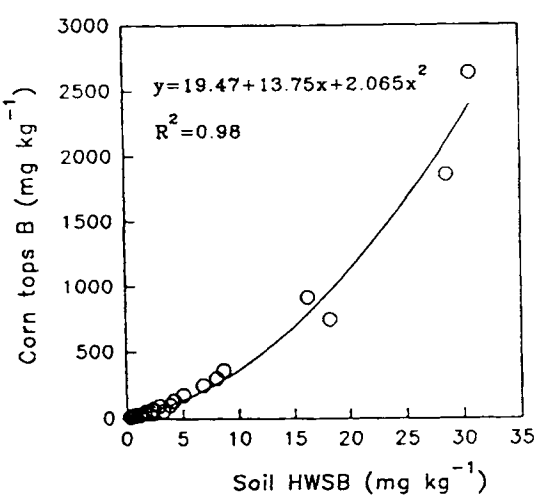


Figure VI.9.1. The relationship between hot water extractable boron in soil amended with different rates of fly ashes and FGD product and corn tissue B (Kukier and Sumner, 1994).

Selenium, while not essential for plants, is essential for animals. Selenium deficiency is a widespread problem with the level in about 30% of the forage and grain crops in the USA being below the optimum for animal nutrition (Mengel and Kirkby, 1987). Combs et al. (1980) in a feeding trial showed high Se bioavailabilty from corn produced on fly ash amended soil with the Se-enriched diet promoting chick growth and plasma Se-dependent glutathione peroxidase. The high plant availability of Se in fly ashes makes this material a potential source for deficient soils.

Furr et al. (1977) found a high correlation between total Se in 15 fly ashes and the Se content in cabbage grown in an amended soil. Shane et al. (1988) found Se uptake by broccoli, endive, lettuce, onions, spinach, tomatoes and perennial ryegrass from a growth medium amended with soft coal fly ash was proportional to the fly ash rate except for broccoli. Increased concentrations of Se from 0.5 to 2.0 mg/kg were detected in five successive cutting of the ryegrass indicating persistence of the effect. We came to similar conclusions based on a pot study with Cecil soil (Typic Kanhapludult) amended with increasing rates of five fly ashes in which corn shoots Se content was directly proportional to the Se rates applied in fly ash but was independent of other fly ash properties (Fig. VI.9.2). If more studies confirm this phenomenon, it would be possible to develop Se uptake equations specific for the soil–crop system which could be useful for the prediction of appropriate fly ash application rates.

An extensive review of the effects of fly ash on plant elemental uptake (Adriano et al., 1980) indicated a consistent increase in plant uptake of B, Mo, Se, As, S and Sr from fly ash amended soils. All anionic species from this list belong to the group of elements highly concentrated on the surfaces of fly ash particles. Other elements including essential plant nutrients such as P, K, Cu, Mg, Mn, Cu, Fe and Zn do not exhibit consistent uptake patterns. Depending on the composition of fly ash, soil properties and plant species, various effects on crop yields have been observed.

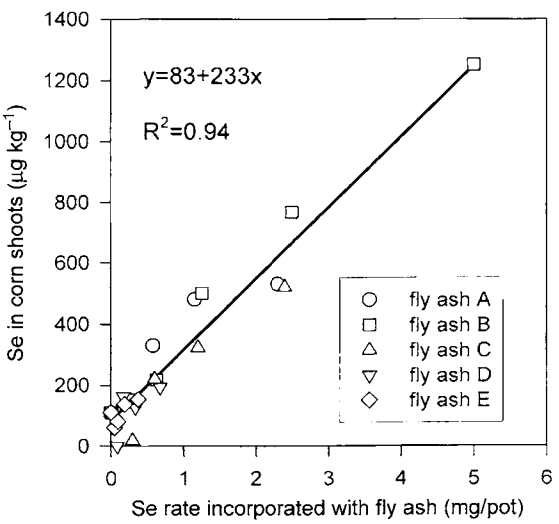


Figure VI.9.2. The relationship between Se rate incorporated with different fly ashes and Se concentration in corn shoots.

VI.9.3.2. Effects on soil physical properties

The effect of fly ash application on soil water content depends on fly ash rate and soil texture. Chang et al. (1977) reported that addition of less than 10% (by volume) of fly ash to soils of various textures (10–55% clay), resulted in a slight reduction in water contents at 20 centibars suction in all soils, except the heaviest. Increased amendment rates, up to 25 and 50% by volume, resulted in significant increases in water contents of almost all soils; however, the amount of plant available water did not change appreciably. Campbell et al. (1983) noted a marked increase in plant available water after addition of 10% fly ash by weight to a sand, which they attributed to an increase in capillary pores. A spectacular example of improving soil water characteristics was demonstrated by Jacobs et al. (1991) in a field study. Fly ash applied to Bayer loamy sand (Typic Hapludalf) and Crosswell sand (Entic Haplorthod) in bands significantly increased corn yield by improvement of the soil water regime. The saturated hydraulic conductivity of the sand was dramatically decreased by additions of fly ash in excess of 10% by weight (Campbell et al., 1983). Chang et al. (1977) observed an increase in hydraulic conductivity in all soils studied from applications of 2.5–5% of alkaline fly ash, above which dramatic decreases in the hydraulic conductivities of the heavy soils (>50% clay) were observed due to a pH rather than soil texture effect. They hypothesized that the pozzolanic reaction of the fly ash caused a clogging of soil pores. It is also likely that clay dispersion played a role in the drastic reduction in hydraulic conductivity of acidic soils. Inconsistent responses of agricultural soils to the application of fly ash indicate the need for further research in order to establish management practices that can assure beneficial modification of soil physical properties. In contrast to agricultural land, potting mixtures and artificial soils create a market for fly ash that can be used to improve their texture and water-holding capacity (Schlosserg et al., 2001).

VI.9.3.3. Observed and potential adverse effects

Although fly ash may have positive effects on soil quality and subsequently on crop yield, various constrains limit its use in agriculture. For example, an improvement in soil water-holding capacity, which requires high fly ash application rates, may result in toxic concentrations of B. Alkaline fly ash used as a lime substitute may add excessive amounts of Mo whose availability increases with pH promoting toxicity. There are numerous examples in the literature demonstrating that improvement of one soil parameter was associated with changes in other soil properties leading to yield reductions or deterioration in crop quality. Many reports emphasized elevated concentrations of elements potentially toxic to animals and humans or adverse balances among elements (Furr et al., 1977; Adriano et al., 1980). Improper Cu:Mo ratios in crops is a common example of such a disorder (Sale et al., 1996).

Because fly ash contains almost all elements and their concentrations depend on coal source, periodic monitoring of the chemical composition should be undertaken to ensure safe utilization.

The situation is further complicated by soil factors that affect plant uptake of elements potentially toxic to animals and human. Kukier et al. (1995) found that As concentrations in corn tops were affected not only by fly ash application rate but also by the addition of

K-fertilizer (Fig. VI.9.3). This could not be attributed to a "dilution effect" because dry matter values were equal for both K treatments at fly ash rates exceeding 3 g/kg soil. Therefore, the effect should be rather attributed to a modification of the uptake mechanism. This example shows that establishing of a safe application rate is a complicated issue and experimentally determined values may vary for the same soil under different management conditions.

Soil microbial population is an important factor influencing cycling of essential elements (C, N, S and P) in soil and the biosphere. Microbial counts, respiration and enzyme activities are the parameters commonly used for evaluation of microbial activity and growth. The changes in soil enzyme activity reflect changes in soil quality (Dick, 1992) and can be a measure of its deterioration. Arthur et al. (1984) found that CO_2 evolution from alfalfa meal and fly ash amended soil was significantly reduced at the higher rates (400–700 t/ha fly ash) indicating a decreased rate of organic carbon mineralization. Reduction of oat grain and alfalfa yields in accompanying field experiment with the same fly ash was noted at these rates. Yield reductions were associated with a B toxicity in plants and an excessive uptake of Mo, Se and As at levels potentially toxic to livestock. Therefore, it was concluded that a CO_2 evolution test may be suitable for prediction of potential phytotoxicity of fly ash.

Soil microbial activity expressed by a microbial respiration and enzyme activity in a fly ash amended Glynwood soil (Aquic Hapludalf) was investigated by Pichtel and Hayes (1990). An alkaline fly ash had no adverse effect on soil respiration at all rates applied (5, 10 and 20% by weight). At the 5% rate, bacterial numbers increased probably due to addition of nutrients but actinomycetes and fungi declined. At the higher rates, numbers of organisms declined in all populations. The decline in fungi was attributed to an increase in soil pH as these organisms are alkali-intolerant. Soil phosphatase, arylosulfatase, dehydrogenase, catalase and invertase activities were strongly inhibited at the 20% rate. Decrease in phosphatase activity was linked to the P added with fly ash, which interferes with activity and production of this enzyme. Overall, it seems that, the adverse effects of fly ash on crop yield and quality are usually observed at lower fly ash rates than those on soil microbial populations.

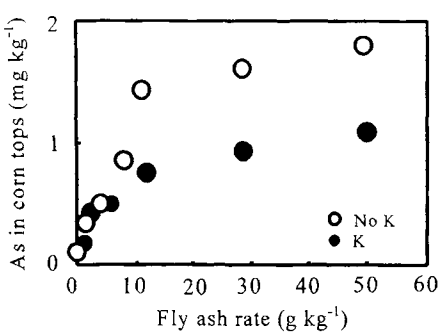


Figure VI.9.3. Effect of K fertilizer and fly ash rate on As concentration in corn shoots (Kukier et al., 1997).

VI.9.4. Forced oxidation FGD gypsum

Gypsum is applied to soils to supply S and Ca for crops, ameliorate subsoil acidity and improve soil physical condition and is recognized as a valuable soil amendment, being used on a commercial scale in many countries. The gypsum produced by a forced oxidation technology has a commercial-grade quality and can substitute mined gypsum in industrial and agricultural applications. Typically, FGD materials have smaller particle sizes than mined gypsum, which affects the dissolution kinetics as demonstrated by Bolan et al. (1991). The dissolution rate of the FGD material was only slightly lower than that of reagent grade gypsum but much higher than that of phosphogypsum and gypsum, which was attributed to a high external surface area of FGD product. This is considered an advantage because a rapid dissolution provides a better protection against crust formation as a rain event occurs and promotes movement of Ca^{2+} and SO_4^{2-} to subsoil. The following section will discuss the beneficial effects of gypsum application and the mechanisms involved. Because forced oxidation FGD gypsum is a recently developed product, most studies on its agricultural utilization are still in progress and few results have been published. For that reason, some examples of the effects of mined gypsum will be presented keeping in mind that FGD by-product has the same or even a better quality than mined gypsum.

VI.9.4.1. Amelioration of subsoil acidity

Highly weathered acid soils are characterized by high levels of Al and often insufficient amounts of Ca. Excessive amounts of Al and insufficient supply of Ca restrict root growth in a subsoil and result in crop susceptibility to drought periods and inhibited nutrient uptake.

Acidity of the topsoil can be ameliorated by application of lime. The Ca applied in this compound remains in the zone of incorporation and for that reason is not an effective ameliorant for subsoil acidity (Sumner, 1993). This can be partly attributed to the low solubility of $CaCO_3$ but also to the lack of a stable soluble anion that would have to accompany the migrating Ca^{2+} cation in order to maintain soil elecroneutrality (Pavan et al., 1984). Surface application or incorporation of gypsum ($CaSO_4 \cdot 2H_2O$) into topsoil was demonstrated to be a cost-effective way of ameliorating subsoil acidity. Both Ca^{2+} and SO_4^{2-} easily migrate down the soil profile changing subsoil chemical properties. Positive crop responses are usually observed after one or two years depending on soil texture, mineralogy and precipitation regime. Both ions, Ca^{2+} and SO_4^{2-}, are involved in reducing Al toxicity. Calcium displaces Al on soil exchange sites increasing Ca and decreasing Al saturation. This was demonstrated in a field experiment on an acid Tupelo soil (Vertic Palequult) amended with commercial-grade FGD gypsum, which was surface incorporated at the rate of 20 t/ha. Deep sampling after 16 months revealed a substantial increase in soil exchangeable Ca and a decrease in exchangeable Al to a depth of 50 cm (Fig. VI.9.4). Alleviation of Al toxicity and improved Ca status in the subsoil result in greater root growth as demonstrated in a number of studies with mined gypsum (Sumner, 1993, 1995) and FGD gypsum (Wendell and Ritchey, 1996). This, in turn, enables a better extraction of water and plant nutrients stored in the subsoil and increases crop yields especially if drought events occur (Sumner, 1993; Farina et al., 2000).

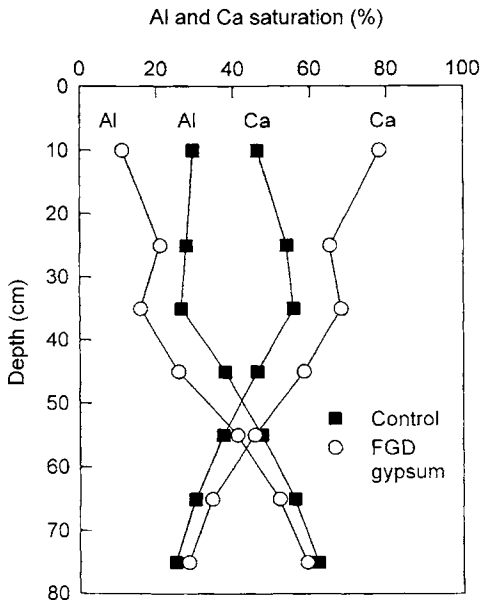


Figure VI.9.4. Al and Ca saturation in the profile of soil amended with 10 t/ha rate of FGD.

Displaced Al is leached out of the root zone or precipitates in a form of various aluminosilicate minerals such as alunite $KAl_3(OH)_6(SO_4)_2$, basaluminite $Al_4(OH)_{10}SO_4 \times 5H_2O$ and jurbanite $AlOHSO_4 \times 5H_2O$. Toxicity of Al in soil solution is reduced by a formation of $AlSO_4^+$ complex. Reeve and Sumner (1972) suggested that ligand exchange of SO_4^{2-} for OH^- on iron and aluminum oxide surfaces would increase soil cation-exchange capacity by creation of a net negative charge. The released OH^- groups would react with Al to form non-toxic $Al(OH)_3$. This process is known as the "self liming effect".

VI.9.4.2. Improvement of soil physical properties

The Ca^{2+} in gypsum promotes flocculation of clay particles, which in turn affects various physical properties of soils containing appreciable amounts of water-dispersible clay. Sodic and many highly weathered acid soils are very susceptible to clay dispersion under conditions of low electrolyte concentration. The energy of raindrops destabilizes aggregates, and clay particles, which separate from other fractions, seal pores to form a layer of reduced permeability at the soil surface (crust). The process is rapid and causes drastic reductions in water infiltration rate accompanied by increased run-off and erosion (Sumner, 1993). Gypsum applications increase final infiltration rates substantially (Miller, 1987, 1988; Miller and Scifers, 1988). Soil losses were reduced from 266, 1315, 1135 and 939 to 96, 732, 442, and 50 kg/ha, respectively. Preventing crust formation by placing gypsum over the row prior to planting improves seedling emergence (Miller, 1988).

Gypsum was also demonstrated to be effective in reducing mechanical impedance of subsoil hardpans (Radcliffe et al., 1986; Sumner et al., 1990) through clay flocculation and improved chemical conditions in the subsoil. Physical, chemical and biological factors working in concert lead to aggregation of the subsoil material, which in turn promotes a better plant rooting and increased stability of the structure.

VI.9.4.3. Observed and potential negative effects

The high application rates of gypsum required for the amelioration of the subsoil acidity may induce losses of Mg and K from the topsoil due to exchange of the Mg^{2+} and K^{+} by Ca^{2+} on the soil exchange sites. Increased mobility and solubility of both cations in soil column amended with gypsum FGD material was reported by Wendell and Ritchey (1996). Severity of the losses depends upon gypsum application rate and soil texture (Fig. VI.9.5).

As mentioned earlier, leaching of Al beyond the root zone is one of the mechanisms alleviating Al toxicity in acid subsoils. This may potentially pose a risk of groundwater contamination with Al. A column study (Wendell and Ritchey, 1996) demonstrated that FGD gypsum dramatically increased concentrations of the Al in leachates. These results may not be directly applicable to field conditions but they indicate the need for further research to answer this question.

These adverse effects are not specific to FGD gypsum and are also observed with mined and any other gypsum materials. They can be overcome by application of K and Mg fertilizers shortly after gypsum application.

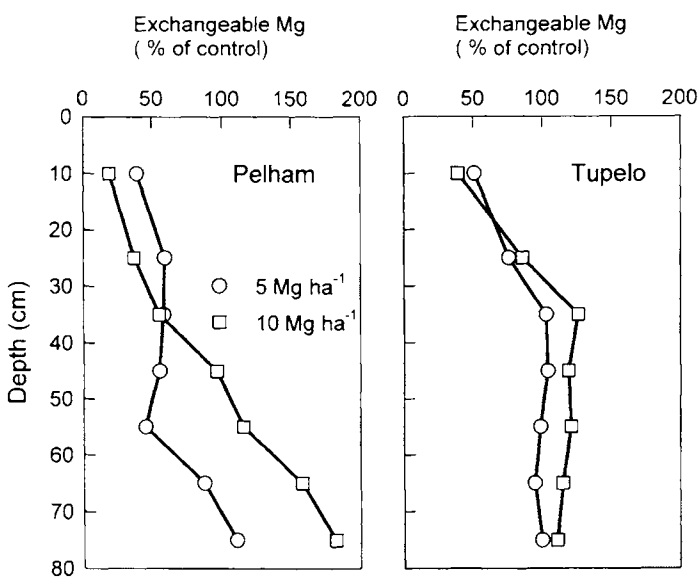


Figure VI.9.5. Distribution of exchangeable Mg in the profiles of soils amended with FGD material.

A salinity problem, which may be potentially associated with high rates of FGD products, is more specific to this material. The electrical conductivity of the mined gypsum saturated extracts is about 2 dS/m while that of FGD gypsum may exceed 30 dS/m. This is due to the presence of soluble salts other than gypsum from process make-up water that is recirculated in order to minimize the volume of wastewater. It is not expected to pose any significant risk to crops and the environment when FGD gypsum is applied at low rates of 0.5–1 t/ha as a source of Ca and S for crops but at high rates a period of time for leaching to take place before planting may be necessary.

A long-term mesocosm study of FGD residue application to South Carolina coastal plain soils showed a short term improvement of the yield of several crops. However, leachate salinity was significantly increased, and both crops and soil were enriched in trace elements As, B and Se; for this reason, 220 T/ha was assumed to be upper limit for the application of this material (Punshon and Adriano, 2001).

In some cases, FGD gypsum is stored in the same settling pond with fly ash, which is a carrier for trace elements. Application of such mixtures may add significant loads of trace elements. Kukier et al. (1997) demonstrated increased plant available As in the mixed vs. the pure FGD gypsum. Although some beneficial effects may result from joint application of both materials, extreme caution is recommended because the agronomic value of FGD gypsum may be offset by the fly ash component.

VI.9.5. Fluidized bed combustion (FBC) material

VI.9.5.1. Beneficial effects

The FBC products are composed mainly of $CaSO_4$, $CaSO_3$, CaO and MgO and ash. Their $CaCO_3$ equivalent typically varies from 50 to over 80% (Stout et al., 1979; Korcak, 1985); therefore their primary agricultural function is a substitute for lime on arable land and orchards (Korcak, 1988; Stehouwer et al., 1999). For this purpose, FBC materials are applied at rates from several to over 70 t/ha. An attempt to apply FBC waste at disposal rates higher than 100 t/ha was also reported (Mays et al., 1991). In every case, except for the highest disposal rates, positive effects were observed. The FBC materials increase soil pH and Ca and Mg levels in plants and soil. No excessive plant uptake of trace elements was reported in any of the field or pot studies. It was established (Terman et al., 1978; Stout et al., 1979) that FBC products may correct S deficiency. The availability of S from this material was comparable to that of Na_2SO_4 and elemental S.

High application rates 100 t/ha of FBC products can be used in orchards. The FBC material is surface applied beneath the trees. In addition to improving Ca status in soil and trees and the liming effect, it provides weed control (Korcak, 1993). A similar method was used with good results for tomato production. The FBC by-product was equal to or better than standard black plastic mulch, bare soil and rolled newspaper in terms of yield and fruit firmness.

High solubility of some components in FBC materials providing electrolytes concentrations sufficient for the flocculation of clay particles can be used for the improvement of water infiltration and the reduction of erosion in variable-charge and swelling soils but with some limitations (Reichert and Norton, 1996). The FBC bottom ash

used in the study was a combination of coal ash, unreacted sorbent material and anhydride ($CaSO_4$). Unlike gypsum, which does not change soil pH, FGD bottom ash increases pH and produces a much stronger electrolyte concentration upon dissolution. Application of FBC bottom ash has two opposite effects on clay dispersion. The increase in pH promotes clay dispersion by generation of negative charge while the increase in electrolyte concentration tends to flocculate clay particles. Reichert and Norton (1996) studied the effect of surface application of 5 t/ha FBC bottom ash on infiltration rate and erosion of seven variable charge soil series from Hawaii, Puerto Rico, Georgia, Brazil and Australia. The FBC ash increased infiltration and reduced erosion only on the soils whose pH was little affected by the application of the by-product. On the permanent charge soils, which respond with a small increase in charge as pH increases, a consistent positive effect expressed in reduced surface sealing and erosion was observed after FBC waste application (Reichert and Norton, 1994).

VI.9.5.2. Potential and observed adverse effects

Very high disposal rates (up to 500 t/ha) of FBC by-product on arable land had an adverse effect on crop yield and soil quality including excessively high pH levels and crust formation due to a pozzolanic effect of the material (Mays et al., 1991).

The potential adverse effect on groundwater quality associated with application of large quantities of FBC product was evaluated by Sidle et al. (1979). Only the Ca, Mg, Mn and SO_4^{2-} concentrations increased in FBC-amended soil. Movement of Ca and Mg could be considered a beneficial effect for subsoil. Concentrations of Mn and SO_4^{2-} in the percolate were within the range for drinking water. No evidence for downward migration of B, Cd, Co, Cu, K, Na, Ni, Pb and Zn was observed.

McCarty et al. (1994) studied the effect of lime ($CaCO_3$) and FBC fly and bed ashes applied at the rates appropriate for substitution as lime on the soil enzyme activity. Significant effects on enzyme activity were observed at 2.8 t/ha rates of FBC products and 4.5 t/ha of $CaCO_3$. The FBC products influenced enzyme activity in a similar manner to $CaCO_3$, which suggests that the influence of the by-products on the enzyme activity was partly due to their liming effect. It appears that in some situations it is very difficult to distinguish the effects of coal combustion by-products from those of traditional fertilizers and lime.

The potential effect on the food chain was studied by Whitsel et al. (1988). Pigs were fed for 8 weeks on a diet produced on soil amended with FBC material. Increased As in urine was the only adverse effect of the diet. None of trace elements investigated (Fe, Mn, Cu, Zn, Cd, Pb and Se) exceeded normal levels in pig organs. A significant depression in weight gain of pigs fed an FBC produced diet was observed when compared to a lime treatment. No explanation of this adverse effect was provided.

VI.9.6. Closing comments

Based on the available literature, it appears that among the coal combustion residues reviewed, fly ashes have the most variable characteristics; therefore their beneficial agricultural utilization should be preceded by a careful evaluation of potential effects on

soil, crop and environment. Co-utilization with other waste materials such as biosolids or manure seems to be a promising alternative (Schumann and Sumner, 2000). Fly ash as a component in such a mixture serves as a dewatering and deodorizing agent and would stabilize P. The organic components are supposed to reduce the toxicity of trace elements present in fly ash. Recent reports give equivocal evidence concerning the environmental effect of biosolids/fly ash mixture. On the one hand, mixture application was found to reduce concentrations of plant available trace elements (Bhumbla et al., 2001). On the other hand, Yuncong et al. (2001) observed an increased phytoavailability of Zn, Ni and Mo in soil amended with a large amount of composted mixture of fly ash and biosolids. Increased mobility of Pb and Zn, following fly ash compost application could pose a risk of groundwater contamination. These results indicate that there is a need to develop guidelines for fly ash application to the agricultural land, either as a sole component or as a mixture with biosolids.

More research is needed in order to explore the possibilities of the agricultural utilization of gypsum-like materials. A greater number of field studies on the environmental impacts of coal combustion by-products is necessary to test under natural conditions hypotheses developed as a result of laboratory studies.

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VI.10
Hazardous waste site remediation technology selection

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VI.10.1. Introduction

Hazardous materials may exist in air, water or soil media and may require treatment, management or disposal relevant to any one of the media. A spill of hazardous material, for example, may affect all three at one time. This chapter deals with selection of technologies for use in site remediation, either for cleanup of areas contaminated with improperly disposed wastes or materials, or for cleanup of sites which are authorized or permitted to dispose of hazardous wastes and materials commercially.

There are a number of possible techniques that may be used to guide the selection of technology for waste treatment or management. There are tens of thousands of chemical compounds, hundreds of different wastes and hazardous materials and dozens of possible treatment processes and technologies applicable to disposal, treatment and management. If it was necessary to examine all possible permutations and combinations of compounds, wastes and technologies, an assessment of millions of options would be required to develop a plan to successfully cleanup a site. The problem is not nearly that complicated, since we may be guided by the experience of past applications of technology, the likelihood that some technologies may work for organics and others for inorganics, and by the fact that technologies must be applied in given sequences, some acting as pretreatment for others that follow in the sequence.

Nevertheless, even after reducing considerably the number of possibilities using the three simplifying strategies mentioned above, the task may be a formidable one. The approach used herein is based on following a number of steps toward developing a treatment or disposal strategy starting with initial data and information about the problem.

One broadly applicable technique for technology selection can be based on a straightforward logic process incorporating the following:

a) the characteristics of the various constituents in the waste,
b) the specific "purpose" of different remediation technologies,
c) inherent restrictions in the applicability of each technology and
d) the specific "cleanup objectives" for the site.

Using this approach, available technologies can be viewed in terms of their functional purpose, i.e. whether their operation achieves one of the following:

- separation
- detoxification/destruction or
- immobilization.

In this tripole context therefore, air stripping, chemical precipitation and soil washing each are examples of separation technologies; chemical dehalogenation and incineration are examples of detoxification or destruction technologies; vitrification is an example of an immobilization technology. Separation technologies may be chosen when the need is to separate contaminants from contaminated media or when the need is to separate contaminants, from each other, especially in those cases where one type of contaminant causes interferences in a technology otherwise suitable for the contaminant mix present. Destruction/detoxification techniques are chosen when all requisite separations have been achieved and a treatable stream of contaminants is available for final destruction or detoxification. Immobilization technologies are used when no remaining destruction/detoxification techniques are appropriate and yet some waste constituents remain whose movement from emplacement must be restricted.

One can then initially select candidate technologies aimed at achieving a specific purpose, i.e. separation, destruction/detoxification or immobilization. Then, using the physical characteristics of the waste constituents (e.g. octanol–water partition coefficient, Henry's law coefficient, water solubility, heat content, etc.), the probable effectiveness of the technology may be estimated. If however, some site characteristic exists, which restricts the use of a specific technology, there is no need to retain such a candidate through the detailed evaluation process. Finally, any candidate technology when evaluated should either meet or move toward the cleanup objectives for the site. Applied remediation strategies will incorporate several technologies in sequence, with following technologies further treating the effluents of earlier technologies until all objectives are met in all media. The technique presented herein follows this logic approach.

VI.10.2. Hazardous waste treatment

VI.10.2.1. Hazardous wastes

The United States Environmental Protection Agency (EPA) has specifically "listed" wastes as hazardous, based on their toxicity, reactivity, corrosivity and ignitability, as measured against specified criteria identified in the Code of Federal Regulations (CFR). Detailed explanations for these wastes are contained in Listing Background Documents. The listing documents are organized as: (i) the EPA basis for listing the waste or waste stream, (ii) a brief description of the industries generating the listed waste stream, (iii) a description of the manufacturing process or other activity that generates the waste, and identification of waste composition, constituent concentrations and annual quantities generated, (iv) a summary of the adverse health effects of each of the waste constituents of concern and (v) a summary of case histories and damage done by the waste. The listed hazardous wastes consist of wastes from non-specific sources (F code), wastes from specific sources (K code) and commercial products (U and P code).

Some of the most commonly found contaminants at hazardous waste sites include *organics* (e.g. VOCs, SVOCs, fuels, etc.), *inorganics* and *explosives*. Organic compounds comprise many classes, including chlorinated solvents, e.g. trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), carbon tetrachloride, dichloroethylene (DCE), methylene chloride, perchloroethylene (PCE), chloroform; fuel constituents such as BTEXs (benzene, toluene, ethyl benzene and xylenes), *n*-alkanes, and substituted alkanes, alkenes and aromatics; polychlorinated biphenyls (PCBs); phenol; pentachlorophenol (PCP); polycyclic aromatic hydrocarbons (PAHs); and pesticides and herbicides (e.g. DDT, chlordane, lindane and dieldrin). Inorganics include toxic metals (e.g. arsenic, cadmium, chromium, copper, lead and zinc), radionuclides and other contaminants, such as asbestos and cyanide. Explosives follow treatment techniques typically applicable to SVOCs and include di- and trinitrotoluene (DNT and TNT), and RDX. Choice of treatment technology for wastes containing one or more of these classes of compounds or other hazardous waste constituents depends on the media (soil, groundwater, surface water, leachate, liquid, air, industrial stream) and other relevant properties (physical, chemical, biological) of the waste media. In the absence of established techniques or historical experience, treatability studies are carried out to determine (i) whether the waste is amenable to the treatment process(es); (ii) what pretreatment, if any, is required; (iii) the optimal process conditions needed to achieve the desired treatment; (iv) the efficiency of a treatment process and (v) the characteristics and volumes of residuals from a particular treatment process.

In this section, a brief overview of some of the commonly used techniques for hazardous waste treatment, and their applications are provided.

The hazardous waste treatment processes can be classified in the following categories:

1. Separation including physical and chemical,
2. Destruction/detoxification including chemical, biological, thermal,
3. Immobilization including chemical or thermal, solidification/stabilization (S/S).

VI.10.2.2. Physical separation processes

In these techniques, physical characteristics are used as means to *separate* or *concentrate* waste constituents. Separation or concentration of target species can be accomplished by affecting or utilizing the changes in *phase* (evaporation, distillation, steam or air stripping), *density* (sedimentation, centrifugation, flocculation, dissolved air floatation), *solubility* (extraction, soil washing, chelation), *adsorptivity* (granulated or powdered activated carbon adsorption), *size* (filtration, reverse osmosis) or *ionic characteristics* (ion exchange, electrodialysis). Some of the commonly used physical processes are briefly described below.

- *Air stripping*: In a typical gas absorption unit, used for air stripping or scrubbing operations, air and water are contacted in a countercurrent fashion in a packed or plate column, as shown in Figure VI.10.1. Water is sprayed through liquid distributors from the top of the tower, while the air is pumped from the bottom. The inert packing, randomly distributed in the tower, provides a large surface area for air–water contact necessary for the mass transfer. The packing material is plastic, ceramic or porcelain, and the typical shapes are rashig rings, berl saddles, intalox and pall rings. The packing must be

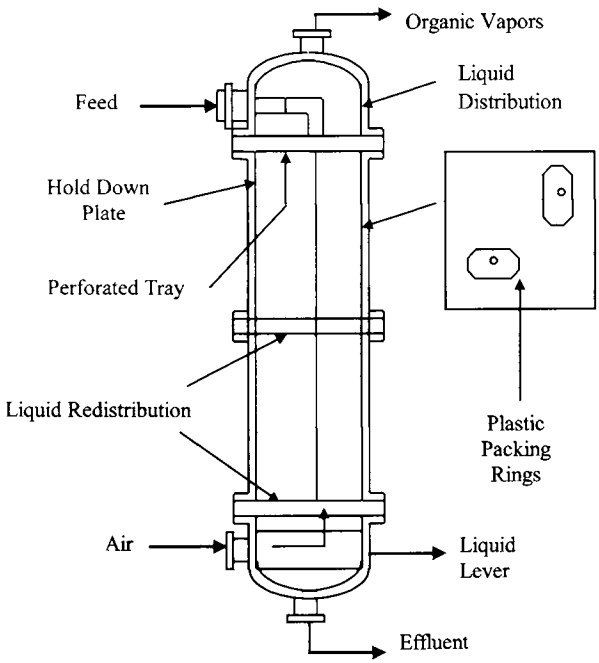


Figure VI.10.1. Schematics of air stripping/scrubbing in a typical gas absorption unit.

chemically inert, strong, lightweight, open to flow, have large surface area and inexpensive. For a given water flow rate and tower packing, there is an upper limit to the air flow rate, flooding velocity, at which the pressure drop is excessive and the column stops to operate. The tower is generally operated at about 50–60% of this flooding velocity. The water stream, leaving the tower is leaner in contaminants, while the air stream is richer in contaminants. The contaminants in the exit air can be further removed by incineration or vapor phase carbon adsorption. Over a sustained operating period of time, the packing and tower internals get clogged because of scale formation due to inorganic impurities in water and suspended solids. Scaling reduces the stripping efficiency by reducing the flow rates and mass transfer surface area, and increasing the pressure drop. Shutdown period for cleaning with appropriate solvents is included in the process design. Air stripping is applicable for low contaminant concentrations, typically less than 100 ppm (mg/kg).

The capital costs for air stripping towers are moderate, compared with other technologies. The operating costs are typically low and include packing material and electricity for pumps and blowers. Since this is a separation/removal technology, off-gases need to be treated in a later step, incurring further treatment costs.

- *Steam stripping*: This is a form of continuous fractional distillation process, in which steam is used to provide the heat instead of reboiler bottoms. The process is similar to air stripping, in the way the column is operated. Liquid feed is introduced from the top in a plate column, while steam is blown from the bottom, as shown in Figure VI.10.2. As the hot steam moves up, it picks up volatile contaminants from the downcoming water

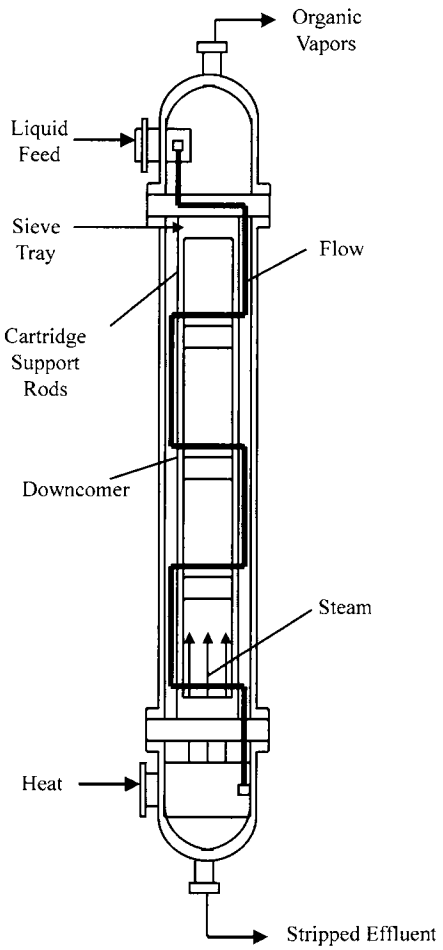


Figure VI.10.2. Steam stripping column – perforated tray type.

stream, in a countercurrent fashion. Some of the steam condenses to provide heat for the contaminant volatilization. The organic vapors in the steam effluent leave the top of the column, while the stripped effluent leaves from the bottom. Steam stripping is applicable to a wider range of organics (less volatile with b.p. $< 150°C$, and more soluble) than air stripping, because of higher operating temperature. Aqueous wastes contaminated with chlorinated solvents (e.g. TCE, TCA) and aromatics (e.g. PCP), fuel aromatics (e.g. BTEXs) and alcohols (e.g. methanol) can be treated by steam stripping, over a wide concentration range, from 100 ppm (mg/kg) to 10%.

- *Carbon adsorption*: Adsorption is a surface-based process as opposed to absorption, which encounters changes at the molecular level. The contaminant transfers from the liquid or vapor phase to the surface of the solid adsorbent (e.g. activated carbon). The ratio of the concentration of the solute on the solid phase to that in the fluid phase, at equilibrium, is known as the partition coefficient and is represented as adsorption

isotherms. Organics from air and water streams are adsorbed on the external and internal surfaces of the porous particles of carbon, which provides high surface area. A typical adsorption design includes two packed adsorption columns – one on line and one being regenerated – pipes and flow control schemes for introducing liquid/gas feed, steam or inert gas inlet for spent carbon regeneration and an effluent port for treated fluid stream (Fig. VI.10.3). The flow arrangement provides for cyclic switching (operation and regeneration) between the two columns. The bed depths and flow rates are generally chosen for an adsorption cycle of 2–24 h. As the bed depth increases, the removal rates increase along with an increase in the adsorption cycle, column length, pressure drop and the cost. On the other hand, a decrease in the bed depth will lower the pressure drop and the cost, but the shallow beds (less than 1 ft = 30.48 cm) do not provide good separation and require more energy for regeneration.

Carbon adsorption may be used to treat single-phase aqueous organic phase, and gas streams contaminated with high molecular weight and boiling point organics with low solubility and polarity. A wide range of contaminants (e.g. chlorinated solvents, trihalomethanes, PCBs, PCP, pesticides, inorganics and metals) is amenable to adsorption. The suggested concentration ranges are: organics $< 10{,}000$ ppm (mg/kg); suspended solids < 50 ppm (mg/kg); dissolved inorganics, and oil and grease < 10 ppm (mg/kg) and removal rates of $> 95\%$ can typically be accomplished.

- *Distillation*: It is a process of separating by vaporization, a mixture of components into individual components or groups of components. The distillation process can be carried out in a batch mode in which feed is partially vaporized into a vapor stream, rich in

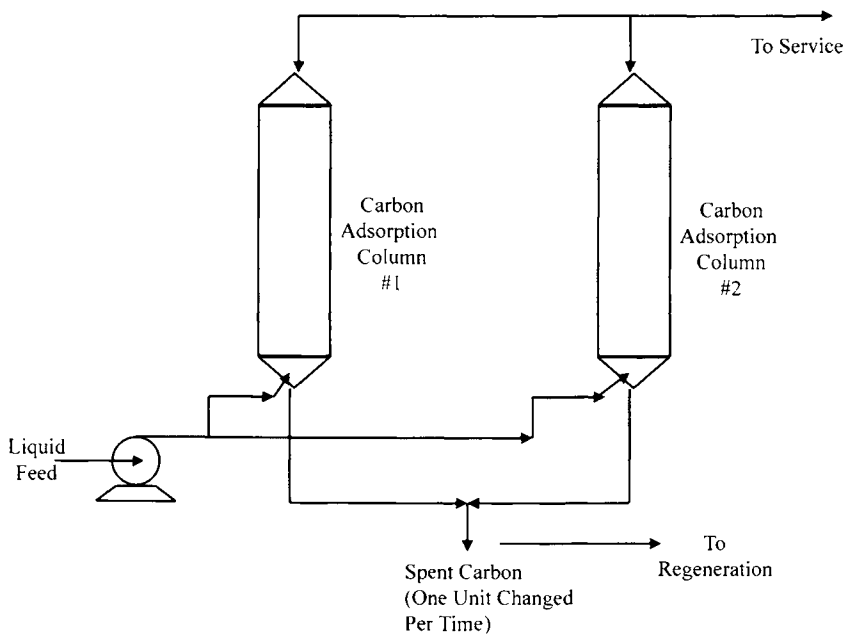


Figure VI.10.3. A typical granular activated carbon adsorption design.

more volatile component and a liquid stream, rich in the lesser volatile components. In the continuous mode, a part of the condensate from the top of the column is returned back to the top of the column where it contacts the upcoming vapor stream. Similarly, a portion of the bottoms stream is vaporized in the reboiler and sent back to the distillation column, as the upflowing vapor stream. This establishes a countercurrent system of liquid and vapor streams contacting throughout the column, establishing equilibrium at the plates, and transferring more volatile components from liquid stream to the vapor stream and lesser volatile components from the vapor stream to the liquid stream. As the vapor moves up, it gets richer and richer in the more volatile components, and the liquid, moving down, gets richer and richer in the lesser volatile components. Figure VI.10.4 shows schematics of batch (A) and continuous distillation (B) processes. Flash distillation is a process in which a portion of the liquid feed is vaporized at a reduced pressure. This results in two streams – a vapor and a liquid – in equilibrium with each other.

Distillation can be used to separate miscible organic liquids for solvent reclamation and waste volume reduction. Most organics with different volatilities can be separated from aqueous streams. Design procedures for distillation processes are outlined in detail in many chemical engineering unit operations textbooks.

- *Soil washing/flushing*: This process is aimed at extracting contaminants from soils and sludges using a liquid medium as the washing solution. The washing solution may be water, surfactants, organic solvents, chelating agents, acids or bases, depending on the type of contaminants to be removed. The process can be operated *in situ* or *ex situ*. The goal of the process is to transfer the contaminants from the solid to the liquid phase. In the post-treatment step, which may be carried out in conjunction, or separately, the contaminants are treated or removed by a chemical, biological or thermal technique.

Soil washing has been successfully applied to various organics, inorganics and heavy metals.

VI.10.2.3. Chemical separation processes

These techniques are usually only appropriate in the liquid phase and involve the addition of specific reagents to change the oxidation state of the target contaminants, followed by pH adjustment to a condition of lower solubility for the target contaminant so that a precipitate forms. Chemical separation is usually accompanied by a physical separation process such as sedimentation or filtration.

VI.10.2.4. Chemical detoxification/destruction processes

In these processes, molecular or structural changes are made on the target waste constituents so that the result is a detoxified form of the original molecule (e.g. dehalogenation) or the target contaminant is completely oxidized to innocuous products (e.g. oxidation of hydrocarbons to CO_2 and H_2O). Chemical destruction/detoxification processes include *chemical hydrolysis* or *ozonolysis*, *redox reactions* (reduction or oxidation of the contaminant by various chemical agents) and *electrolytic oxidation*.

- *Precipitation/flocculation/sedimentation*: Precipitation is a physio-chemical process, based on the reduction of solubilities of inorganic species, resulting in change of phase of the species to solid. Metals can be precipitated as hydroxides or sulfides by

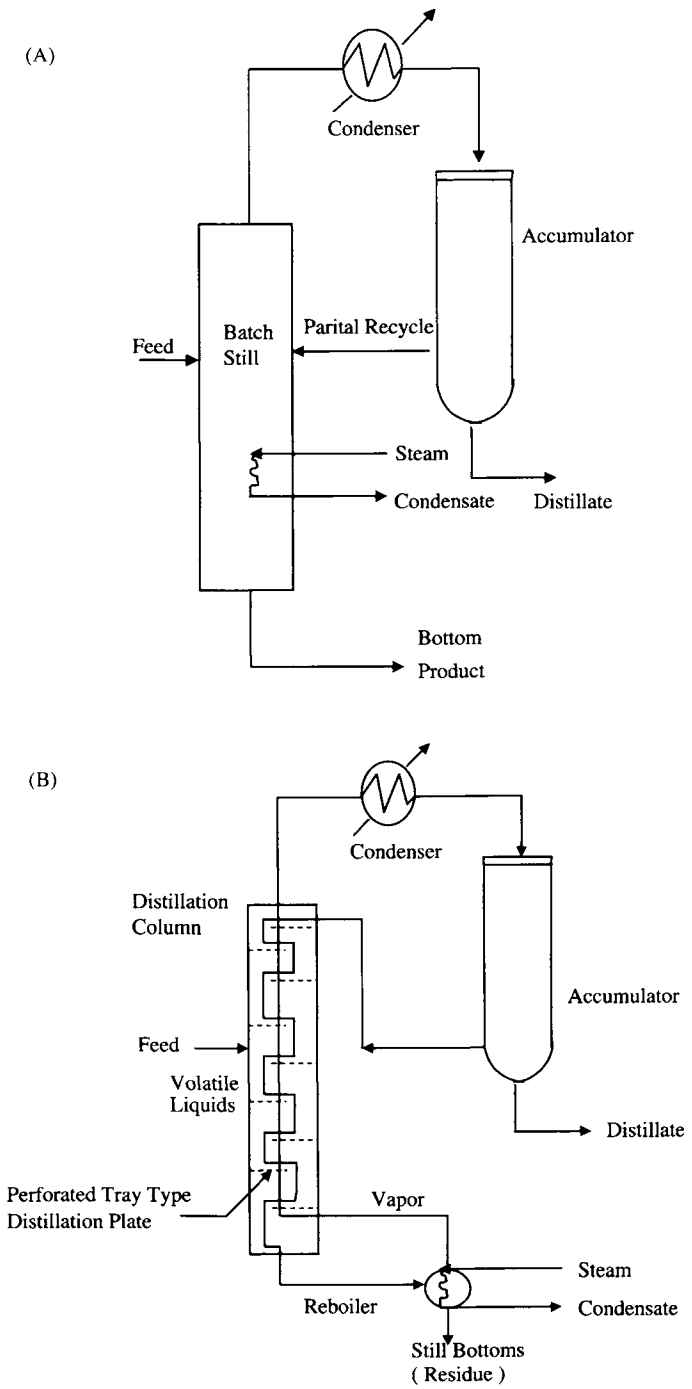


Figure VI.10.4. Schematics of batch (A) and continuous fractional distillation (B) processes.

changing pH, as shown in Figure VI.10.5. For instance, lead can be precipitated as PbS by changing the pH from 4 to 11.5; the solubility drops by seven orders of magnitude, precipitating Pb as lead sulfide. Addition of flocculating agents causes the precipitated particles to agglomerate. Agglomerated particles are separated from the liquid phase by sedimentation or filtration. Figure VI.10.6 shows a typical configuration of precipitation/flocculation/sedimentation process.

- *Neutralization*: Neutralization is the process of adjusting pH by the addition of acid or base to a mixture. It can be a treatment technology in itself, or a pretreatment step for chemical or biological treatment processes. Sulfuric acid or hydrochloric acid is generally used as acidic agents, while sodium hydroxide or limes are used as alkaline agents. The neutralization system is a simple mixing unit, with feed controls, and chemical storage units. Simultaneous neutralization of acid and caustic waste is shown in Figure VI.10.7. Acidification of certain hazardous wastes produces heat and toxic off-gases, and should be handled with caution.
- *Ion exchange*: The process is carried out in packed towers, filled with ion exchange resins (Fig. VI.10.8). The target ions from the aqueous phase are removed and substituted by the harmless ions from the resin. The resins are temperature and pH tolerant, and can be tailored specifically for particular waste applications. Ion exchange can remove a wide variety of organics, inorganics and metals. Some of the design challenges are similar to traditional packed tower mass transfer processes, e.g. absorption and adsorption, and the resin has to be regenerated periodically. Plugging and scaling problems, because of suspended solids and mineral scaling, need to be resolved in regular cleaning operations.

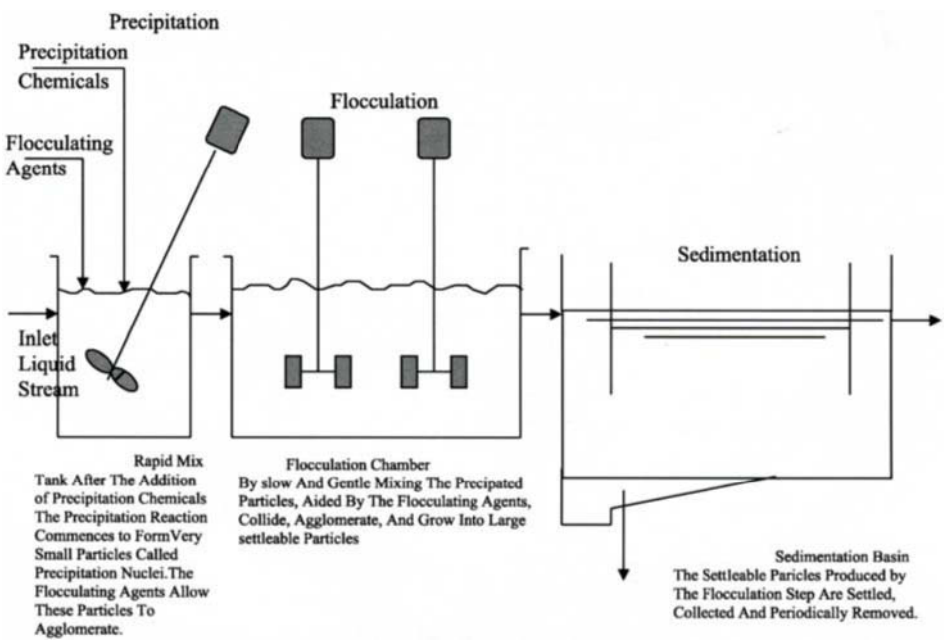


Figure VI.10.5. Schematics of chemical precipitation/flocculation/sedimentation process.

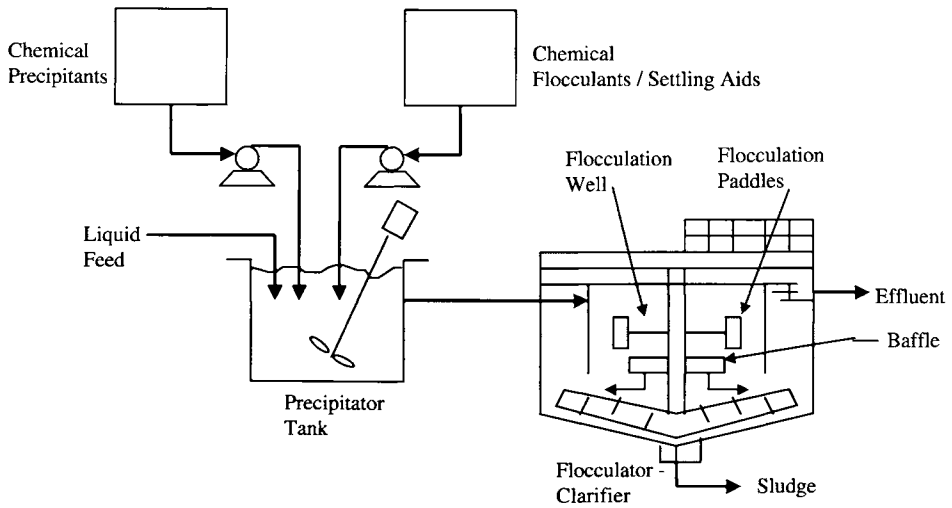


Figure VI.10.6. Typical configuration of chemical precipitation and associated flocculation/sedimentation process steps.

- *Reduction–oxidation reactions*: In redox reactions, one of the reactants is reduced while the other is oxidized. In chemical oxidation, the waste is oxidized to a higher oxidation state, a less hazardous or toxic form. Oxidation power of some common oxidants is included in Table VI.10.1.

Chemical oxidation is used for cyanide wastes and oxidizable organics. Chemical oxidation can also be used as a pretreatment technique for refractory organics, partially oxidizing them in preparation for biological treatment.

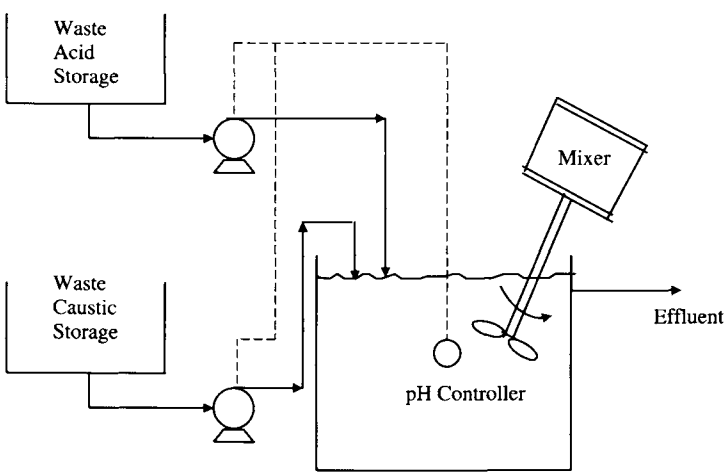


Figure VI.10.7. Simultaneous neutralization of acid and caustic waste.

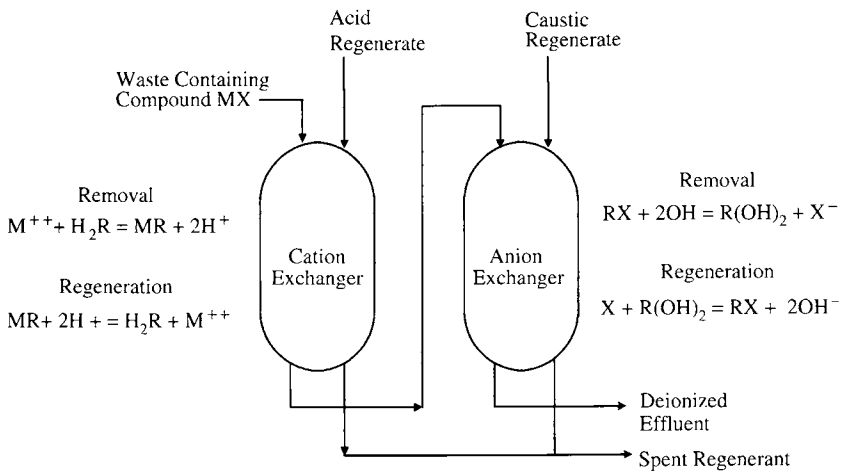


Figure VI.10.8. Schematics of the ion exchange processes.

Chemical reduction is the opposite process to chemical oxidation. Reducing agents are added to lower the oxidation state of a waste compound, e.g. addition of sulfur dioxide converts toxic Cr^{+6} to the less toxic Cr^{+3} form, as shown below:

$$2H_2CrO_4 + 3SO_2 + 3H_2O = Cr_2(SO_4)_3 + 5H_2O \qquad \text{(VI.10.1)}$$

Some common reducing agents include sulfite salts, sulfur dioxide and base metals, Fe, Al and Zn.

Table VI.10.1. Oxidation power of some oxidants.

Oxidants	Oxidation power
Fluorine	2.23
Hydroxyl radical	2.06
Atomic oxygen	1.78
Hydrogen peroxide	1.31
Perhydroxyl radical	1.25
Permanganate	1.24
Hypobromous acid	1.17
Chlorine dioxide	1.15
Hypochlorous acid	1.10
Hypoiodous acid	1.07
Chlorine (reference)	1.00
Bromine	0.80
Iodine	0.54

VI.10.2.5. Biological destruction/detoxification processes

These techniques utilize microorganisms to break down organic wastes into products such as CO_2, H_2O, CH_4 and others. Depending on the type of electron acceptor used, biological processes are classified as *aerobic* (oxygen as terminal electron acceptor) or *anaerobic* (sulfate or nitrate as terminal electron acceptor). Indigenous microorganisms, as well as specially adapted or genetically manipulated microorganisms can degrade a wide range of compounds under proper conditions of nutrients and electron acceptor concentrations.

Bioremediation techniques involve the use of naturally occurring microorganisms for contaminant degradation by providing favorable conditions for the growth of microorganisms, which in turn use contaminants as a source of food and energy. The favorable conditions for the growth of microorganisms include appropriate values of oxygen, nutrients, moisture, temperature and pH. Bioremediation can be used to remediate soils, sludges, sediments, groundwater, leachate and surface water. Biotreatment is generally applicable to a wide variety of organics – VOCs, SVOCs, fuels and explosives. A large number of sites contaminated with petroleum hydrocarbons, halogenated and non-halogenated solvents, pesticides, wood preservatives and other organic chemicals have been studied for the application of biological techniques for the destruction of hazardous wastes. Inorganics are generally not amenable to biological treatment.

VI.10.2.6. Thermal destruction/detoxification processes

These methods use high temperature under controlled conditions to change the physical, chemical or biological character or composition of the waste. An incinerator is any enclosed device using controlled flame combustion. Figure VI.10.9 shows a schematic of a rotary kiln incineration device. Thermal oxidation degrades wastes into products such as CO_2, H_2O, SO_2, NO_x, HCl, products of incomplete combustion (PICs) and ash. In general, air pollution control devices (APCDs) are required to control the release of air contaminants into the atmosphere. Thermal techniques can be used to destroy organic contaminants in all three phases (liquids, solids and gases) and various waste media – water and leachate, soils and sediments and air and off-gases. Other forms of thermal treatment include pyrolysis, microwave discharge, wet air oxidation and molten salt processes.

EPA RCRA regulations use destruction and removal efficiency (DRE) as a measure of a hazardous waste incinerator performance. Destruction applies to the waste combustion, while removal applies to the cleansing of the combustion gases in APCDs, before release to the atmosphere. Because of the complexities and potentially large number of constituents involved in a waste stream, representative hazardous compounds, called the principal organic hazardous constituents (POHCs) are selected as surrogates to determine the DRE performance of the incinerator during testing for a RCRA permit. POHCs are selected based on their high concentration in the waste feed and their high resistance to destruction compared to other waste constituents. The logic is that if the required DRE is achieved for the POHCs during testing, then the other compounds in the feed should perform at the same or better DRE values.

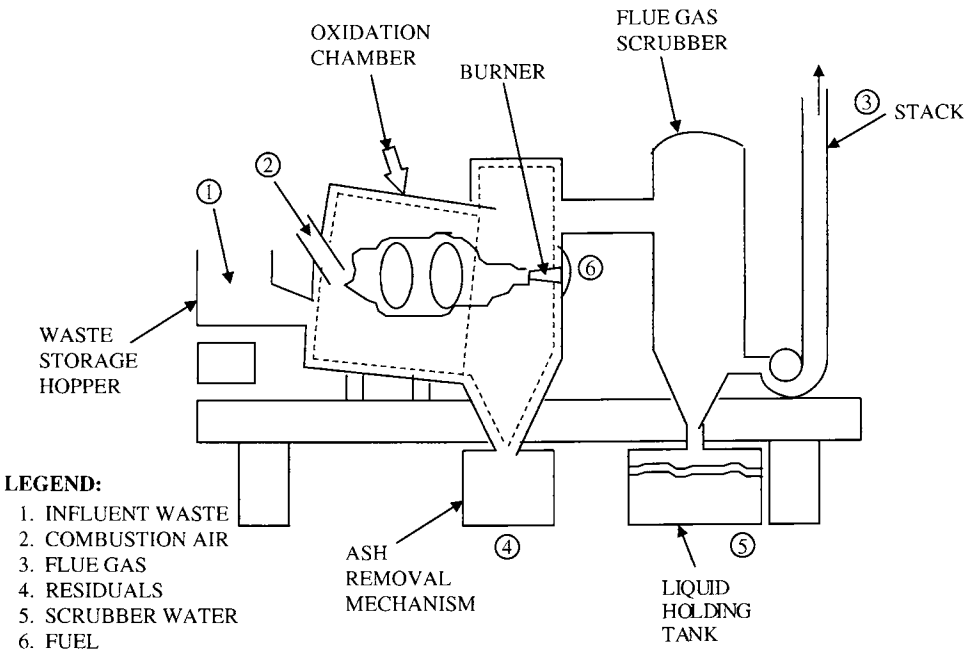


Figure VI.10.9. Schematics of a rotary kiln incineration device.

VI.10.2.7. Immobilization

Immobilization, or more commonly S/S is a technique to immobilize hazardous contaminants within a matrix (e.g. soil, sand, glasses, building materials). Immobilization can be achieved by physical, chemical or thermal means. Contaminants are physically bound or enclosed within a solid mass of high compressive strength and low permeability (solidification); or immobilized via chemical reactions between the contaminants and stabilizing agents (stabilization). The major factors contributing to the success of a good S/S application include: (i) pH, (ii) redox potential, (iii) permeability, (iv) diffusion coefficients, (v) solubility characteristics and (vi) chemical interactions between the wastes and the binding agents. A criterion used for measuring the success of S/S is leachability testing. S/S techniques can be used alone or in conjunction with other treatment and disposal methods to yield a product for some beneficial use. This technology is typically used for inorganics and has limited effectiveness in the case of SVOCs and pesticides. Some S/S processes cause large increases, up to 100%, in the volume of the waste matrix. VOCs do not respond favorably to S/S technology. S/S methods can be categorized as follows:

- *Cement-based solidification*: The waste is directly mixed with Portland cement and incorporated into the hard cement matrix. The bonds may be physical or chemical. Over a period of time, with erosion, physical bonds may weaken, causing the leaching of contaminants. Metals are good candidates for this process, because they form insoluble

hydroxides or carbonates. However, the insolubility is highly pH dependent, and even a slightly acidic condition could cause solubility to increase, resulting in the leaching of metals. A major disadvantage of this process is that the cement–waste matrix often weighs twice as much and occupies twice as much volume as the waste itself, making it more expensive for transportation. Certain wastes (organics, some salts of Na, Mg, Sn, Cu, Pb and Zn) can cause problems with the setting, curing or stability process of cement, and are not suitable for cement-based solidification.

- *Silicate-based solidification*: These processes use siliceous material along with additives, such as lime, cement, gypsum and other settling agents. Silicate material reacts with polyvalent metal ions, and the technique is applicable to a wide range of metals and organics (waste oils and solvents). The silicate material is fly ash, blast furnace slag or soluble silicates of Na or K.
- *Thermoplastic solidification*: The waste is dried, heated and incorporated in a heated plastic matrix. The mixture is then cooled to a rigid, deformable solid. Compared to cement solidification, the rates of leaching and increase in weight and volume are significantly lower. The effects of water and microbial attack are not present. Major disadvantages include high energy usage, high equipment and processing costs, and the need for specialty equipment and highly trained labor. Some wastes are not compatible with thermoplastic solidification. They include oxidizers such as perchlorates or nitrates, which can react with the solidification materials to cause an explosion, and some solvents and greases can cause asphalt materials to soften and never become rigid.
- *Encapsulation*: Waste material is mixed and churned with polymeric materials, physically encapsulating waste by sealing them in an organic binder or resin. An advantage of this approach is that the waste is completely isolated from leaching solutions. Depending on the size of the resulting particles, these are called, micro-encapsulated or macro-encapsulated. Organic as well as inorganic wastes can be encapsulated. Some disadvantages of the process include high cost, skilled labor needs and high energy requirements.
- *Vitrification*: Wastes are combined with molten glass at temperatures above 1350°C, and the melt is then cooled into a stable, non-crystalline solid. This can be a very expensive process and therefore limited to the worst wastes – radioactive and highly toxic.

VI.10.2.8. Site remediation

Hazardous waste site remediation can be very complex and involves treatment of contaminants in various media. These media include groundwater or aqueous phase, soil, gaseous phase in the unsaturated zone and immiscible phase. For instance, VOCs can dissolve in groundwater in both saturated zone and unsaturated zone, and exist as soluble organic contaminants up to their solubility limits. VOCs can also adsorb as liquid, on the soil particles in both saturated and unsaturated zones. In the unsaturated zone, VOCs can also exist as vapors at concentrations which are dependent on the Henry's law coefficient and the vapor pressure of the particular VOC. Additionally, due to the capillary action in the porous media of the unsaturated zone and the up and down movement of the water table, organic contaminants can exist as isolated blobs or globules in the pore space, and

not as a continuous phase. In this form, organic phase exists as non-aqueous phase liquids (NAPLs). If the organic phase has a specific gravity greater than unity (denser than water), it is known as DNAPL, and conversely, if it is lighter than water, it is called LNAPL. Once they are released from the interfacial forces of soil pores, NAPLs move downwards toward the groundwater or aquifers. NAPLs dissolve in water up to the solubility limit and the excess DNAPLs sink to the bottom while LNAPLs float on the surface. These "sinker" DNAPLs and "floater" LNAPLs stay in the water and cause a long-term continuous source of contamination in the groundwater. Continuous leaching or desorption of organics from the soil particles and dissolution of DNAPLs and LNAPLs in the groundwater cause most "pump and treat" techniques for groundwater to fail and/or require years of continuous or intermittent action. Inorganics and SVOCs may not exist in the vapor phase to the same extent as VOCs.

An overview of various options in media, mode, remedial action and types of contaminants encountered at a hazardous waste site is presented in Figure VI.10.10.

VI.10.2.9. Permitting – treatment goals and criteria

There are goals and criteria that determine the selection of a treatment technology for a particular application. The basic question one must ask is "how clean is clean". The answer may vary depending on the perspective of the stakeholder – principal responsible parties (PRPs) for cleanup, regulators, community and other interested parties such as insurance companies, banks and environmental organizations. For a typical CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act, commonly

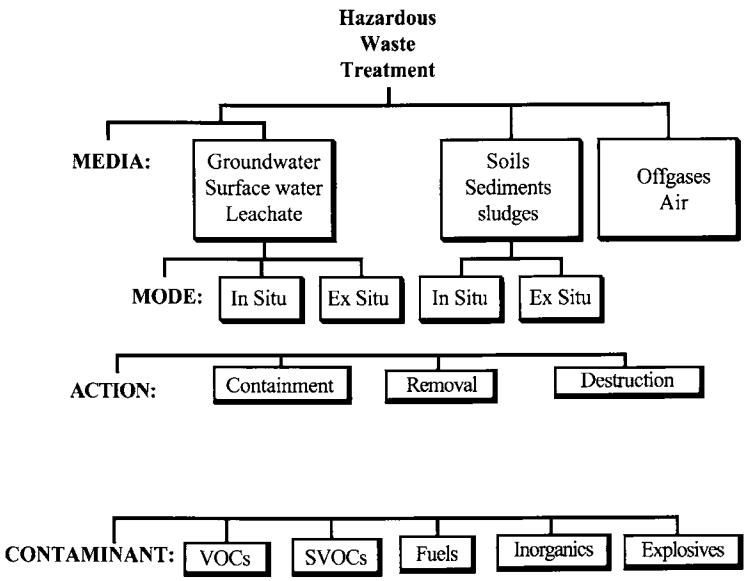


Figure VI.10.10. Hazardous waste treatment: an overview of mode and kind of remedial action and types of contaminants encountered at a hazardous waste site in different media.

known as Superfund), site remediation process, a Preliminary Assessment/Site Investigation (PA/SI) is undertaken to identify areas needing further investigation. A subsequent Remedial Investigation/Feasibility Study (RI/FS) is carried out to determine the nature and extent of contamination, and evaluate and select a remedy. After negotiations, based on technical and economic feasibility, and other factors, permits are issued and Record of Decision (ROD) signed between the PRPs and the regulating agencies for cleanup of the contaminated media. A Remedial Design/Remedial Action (RD/RA) is instituted to design and implement the chosen remedy. A similar corrective action process for RCRA (Resource Conservation and Recovery Act) facilities also exists.

EPA's general operating requirements for the treatment technique and units require that they must be located, designed, constructed, operated, maintained and closed in a manner that will ensure protection of human health and the environment. Conditions must be included for appropriate design and operating requirements, detection and monitoring requirements and requirements for responses to release of hazardous waste or constituents from the unit. To meet the performance standards, the principal hazardous substance migration pathways (groundwater, surface water, wetlands, air and soil) must be protected.

Factors for the protection of groundwater and subsurface pathways:

1. Physical and chemical characteristics, and volume of the waste.
2. Patterns for land use in the region.
3. Hydrogeological characteristics of the site.
4. Potential for damage to food-chain crops, wildlife, vegetation, physical structures and domestic animals.

Factors for the protection of surface water, wetlands and surface soil pathways:

1. Physical and chemical characteristics, and volume of the waste.
2. Existing quality of surface water and soil.
3. Current and potential surface water and land use in the nearby area.
4. Hydrology and surrounding topography of the site.
5. Proximity to surface water.
6. Operating characteristics, and effectiveness and reliability of systems and structures that contain, confine and collect migrating substances.
7. Potential for damage to food-chain crops, wildlife, vegetation, physical structures and domestic animals.

Factors for the protection of the air pathway:

1. Physical and chemical characteristics, and volume of the waste, including its potential to emit gases, aerosols and particulates.
2. Existing quality of air.
3. Atmospheric, meteorological and topographic characteristics of the surrounding area.
4. Operating characteristics including the effectiveness and reliability of systems and structures to reduce or prevent emissions of hazardous wastes or constituents to the air.
5. Potential for damage to food-chain crops, wildlife, vegetation, physical structures and domestic animals.

VI.10.2.10. Mode of treatment

Hazardous waste site remediation can be attempted either *in situ* (in place, without excavation) or *ex situ*. The mode of treatment is very site specific and depends on the site characteristics and the extent of contamination, contaminant type and concentrations, level of cleanup desired and future use, treatment technology and costs.

VI.10.2.10.1. In situ treatment

The main advantage of *in situ* treatment is that it can save the time, effort and money required for excavation and transport of soil both before and after treatment. Additional expense of site reparation is also avoided in the *in situ* treatment. The negative side of this treatment mode is that it generally requires longer time periods than *ex situ* treatment. Because of the variability in the soil and aquifer characteristics, and development of preferential fluid flow, the treatment is non-uniform and pockets of high contaminant concentration may remain in the subsurface soil.

Physical/chemical separation techniques use the physical or chemical properties of the soil-contaminant–aquifer system, such as volatility in the soil vapor extraction (SVE) or solubility in the soil washing/flushing operations. Physical operations combined with chemical reactions or biological degradation may also be used to enhance the contaminant destruction by either increasing the reaction rates (chemical) or making the contaminant more bioavailable (biological), as in surfactant-enhanced bioremediation applications.

In the case of *in situ* biological processes, organic contaminants are either targeted directly for biological treatment or mobilized to groundwater or collection wells for *in situ* treatment. In some cases, groundwater may be extracted aboveground and treated on-site.

To provide an aerobic environment, oxygen concentration in the soil can be increased by injecting air or hydrogen peroxide. Care must be taken to avoid saturating the soil with water (thus inhibit the movement of oxygen through the soil), compaction of the soil (thus lowering the mass transfer rates) and diluting the contaminant (thus decreasing the rate of biodegradation). The use of hydrogen peroxide is limited, because at concentrations above 100 ppm, it can be toxic to microorganisms. Anaerobic conditions, which are prevalent in the subsurface soil, are amenable, although at a very slow rate, to degrade highly chlorinated contaminants such as PCBs. This can be followed by the aerobic treatment to complete biodegradation of the partially degraded compounds.

Nutrients, especially nitrogen and phosphorus, are likely to be deficient in the contaminated environment, and can be added in a useable form (as ammonium and phosphate). Care must be taken as phosphates can react with soil minerals, iron and calcium, and form stable precipitates that can cause soil plugging. Temperature and pH can affect the biological activity and must be maintained at certain values, depending on the microorganisms, contaminants and site characteristics. Temperature can be increased in colder climates by warm air injection to maintain microbial activity at a high level, but the technology is in experimental stages. On the other hand, too high a temperature can be detrimental to the microorganisms and may increase the volatility of contaminants. Alkaline conditions ($pH > 7$) are generally more favorable to microbial activity than acidic conditions ($pH < 7$). Many metals that are potentially toxic to microorganisms are

generally insoluble at high pH values. Therefore, generally a higher pH value would favor an increased degradation.

Sometimes, indigenous microorganisms collected from the contaminated targeted site, or other similar microorganisms, are cultured and grown for the degradation of specific contaminants, or for survival under unusually severe environmental conditions. Addition of these microbial cultures to the contaminated site is known as bioaugmentation. In some cases, the contaminants cannot be utilized directly by the microorganisms for growth or energy, without the presence of a specific enzyme. In some of those cases, a primary substrate is used to produce that enzyme, which aids the subsequent utilization of the contaminant (secondary substrate) by the microorganisms for energy. An example of a co-metabolic process is the aerobic biodegradation of TCE in the presence of methane or gasoline constituents as co-substrates.

Bioventing is another biological technique for *in situ* soil remediation that achieves the biodegradation of VOCs and adsorbed fuel residuals, by providing oxygen via low air flow rates, just enough to sustain microbial activity. Saturated soils, especially in the vicinity of water table or low permeability soils may limit bioventing performance.

In situ application of a solidification technique can be achieved via thermally enhanced SVE or vitrification, which uses electrically generated heat to melt the soil. The vitrification process destroys some organics by oxidation due to extremely high temperatures (1300–2000°C) and encapsulates inorganics in the vitrified glass and crystalline mass.

Solidification/stabilization processes use both physical and chemical changes by encapsulating the contaminant (solidification), or altering or binding (stabilization) with the contaminant.

VI.10.2.10.2. Ex situ treatment

The advantages of *ex situ* process are that the contaminated media (soil, sediments and groundwater) can be thoroughly mixed and homogenized for more uniform treatment, degradation rates are higher and therefore it takes less time for remediation than *in situ* treatment. The major disadvantage is that there are a number of problems associated with the excavation of soil, such as, increased cost, additional equipment, material handling, worker exposure, extra permitting and space considerations. *Ex situ* treatment can be carried out on- or off-site. Off-site treatment further adds transportation costs for contaminated and fill soils, and has the potential to expose a larger population.

The treatment techniques for *ex situ* processing are less limited than *in situ* processing. Additionally, the delivery of chemicals and materials to the contaminated medium is much easier, and can be better targeted than for *in situ* treatment. Operating conditions, such as temperature, pH, mixing, oxygen level, nutrients, chemical additives, binders, surfactants and other parameters can also be optimally controlled in *ex situ* situations.

Treatment technologies for *ex situ* remediation of hazardous wastes include soil washing, solvent extraction, SVE, redox reactions, dehalogenation, biodegradation, composing, landfarming, solid and slurry phase biological treatment, thermal desorption, incineration, pyrolysis and vitrification.

In *ex situ* thermal treatment, waste gases, ash and slag may be generated during the destruction process, which may require additional disposal/treatment.

VI.10.3. Decision steps in technology selection

Selecting corrective measures objectively is a challenge for several reasons. The individual evaluator is usually biased toward one or a group of technologies with which he/she has had experience. Personal experience often generates more confidence than a broader experience would justify. Similarly, a more conventional technology such as landfill or incineration, usually exhibits more background experience and operational data and information, than a newer technology. On the other hand, there may be "pressure" to select alternative or innovative technologies over more conventional applications on the basis that "newer is better", or that conventional technology is flawed to the extent of "having brought us to where we are now". In certain cases, innovative technology may, in fact, be more suitable and/or more cost effective but design may be more uncertain because of lack of data.

This section is meant therefore, to provide guidelines for selecting any technology, but because of the information offered, to provide additional assurance for selecting emerging technology for application to site remediation. A series of decision steps are provided to serve as a basis for a regularized approach to selection of appropriate technology for application at a given site. The eight decision steps are as follows (Williams et al., 1992):

1. Identify contaminants present in each medium.
2. Identify candidate technologies.
3. Screen candidates by evaluating the probable effect(s) of application on target contaminants.
4. Estimate effect on non-target contaminants of technically acceptable candidate technologies.
5. Repeat steps 1–4 until each contaminated medium is assessed and all contaminants are addressed in each medium.
6. Compare acceptable processes for similar treatment steps applied to different media.
7. Compare all acceptable treatment process concepts.
8. Select corrective measure(s) for implementation.

A discussion of each of the steps is given below.

1. *Identify contaminants present in each medium.* Often there appear to be too many compounds represented in each medium to allow a reasonable analysis to proceed. Several contaminants may be selected from the full array on the basis of toxicity, mobility and amount present, and listed in the category of "target contaminants". It may be useful to categorize contaminants into "families", representatives of each of those that may be used to evaluate potential technology applicability. The three criteria, toxicity, mobility and amount must be jointly considered and care must be taken to avoid selecting contaminants on the basis of a single criterion, such as amount present or concentration. Toxicity of individual compounds may vary by orders of magnitude. Thus, contaminants present in low concentrations may be included in the preliminary array of high priority compounds on which decisions are based.

2. *Identify candidate technologies.* Table VI.10.2 is provided to guide the collection of contaminant and site related data. During early site investigations and feasibility studies in the United States, the tendency was to gather all possible data on the contaminants and the site. This resulted in significant expenditures for collection of data and information that

Table VI.10.2. Data needed for different technologies.

Data needed	Containment	Volatility separation	Soil flush/ soil wash	Density separation	Adsorption	Phase separation	Size separation	Biological oxidation	Chemical oxidation	Thermal destruction	Biological reduction	Chemical reduction	Vitrification	Chemical immobilization
Contaminant characteristics														
Topography	•													
Weather (monthly average and annual extremes)														
Precipitation	•		•					•	•		•	•	•	
Temperature	•							•			•			
Wind rose										•				
Soil, infiltration rate	•		•					•	•		•	•		
Subsurface profiles														
Stratigraphy	•	•	•					•	•			•	•	
Groundwater potentiometry	•	•	•					•	•			•	•	
Water table annual variability	•	•											•	
Groundwater velocity and direction	•		•					•	•		•	•	•	
Depth to aquitard	•	•									•		•	
Soil physical and chemical characteristics														
Hydraulic permeability	•	•	•					•	•		•	•		
Steam permeability		•	•											
Gas permeability	•	•											•	
Porosity	•	•	•					•	•		•	•	•	
Hydraulic conductivity	•												•	
pH								•	•		•	•	•	
Organic carbon content		•	•					•	•		•	•	•	
Ion exchange capacity			•						•			•		
Nutrient content								•			•			
Iron and manganese		•			•			•	•		•	•	•	
Soil particle size distribution			•				•	•	•	•	•	•	•	
Presence of debris	•	•	•				•	•	•	•	•	•	•	

Contaminant profile	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Contaminant isopleth (major contaminants)	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Physical chemical constants for each target														
Water solubility		•	•	•	•			•	•		•	•		•
Vapor pressure		•				•							•	•
Boiling point		•								•			•	•
Density				•		•				•				•
Viscosity (liquids)				•					•	•				•
Henry's coefficient		•	•	•									•	
K_{ow}			•	•	•									
K_{oc}			•	•	•									
Biorefractory index								•						
Heat content									•	•			•	
Ignition temperature		•								•			•	
Measured characteristics														
BOD5								•			•			
COD								•	•		•	•		
TOC								•	•		•	•		
Biodegradation rate								•			•			
Freundlich isotherms					•								•	•
Particle size distribution							•						•	•

were often not needed to guide the performance of remediation actions. On the other hand, the dilemma associated with the amount and scope of data collection is not easily resolved at many sites because the selection of possible technologies is intimately tied to the contaminants present and their form(s). If the general character of the contaminants present is known, then Table VI.10.2 is useful in limiting the scope of data collection.

The contaminant-related selection criteria for technologies include: organic/inorganic contaminants or both; media or phase(s) in which contaminants are present; solid, liquid, gas; a real extent of the contamination; "as-found" matrix in the field, i.e. the chemical and physical context in which the waste is found at a given site. Perhaps the most important set of criteria related to the contaminants are the cleanup objectives.

Cleanup objectives are numerical values for the required maximum concentration(s) of contaminants remaining in the treated media after full implementation of the remediation strategy. These values comprise the end point of the system effectiveness, but may be considered as the beginning step for the system component selection. The final treatment process in the system array must be capable of achieving the stated cleanup objective(s) as an output. Similarly, the next-to-last process must be capable of achieving as output, the required input for the final process. The selection process proceeds *backwards* to the point where the whole system can accept both the site contamination levels and the media involved (also refer to Step 6).

3. *Screen candidates by evaluating the probable effect(s) of application on target contaminants.* After the contaminants have been grouped into chemical families, Table VI.10.3 may be used as a first cut to screen technologies for potential applicability. This screening step may be based on rejection rather than potential applicability (i.e. by rejecting those which potentially fail). At the screening step, technologies should be kept in the analysis as long as possible rather than eliminated if applicability is questionable. Eliminating technologies too soon in the analysis may negatively impact the effectiveness of cleanup actions. Other than those with an open circle in Table VI.10.3, the technologies may have applicability.

Alternatively, carrying processes through the analysis that have limited applicability may expand the analysis unnecessarily. For example, S/S does not work well on organic compounds (especially volatiles) unless special steps are taken, such as using specially treated clays or chemical additives, and/or pretreatment. Therefore, S/S should not be used in situations that contain largely organic contamination. Treatability studies will almost certainly be required for applications showing a diamond shape ("potential effectiveness") in Table VI.10.3. Treatability studies may even be required for those applications showing a filled square ("demonstrated effectiveness") in Table VI.10.3. Biological treatment applications will probably require treatability studies in all cases. A complete assessment of removal and/or destruction effectiveness is given by Martin and Johnson (1987). The procedure, though developed long ago, is still valid nowadays.

The chief basis of the analysis in Step 3 is treatability. Considerable data are available about treatability but often not specifically relevant to the "as-found" matrix at a given site. Therefore, criteria for screening should be developed and used for the analysis. Treatability consists of many subcategories of more specific "-ability" characteristics, some of which are discussed below.

Biodegradability is clearly important for applicability of biological processes. "Biodegradability" can often be an amorphous term when applied to specific cases.

Table VI.10.3. Selection matrix for hazardous – solid waste technologies.

Contaminant	Technology																
	Fluidized bed incineration	Rotary kiln incineration	Infrared thermal treatment	Pyrolysis–incineration	Vitrification	Chemical extraction	*In situ* chemical treatment	Soil washing	*In situ* soil flushing	Dechlorination	Low temperature thermal stripping	*In situ* vacuum stream extraction	Stabilization/solidification	*In situ* vitrification	Biodegradation	*In situ* biodegradation	Other
Organic																	
Halogenated volatiles	◆	■	■	◆	◆	◆	○	◆	◆	◆	◆	■	○	○	◆	◆	
Halogenated semivolatiles	◆	■	■	◆	◆	◆	○	◆	◆	◆	◆	■	◆	◆	◆	◆	
Non-halogenated volatiles	◆	■	■	◆	◆	◆	○	◆	◆	○	◆	■	○	○	◆	◆	
Non-halogenated semivolatiles	◆	■	■	◆	◆	◆	○	◆	◆	○	◆	■	◆	◆	◆	◆	
PCBs	◆	■	■	◆	◆	◆	○	◆	◆	◆	○	■	◆	◆	◆	◆	
Pesticides	◆	■	◆	◆	◆	◆	○	◆	◆	◆	○	◆	◆	◆	◆	◆	
Organic cyanides	◆	■	◆	◆	◆	◆	◆	◆	○	○	○		◆	◆	◆	◆	
Organic corrosives	◆	■	◆	◆	◆	◆	◆	◆	◆	○	○	○	◆	◆	×	×	
Inorganic																	
Volatile metals	◆	◆	◆	○	×	◆	◆	◆	◆	○	◆	◆	■	○	×	×	
Non-volatile metals	◆	◆	◆	○	◆	◆	◆	◆	◆	○	○	○	■	◆	×	×	
Asbestos	○	○	○	◆	■	○	○	○	○	○	○	○	■	◆	×	×	
Radioactive materials	○	○	○	○	■	◆	◆	◆	◆	○	○	○	■	◆	×	×	
Inorganic corrosives	○	○	○	◆	◆	◆	◆	◆	◆	○	○	○	■	◆	×	×	
Inorganic cyanides	◆	◆	◆	◆	◆	◆	◆	◆	○	○	○	○	■	◆	×	×	
Reactive																	
Oxidizers	■	■	■	■	◆	◆	◆	◆	◆	○	○	○	◆	◆	×	×	
Reducers	■	■	■	■	◆	◆	◆	◆	◆	○	○	○	◆	◆	×	×	

Demonstrated effectiveness ■; Potential effectiveness ◆; No effectiveness ○; Potential adverse impacts to the process ×.

There are, however, much data on the use of biological processes for removal of toxic and hazardous compounds. For example, for most organic compounds, significantly high (>90%) removability data can be found for wastewaters. Similarly, most metals in the compound state(s) found in municipal wastewaters are removable by biological processes (Martin and Johnson, 1987), again to a significant extent (often between 50 and 90%; sometimes even higher removals are possible).

Special considerations may be necessary for certain screening evaluations. For example, strippability and solubility can have variable definitions. Strippability has been defined as compounds having a Henry's law coefficient $H_L > 3 \times 10^{-3}$ atm m^3/mol at 20°C. Henry's law coefficients, however, are often difficult to find, although software is now common for determining values. Acceptable values for solubility may vary depending on the treatment strategy; a solubility cutoff value for carbon adsorption may be different from one applicable to soil washing (depending on the solvent). One definition may be, solubility in water at 20°C > 200 mg/l. In this case, 200 mg/l is felt to be a reasonable cutoff for the treatment strategy being considered. Octanol–water partition coefficient (K_{ow}) values $>10^4$ may be considered a good range for high efficiency depending on the solvent being used.

4. *Estimate effect on non-target contaminants of technically acceptable candidate technologies.* Some strategies for remedial investigations and site evaluations suggest that a short list of compounds representing the most ubiquitous, most toxic or hazardous, and those present in the greatest quantities be developed and used for the screening evaluations. Some of the compounds not being carried completely through the evaluation process may not be efficiently removed and/or managed by the selected strategies. Indeed, some compounds may have negative impacts on the treatment process(es) being considered. Table VI.10.3 contains information on "no effectiveness" and "potential adverse impacts on the process".

At this point in the analysis, it is necessary to revisit compounds that may not have been included in the short list array. Sometimes the list can be quite extensive but it is necessary to determine potential adverse impacts on the treatment strategy. Two examples are: volatile organic compounds are likely to escape during *in situ* vitrification and thus may not be effectively controlled; corrosives (both high and low pH) will probably be deleterious in a biodegradation strategy (see Table VI.10.3).

5. *Repeat steps 1–4 until each contaminated medium is assessed and all contaminants are addressed in each medium.*

6. *Compare acceptable processes for similar treatment steps applied to different media.* The approaches to different media may be combined when appropriate to build multimedia treatment trains.

Technologies that may be included in a corrective measure fall into three categories: separation technologies, detoxification–destruction technologies and immobilization technologies. Treatment processes that achieve removal but not destruction will generally require additional management and may be implemented in a separate system. Thus, both separation and detox–destruct technologies may be required in the same system.

General considerations for media are presented in Tables VI.10.4–VI.10.7. Table VI.10.4 presents *in situ* strategies for various major contaminant families and Tables VI.10.5–VI.10.7 do the same for *ex situ* strategies.

Table VI.10.4. Technologies and suitability for *in situ* application.

Technology	Chemical families potentially treatable
Technologies for *in situ* application in the vadose zone	
Air stripping	All volatile and semivolatile organics
Steam stripping	All volatile and semivolatile organics
Vacuum extraction	All volatile and semivolatile organics
Soil flushing	All water-soluble organics and inorganic salts
Radio frequency heating	Simple aromatics, paraffins, olefins and PAHs
Biological oxidation	Many organics and some inorganics
Chemical oxidation	Most organics and some inorganics to a degree
Dechlorination	Haloaromatics and persistent pesticides
Solidification (injected cement)	Inorganics
Vitrification	Inorganics and up to 10% organics
Excavation	All contaminants
Technologies for *in situ* application in saturated soils	
Air stripping	All volatile and semivolatile organics
Soil flushing	All water-soluble contaminants
Radio frequency heating	Simple aromatics, paraffins, olefins and PAHs
Biological oxidation	Many organics and some inorganics
Chemical oxidation	Most organics and some inorganics to a degree
Solidification (injected cement)	Inorganics
Technologies for *in situ* application in groundwater	
Biological oxidation	Many organics and some inorganics
Steam stripping	All volatiles
Radio frequency heating	Simple aromatics, paraffins, olefins and PAHs
Chemical oxidation	Most organics and some inorganics
Pumping	All contaminants
Technologies for application to surface water and sludges (*in situ*)	
Biological oxidation	Many organics and some inorganics
Air stripping	All volatiles
Steam stripping	All volatiles
Chemical oxidation	Most organics and some inorganics
Pumping	All contaminants
Dredging	All contaminants

It is desirable to combine treatment process applications where possible, e.g. treating sludge residue from a liquid process sequence along with contaminated soil in the same process(es), if both sludge and soil contain similar or the same contaminants.

Every treatment process will generate a residue; sludge, brine, ash, dust, etc. All but the simplest treatment systems will therefore likely generate an array of residues, which considered as a group, will provide combination treatment possibilities. Comparison

Table VI.10.5. Separation technologies and suitability for *ex situ* application.

Technology	Chemical families potentially treatable
Separation technologies for use in contaminated waters	
Air stripping	All volatile organics
Steam stripping	Volatile and semivolatile organics
Distillation	All organics
Solvent extraction	All organics soluble in the selected solvent
Centrifugation/sedimentation	All insoluble contaminants with densities different from water
Dissolved air flotation	All insoluble contaminants with densities less than water
Carbon adsorption	All insoluble contaminants and many non-volatile, soluble organics
Oil/water separation	All insoluble organics with densities different from water
Ion exchange	Most metals and exchangeable anions
Precipitation/pH adjustment	Most metals
Freezing	Most organics and inorganics
Separation technologies for use in excavated soils	
Air stripping	All volatile contaminants
Soil washing	All contaminants soluble in the selected solvent
Solvent extraction	All organics soluble in the selected solvent
Low temperature thermal desorption	All organics
Separation technologies for use in aboveground sludge streams	
Oil sludge separation – acid cracking	All insoluble organics with densities different than water
Air stripping	All volatile organics
Soil washing	All contaminants soluble in the selected solvent
Solvent extraction	All organics soluble in the selected solvent
Sedimentation	All insoluble contaminants with densities different than water
Filtration	All insoluble contaminants
Dissolved air flotation	All insoluble contaminants with densities less than water
Precipitation/pH adjustment	Most metals
Ion exchange	Most metals and exchangeable anions
Separation technologies for use in air streams	
Condensation	All organics and volatile inorganics
Carbon adsorption	All insoluble contaminants and most non-volatile, soluble organics

Table VI.10.6. Detoxification/destruction technologies and suitability for *ex situ* application.

Technology	Chemical families potentially treatable
Chemical oxidation	Sludges and aboveground waters
Biological oxidation	Excavated soils, sludges and aboveground waters
Catalyzed chemical oxidation	Sludges and aboveground waters
Incineration	Sludges, excavated soils and sludges
Chemical reduction	Aboveground waters, sludges and excavated soils
Catalyzed chemical reduction	Aboveground waters, excavated soils and sludges
Anaerobic bio-reduction	Aboveground waters and sludges

criteria for this step will therefore include treatment combinations that make best use of treatment process applications to mixed media, e.g. soils and sludges.

7. *Compare all acceptable treatment process concepts.* The basis for comparison may include many factors but at least the following should be addressed: (1) the cleanup level achieved compared to cleanup objectives, (2) elapsed time to complete the remediation, (3) cost of remediation and (4) short- and long-term effectiveness.

Comparisons should be drawn only among carefully selected systems that achieve the same or similar outputs. For example, a landfill achieves storage of organic contaminants while incineration is a destruction process for organics. Direct comparisons between these two technologies are often made and are usually inappropriate. It is important to consider all four of the factors listed above, *together*. A joint comparison of the factors will require, for example, matching achieved cleanup levels with cost. Thus, a choice of a less costly landfill will become more clearly unacceptable against incineration, when considering also cleanup levels and long-term effectiveness. A simple comparison of the two technologies for managing organics is given in Table VI.10.8.

8. *Select corrective measure(s) for implementation.* There often is an attempt made to reduce the number of selection criteria because of the difficulty of quantifying values of the various criteria. Shortening the list of selection criteria should be avoided.

Table VI.10.7. Immobilization technologies for use in corrective measures.

Technology	Contaminant streams potentially treatable
In situ vitrification	Vadose zones containing hazardous inorganics and $<5\%$ organics
Vitrification furnace	Soils and sludges containing hazardous inorganics and $<3\%$ organics
Cement Pozzolan immobilization	Metal bearing wastes (solids, liquids or sludges) with $<1\%$ organics
Lime-based immobilization	Waters containing dissolved heavy metals and $<1\%$ organics

Table VI.10.8. Example comparison of the two treatment process concepts for organic waste.

Treatment process	Cleanup level	Elapsed time	Cost	Effectiveness
Incineration	High	Same	Higher	Permanent
Landfill	Low or zero	Same	Lower	Landfill life

A rigorous selection analysis need not be based on quantifiable or quantified selection criteria. Therefore, the list of selection criteria should be made as long as needed in order to satisfy all parties involved in the process. Indeed, the selection will be more acceptable to all and therefore more implementable, the more extensive the list of criteria. The plus (+), zero (0), minus (−) approach has been used successfully in many cases to evaluate the overall impact of both quantifiable and non-quantifiable selection criteria. Table VI.10.9 was constructed using this approach for a simplistic landfill–incineration case. In many cases, it is unnecessary to provide any quantification. Usually, however, participants in the analysis will want to know costs.

Based on the analysis in the table alone, incineration should be chosen. Zeros (0) count neither plus nor minus in the summation, since the determination of a zero for a criterion suggests neither benefit nor deficit in the evaluation. The list may be extended to include other criteria, e.g. emission of combustion by-products in the case of incineration and cost of re-landfilling in the case of landfill, thus making the evaluation more complex.

VI.10.4. General economics

This section deals with the generalized costs of hazardous waste site remediation in the United States. A later section of this chapter presents costs for several processes for which experience provides more recent costs. Typical soil remediation projects involve excavation, treatment of processing waste streams, measurement and monitoring and site restoration. EPA's SITE (Superfund Innovative Technology Evaluation) Program evaluates and publishes Technology Evaluation and Applications Analysis Reports for new or innovative technologies, after they are being demonstrated in the field (see Chapter VI.11). These reports include economic analysis of the particular technique by breaking down the costs, typically, into 12 categories. The costs are site and contaminant specific,

Table VI.10.9. Example selection analysis of the treatment process using the plus (+), zero (0), minus (−) approach.

Treatment process	Cleanup level	Elapsed time	Cost	Effectiveness
Incineration	High	Same	Higher	Permanent
Landfill	Low or zero	Same	Lower	Landfill life

and can only provide general comparisons and guidance. However, the total cost based on these 12 cost categories can be widely applied for comparison of different remediation techniques for the same site, and help in the selection of the candidate technologies. The 12 cost categories are given below:

1. Site preparation costs
2. Permitting and regulatory costs
3. Equipment costs
4. Startup and fixed costs
5. Labor costs
6. Supply costs
7. Supply and consumables cost
8. Effluent treatment and disposal costs
9. Residuals and waste shipping, handling and transportation costs
10. Analytical costs
11. Facility modification, repair and replacement costs
12. Site demobilization costs.

These cost estimates are highly site dependent, and should be used with caution, only for qualitative comparisons. A summary of processes, their status and their estimated cost ($/ton) in 1994 are included in Table VI.10.10 to be used for the comparative analysis. The subject of current remediation economics is discussed in the following section.

VI.10.5. Detailed selection criteria and considerations

The contaminant destruction and removal strategies for groundwater and surface water, soil, and gas treatment are tabulated in detailed remediation technology selection matrices: Tables VI.10.11–VI.10.13. The tables list remediation strategy, media, remediation technology, conditions favorable and unfavorable and economic factors including unit cost ranges and major cost drivers.

Additional remarks are provided that are specific to particular contaminant technology applications.

VI.10.6. Costs of remediation technologies

A number of technologies have been developed and applied for hazardous waste management in the past few years (McCabe et al., 2001, see also Chapter VI.10). For these technologies, cost data have been determined based on the experience at the sites. This section contains recent available cost data for the following: bioremediation, thermal desorption, SVE, on-site incineration, groundwater pump and treat (P&T) systems, and permeable reactive barriers. A cost plot was not prepared for permeable reactive barriers because of the difficulty and uncertainty of determining the quantity treated by barriers placed within the underground context of the site being remediated. Therefore, unit costs could not be determined.

Table VI.10.10. Summary of some processes for hazardous waste site remediation (status and estimated costs in 1994).

Process	Status in 1994	Estimated cost ($/ton)
Chemical extraction		
CF Systems	Full-scale	80–450
BEST	Full-scale	75–175
Carver–Greenfield Process	Pilot-scale	100–220
Low-energy solvent extraction process (LEEP) Acurex	Pilot-scale	70–150
OHM Corp. Methanol Extraction Process	Field-tested	75–230
Soil washing		
OHM Corp. Soil Washing	Full-scale	50–125
BioGenesis Soil Cleaning Process	Full-scale	40–140
BioTrol Soil Washing System	Full-scale	100–125
Westinghouse Soil Washing System	Full-scale	150–250
Canonie Environmental Services Soil Washing	Full-scale	50–100
Bergmann USA Particle Separation Process	Full-scale	75–125
Divesco, Inc. SRS-10	Full-scale	50–65
Alternative Remedial Technologies, Inc. Soil Washing	Full-scale	85–225
Thermal extraction		
X* TRAX	Full-scale	100–200
Anaerobic Thermal Processor (ATP) or Taciuk Process	Full-scale	120–300
Williams Thermal Desorption System	Full-scale	125–250
Canonie Environmental Services LTTA System	Full-scale	60–150
Roy F. Weston, Inc. LT	Full-scale	100–150
Maxymillian Mobile Thermal Desorption	Full-scale	40–300
Westinghouse Thermal Desorption	Full-scale	150–300
Advanced Soil Technologies Thermal Desorption	Full-scale	35–150
Physical extraction		
Hydrocyclones	Full-scale	
Sedimentation	Full-scale	
Centrifugation	Full-scale	
Flocculation	Full-scale	
Oil/water separation	Full-scale	
Mechanical screening	Full-scale	
Chemical destruction		
SDTX KPEG Dechlorination	Full-scale	100–300
Base-catalyzed decomposition (dechlorination) process	Full-scale	150–250
G. E. M., Inc. Oxidation	Bench-scale	150–500

(*continued*)

Table VI.10.10. (Continued)

Process	Status in 1994	Estimated cost ($/ton)
Agent 313	Bench-scale	100–175
APEG Dechlorination	Full-scale	200–500
ETUS, Inc. TR-DETROX	Full-scale	20–50
Eco Logic Reduction	Full-scale	400–500
Radiant energy		
Light activated reduction of chemicals (LARC)	Pilot-scale	90
Perox-Pure	Full-scale	
Ultrox UV Radiation and Oxidation	Full-scale	
Laser-induced photochemical oxidative destruction (excimer laser)	Lab-scale	
Titanium Dioxide Photocatalytic Oxidation System/Nulite Technology	Bench-scale	
Photothermal detoxification unit (PDU)	Lab-scale	
Thermal destruction		
Eco Logic Thermal Gas Phase Reduction Process	Full-scale	300–400
Molten salt oxidation (MSO) process	Pilot-scale	
Biological destruction		
Cognis Bioremediation Technology	Full-scale	40–80
Envirogen	Full-scale	40–170
BIOFAST	Full-scale	35–75
Petroclean Bioremediation System	Full-scale	25–50
Remediation Technologies, Inc.	Full-scale	15–100
Earthfax Engineering, Inc.	Pilot-scale	200
CNP-PLUS	Full-scale	15–30
Solidification		
Geo-Con, Inc. Solidification Process	Full-scale	30–100
Wastech, Inc. Solidification Process	Full-scale	70–250
Advanced Remediation Mixing, Inc.	Full-scale	35–100

The selection of these six technologies by site cleanup managers is a major indication of the status of the technologies for application at other sites. Even in those cases referred to as "demonstration scale" in the reference material, the applications are at sufficiently large scale to set these apart from technologies mentioned earlier in this chapter for which smaller scale data are available. In previous sections, a wide array of technologies, indeed almost the full assortment has been presented along with generalized descriptive and cost information in order to provide a platform for a full technical assessment of possibilities.

Cost data were obtained from US federal agency sources, including case studies and reports prepared by the Federal Remediation Technologies Roundtable (FRTR), the US

Table VI.10.11. Remediation technology selection matrix I.

Remediation strategy	Media	Remediation technology	Conditions favorable to use	Conditions unfavorable to use	Unit cost range (US $)	Major cost drivers	Additional comments
• A strategy should be developed prior to technology selection • A strategy may include any combination of these options • No containment measure should be considered permanent • Removal and destruction are often used together	• Each medium affected by a completed risk exposure pathway should be remediated • The majority of contaminant mass is likely to be located in soil • Groundwater remediation should be coordinated with source remediation in the unsaturated zone	These technologies may be considered to be proven technologies: innovative technologies are not included Technology selection can be guided by performance of nearby remediation projects at similar sites. IRPIMS may be used to locate sites having similar media stratigraphy and contaminants concern	• These generalizations are based on projects demonstrating acceptable performance and cost effectiveness: they are not presented as rigid guidelines because each project needs to be evaluated individually	• These generalizations are based on projects demonstrating acceptable performance and cost effectiveness: they are not presented as rigid guidelines because each project needs to be evaluated individually	• These costs are typical of successful projects conducted by the Air Force and private industry • These costs may be used for budget planning and as a rough check of contractor proposals • These costs are typical of those charged by companies specialized in each technology • A useful measure of merit for evaluating costs is to compute the project cost per pound of contaminant – Cost effective projects typically run < $200/lb – Projects where the costs are orders of magnitude higher	• Reviews of project cost estimates can focus on these areas to expedite the reviews • Regulatory requirements for monitoring and preparing project documentation can be major cost drivers for any project, and they are not addressed in this guide because of the wide range of variability in regulatory requirements among state and local agencies	• These comments and performance estimates are provided as helpful hints and observations based on successful projects
Contaminant	Groundwater	Groundwater pumping	Receptors actually or immediately at risk	Active source of contamination remains because soil and free product sources not isolated or removed such as pooled DNAPLs in the saturated zone	$40–$80/ft of well for installation $4000–$9000/well for pumping system Water treatment systems costed below	Power Effluent treatment (options listed below)	Not a cost-effective method for remediating contaminant mass
		Solidification	Inorganic contaminants present Non-volatile organics < 1%	Volatile organic present High-clay soils High debris content	$30–$150/ton of soil treated (*ex situ*) $60–$200/ton of soil treated (*in situ*)	Reagents and transportation materials handling (large volume increase)	Site-specific treatablilty testing mandatory Very long-term stability difficult to predict

		Stabilization	Inorganic contaminants present Non-volatile organics < 1%	Volatile organic present High-clay soils High debris content	$30–$150/ton of soil treated	Reagents and transportation materials handling	Site-specific treatablilty testing mandatory Very long-term stability difficult to predict
		Asphalt blending ("soil recycling")	Petroleum product contamination	Volatile organic present High-clay soils High debris content Halogenated organic present	$55–$100/ton of soil treated	Feed material preparation (crushing, screening, aggregate addition)	
Contaminant		Slurry walls Sheet piling HDPE walls	Groundwater levels < 20 ft Receptors imminently at risk Availability of aquitard within 40 ft of ground surface to anchor walls	Corrosive contaminants and strong electrolytes High expensive soils High climate moisture variation (extreme wet–dry cycles) Complex terrain	$7–$10/sq. ft of wall	Trenching depth Soil additives (cements, aggregate)	Site-specific compatibility testing recommended Wall may degrade over time
	Soil	Capping	Rainfall > 10 in./year Large contaminated soil volume Relatively low hazard Use as an interim measure	Presence of material that will settle in landfill Dry climates	$25–$30/sq. yd for RCRA cap $10–$15/sq. yd for clay cap	Long-term monitoring and maintenance requirements Regulatory specifications for cap construction Gas collection and treatment	Construction quality assurance to ensure low conductivity of the cap is critical Gas collector may be necessary Cap can enhance soil vapor extraction efficiency
		Off-site landfilling	Quick remediation required	Concern about long-term liability	$200–$500/ton tipping fee $0.40–$0.90/ton-mile for transportation	Disposal fee Transportation	Costs provided for hazardous material landfilling
		Dust control	Short-term control of exposure pathway Dry climate	High soil moisture content	$0.02–$0.04/sq. ft for sending or one chemical spray application $0.30–$0.40/sq. ft for one foam application $0.25–$0.60/sq. ft for synthetic cover	Labor	Foam application and synthetic cover can also inhibit contaminant volatilization

Note: US units used: 1 in. = 2.54 cm; 1 ft = 0.3048 m; 1 sq. ft = 0.0929 m^2; 1 sq. yd = 0.8361 m^2; 1 lb = 0.45359 kg.

Table VI.10.12. Remediation technology selection matrix II.

Remediation strategy	Media	Remediation technology	Conditions favorable to use	Conditions unfavorable to use	Unit cost range	Major cost drivers	Additional comments
• A strategy should be developed prior to technology selection • A strategy may include any combination of these options • No containment measure should be considered permanent • Removal and destruction are often used together	• Each medium affected by a completed risk exposure pathway should be remediated • The majority of contaminant mass is likely to be located in soil • Groundwater remediation should be coordinated with source remediation in the unsaturated zone	These technologies may be considered to be proven technologies: innovative technologies are not included Technology selection can be guided by performance of nearby remediation projects at similar sites. IRPIMS may be used to locate sites having similar media stratigraphy and contaminants concern	• These generalizations are based on projects demonstrating acceptable performance and cost effectiveness: they are not presented as rigid guidelines because each project needs to be evaluated individually	• These generalizations are based on projects demonstrating acceptable performance and cost effectiveness: they are not presented as rigid guidelines because each project needs to be evaluated individually	• These costs are typical of successful projects conducted by the Air Force and private industry • These costs may be used for budget planning and as a rough check of contractor proposals • These costs are typical of those charged by companies specialized in each technology • A useful measure of merit for evaluating costs is to compute the project cost per pound of contaminant – Cost effective projects typically run < $200/lb – Projects where the costs are orders of magnitude higher	• Reviews of project cost estimates can focus on these areas to expedite the reviews • Regulatory requirements for monitoring and preparing project documentation can be major cost drivers for any project, and they are not addressed in this guide because of the wide range of variability in regulatory requirements among state and local agencies	• These comments and performance estimates are provided as helpful hints and observations based on successful projects

	Liquid phase carbon adsorption	Contamination < 10 ppm Presence of semivolatile halogenated and on-halogenated contaminants Flow rate < 10 gpm id Contamination > 10 ppm	Suspended solids > 50 ppm Oil, grease content > 10 ppm High volatile organic content Presence of humic and fulvic acids	Capital cost: 10–30 gpm: $200/gpm 30–500 gpm: $130/gpm Operating cost: $20–$50/lb of contaminant removed	Carbon regeneration	Best suited for low volume, low concentration applications such as effluent polishing Removal efficiencies of 100% can be attained On-site regeneration usually not cost effective
Groundwater or surface water	Air stripping	Volatile organic contaminants > 10 ppm	Presence of non-volatile organics Iron content > 10 ppm Hardness > 800	Capital cost: $250–$400/gpm throughput up to 100 gpm Operating cost: $20–$50/lb of contaminant removed	Instrumentation for automated operation Power consumption Air reheat Offgas treatment (options listed below)	Tray strippers have less visual impact than packed towers and tray strippers may be less prone to fouling Units designed for removal efficiencies around 99%

(*continued*)

Table VI.10.12. (Continued)

Remediation strategy	Media	Remediation technology	Conditions favorable to use	Conditions unfavorable to use	Unit cost range	Major cost drivers	Additional comments
		Free product removal by pumping	Measured thickness of organic layer > 6 in. Water depth < 50 ft below ground surface	Viscous free product that is difficult to pump Thin free product layersWater table depth > 100 ft below ground surface	$3000–$5000 for a single well $1500/well for additional wells in multi-well systems	Product treatment or disposal (excluding recovery credits)	Should be initiated immediately upon discovery of free product layer Single phase pumping less costly than two phase pumping which requires water treatment
Contaminant		Phase separation (oil–water)	Contamination > 200 ppm Flow rate > 100 gpm	Presence of emulsions	$10–$20/gpm capacity of separator	Equipment	Effluent concentration seldom < 10 ppm
		Air sparging	Volatile contaminants present	Low permeability aquifer Presence of free product > 6 in. thick	Capital cost: $75/ft for injection wells $5000–$25,000 for air injection pumps	Trial test Implementation	Small scale (1 or 2 wells) pilot test recommended Sparging may spread contamination to clean areas, such as basements or utility lines May be used with SVE

Removal	Soil	Soil vapor extraction	Volatile contaminant concentrations > 1000 ppmv in soil gas Presence of low permeability surface cap Presence of contamination > 30 ft below ground surface Structures or utilities present that would hinder excavation	Water table < 10 ft below ground surface Clay content > 20%	Capital cost: $15–$25/scfm capacity for extraction skid with no emission controls (see contaminant destruction by thermal treatment for emission control costs) $40–$75/ft for extraction wells	Equipment Process monitoring Trial test if no nearby SVE applications	Emission control equipment probably necessary: contaminant destruction by thermal treatment is the preferred alternative Operation is generally not cost effective at removal rates < 10 lb/day Air flow promotes biodegradation Can be used with air sparging
		Excavation	*Ex situ* treatment planned, such as thermal, soil washing or biological treatment Off-site treatment available Contamination < 20 ft below ground surface	Presence of structures and utilities Very volatile or toxic contaminants Noise sensitive environments	$2–$25/cu. yd for excavating and loading $1–$3/cu. yd for backfilling and compacting Treatment costs additional	Field implementation Treatment or disposal of contaminated material	
		Soil washing	Thermal treatment prohibited Soil cannot be disposed of off-site	Presence of >30% silt and clay Presence of a sensitive aquifer that may be affected by residual washing chemicals	$100–$500/ton of soil treated	Number of extraction stages required Waste stream management or decontamination	Due to the complexity of this technology, a compelling reason for use should exist Treatment of numerous waste streams required

(*continued*)

Table VI.10.12. (Continued)

Remediation strategy	Media	Remediation technology	Conditions favorable to use	Conditions unfavorable to use	Unit cost range	Major cost drivers	Additional comments
	Gas SVE exhaust Air Stripper exhaust	Condensation	Gas flow rate < 200 scfm High contaminant concentrations Collection efficiencies > 80–90% are not required	Gas flow rate > 200 scfm Dense or viscous condensate	$15,000–$20,000 for a 200 scfm unit	Equipment Compressor power	Both contaminants and water will condense, water will require treatment prior to discharge Recovered product may be partially oxidized, unfit for reuse, and may plug the condenser
		Vapor phase carbon adsorption	Application on trial test SVE units Short term (< 1 month) emission control required Contaminant concentrations < 100 ppmv	Application on air strippers Flow rates > 200 scfm Application to water-saturated gas streams	Capital cost: <$1000 for units 200 scfm or less $3–$4/scfm capacity for larger units Operating cost $40–$100/lb of contaminant removed	Equipment Carbon replacement	On-site carbon reactivation is generally not cost effective: vendors provide carbon replacement service Removal efficiencies of 100% can be attained but saturated gases impede performance

Note: US units used: 1 in. = 2.54 cm; 1 ft = 0.3048 m; 1 sq. ft = 0.0929 m^2; 1 sq. yd = 0.8361 m^2; 1 cu. ft = 28.317 dm^3; 1 cu. yd = 0.7646 m^3; 1 lb = 0.45359 kg; 1 US ton (short) = 0.90718 ton; 1 US gal = 3.78533 l; 1°F = 5/9°C; ppm, parts per million; gpm, gallons per minute; scfm, standard cubic feet per minute.

Table VI.10.13. Remediation technology selection matrix III.

Remediation strategy	Media	Remediation technology	Conditions favorable to use	Conditions unfavorable to use	Unit cost range	Major cost drivers	Additional comments
• A strategy should be developed prior to technology selection • A strategy may include any combination of these options • No containment measure should be considered permanent • Removal and destruction are often used together	• Each medium affected by a completed risk exposure pathway should be remediated • The majority of contaminant mass is likely to be located in soil • Groundwater remediation should be coordinated with source remediation in the unsaturated zone	These technologies may be considered to be proven technologies: innovative technologies are not included Technology selection can be guided by performance of nearby remediation projects at similar sites. IRPIMS may be used to locate sites having similar media stratigraphy and contaminants concern	• These generalizations are based on projects demonstrating acceptable performance and cost effectiveness: they are not presented as rigid guidelines because each project needs to be evaluated individually	• These generalizations are based on projects demonstrating acceptable performance and cost effectiveness: they are not presented as rigid guidelines because each project needs to be evaluated individually	• These costs are typical of successful projects conducted by the Air Force and private industry • These costs may be used for budget planning and as a rough check of contractor proposals • These costs are typical of those charged by companies specialized in each technology • A useful measure of merit for evaluating costs is to compute the project cost per pound of contaminant – Cost effective projects typically run < $200/lb – Projects where the costs are orders of magnitude higher	• Reviews of project cost estimates can focus on these areas to expedite the reviews • Regulatory requirements for monitoring and preparing project documentation can be major cost drivers for any project, and they are not addressed in this guide because of the wide range of variability in regulatory requirements among state and local agencies	• These comments and performance estimates are provided as helpful hints and observations based on successful projects
	Groundwater	Intrinsic remediation or natural attenuation	Contaminant mass < 2000 lb No receptors at risk	Presence of halogenated organics or heavy metals Presence of free product	No capital or O&M costs	Monitoring	Halogenated organics degrade slowly
Contaminant	Soil	Biotreatment: *In situ* *Ex situ*	Presence of water-soluble organic contaminants For *in situ* treatment, aquifer must have permeability > 10^2 ft/day	Presence of halogenated organics Presence of free product Presence of inorganic contaminants	$13–$50/cu. yd for *in situ* $40–$175/cu. yd for *ex situ*	Trial test Monitoring	Trial test is recommended to determine performance

(continued)

Table VI.10.13. (Continued)

Remediation strategy	Media	Remediation technology	Conditions favorable to use	Conditions unfavorable to use	Unit cost range	Major cost drivers	Additional comments
			Contaminant mass ranging from 1000 to 8000 lb				
		Biotreatment: *In situ* *Ex situ* (composting) Bioventing	Moist, permeable soil, neutral to basic pH Temperature > 40°F	Presence of free product Presence of halogenated organics or inorganics Saturated soil or water content ?50% Rapid remediation required	$15–$50/cu. yd	Trial test Field implementation	Trial test is recommended, especially if microorganisms are added to soil Nutrient requirement need to be determined Performance depends on soil pore structure, low ppm levels may not attained
		Thermal treatment: Low temperature High temperature	High contaminant concentrations and presence of free product Water content < 20% Contaminant mass > 2000 lb for on-site treatment Rapid remediation required	High clay content	$15–$150/ton for POL only (low temperature treatment) $300–$600/ton for halogenated organics (high temperature treatment) $700–$1500/ton if PCBs present $6000/ton if process-related dioxins are present in soil	Contaminant type determining whether high or low temperature treatment is required On-site or off-site location of treatment unit Need for air emission controls	Off-site treatment at high range of costs, on site at low range of costs Soils with water content > 25% require drying High temperature treatment units achieve DREs > 99.99% and often require acid gas scrubbing and pollution control systems

Destruction	Gas SVE exhaust Air stripper exhaust Air sparging emissions	Thermal treatment: Catalytic Flame Reactive bed	Emission control stipulated by regulatory agencies Contaminant concentrations > 1000 ppmv favors use of flame units Concentrations from 100–5000 ppmv can be treated in catalytic oxidizers	High particulate or water droplet loading requires filtering or separation	Capital cost: $65–$100/scfm throughput for thermal equipment cost $60–$90/scfm throughput for acid gas emission control equipment Operating cost: – $50/scfm throughput annual O&M cost for thermal unit – $250–$400/scfm throughput annual O&M cost for thermal unit with scrubber	Gas flow rate Presence of halogens requiring acid gas cleaning	Performance > 95% DRE usually attained Base metal catalysts may be more cost effective than precious metal catalysts if halogens are present Units available that convert from flame to catalytic operation as concentrations decrease Influent concentration generally kept < 25% of lower explosive limit by dilution

Note: US units used: 1 in. = 2.54 cm; 1 ft = 0.3048 m; 1 sq. ft = 0.0929 m^2; 1 sq. yd = 0.8361 m^2; 1 cu. ft = 28.317 dm^3; 1 cu. yd = 0.7646 m^3; 1 lb = 0.45359 kg; 1 US ton (short) = 0.90718 ton; 1 US gal = 3.78533 l; ppm, parts per million; gpm, gallons per minute; scfm, standard cubic feet per minute.

Department of Energy's (DOE) Los Alamos National Laboratory (LANL); the US Army Corps of Engineers (USACE) Hazardous, Toxic, and Radioactive Waste Center for Expertise; and the US Air Force Center for Environmental Excellence (AFCEE). Those sources provided cost data for approximately 150 projects. The data were sufficient to begin identifying patterns in costs of several technologies. However, additional cost data for remediation technologies, collected through the use of standard procedure will help to further increase understanding of the factors affecting the cost of technology applications in the future.

VI.10.6.1. Sources of cost data

The FRTR gathers data on costs and regularly adds those data to its web site at http://www.frtr.com.

Additional information about the FRTR and its recommended procedures for documenting case studies is included in the FRTR's *Guide to Documenting and Managing Cost and Performance Information for Remediation Projects* (the guide), EPA 542-B-98-007, October 1998, which is available through the FRTR web site. FRTR case studies present information from more than 200 reports about remedial technology projects, including cost data for the six remediation technologies of interest herein. Each case study provides information about the site background, technology design and performance, cost and lessons learned. Cost data generally were reported in the format provided in the FRTR's *Guide to Documenting and Managing Cost and Performance Information for Remediation Projects*, with the level of detail of the cost data varying by case study (FRTR, 1995, 1997, 1998, 2000). Case studies are available at the FRTR web site at http://www.frtr.gov/cost.

Many USEPA reports are available at http://www.epa.gov in downloadable formats.

A major source of data used for the cost of bioventing technology was the report *Bioventing Performance and Cost Results from Multiple Air Force Test Sites, Technology Demonstration, Final Technical Memorandum*, prepared by the AFCEE (1996). This Air Force report presents cost data on 45 bioventing projects that were performed at Air Force bases throughout the United States. For each project, information is provided about site name, location, total cost of bioventing and volume of soil treated. A standard protocol was used in collecting the cost data. This report was the major source of data on bioventing in this document. The data from the Air Force report are considered unique in the field because they represent a comprehensive effort to collect costs through use of standard procedures. The report is available at http://www.afcee.brooks.af.mil/er/ert/costperf.htm web site.

The report *A Compendium of Cost Data for Environmental Remediation Technologies*, Los Alamos National Laboratory (LANL), LA-UR-96–2205, August 1996 presents summary information about 250 commercial or pilot-scale remedial projects, including actual costs, site characteristics and comments about the project. Cost data were provided by a variety of sources (including FRTR case studies) and vary in level of detail. The report is available at http://www.lanl.gov/orgs/d/d4/enviro/etcap.

Bioremediation in the Field Search System (BFSS), Version 2.1 is a USEPA database of information about waste sites in the United States and Canada where bioremediation is being tested or implemented or has been completed. The database contains information

about 450 full-scale bioremediation efforts and treatability and feasibility studies. BFSS is available at http://www.clu-in.org/PRODUCTS/MOREINFO/Bfss.htm.

The report *Cost Data for Innovative Treatment Technologies*, Internal Draft USACE, July 1997 by the US Army Corps of Engineers, presents information about the cost of selected technology applications, drawn from data available in public sources and from personal communications with site managers.

The costs for technology applications in this section were standardized for both time (to 1999 US$), and location. The inflation factor was applied to most data (except bioventing) using the Engineering News Record (1999) information, available at http://www.enr.com/cost/costcci.asp.

In addition to the sources listed, individual case study reports are available at the USEPA site.

VI.10.6.2. Cautions for use of the data

The cost data throughout this chapter are for use by site managers, engineers, decision makers and other parties interested in assessing remedies on a relative basis, and should not be used for predicting the costs for application because of the significant effects of site-specific factors. The plots in this section may be useful early in the planning process when an analysis of technology costs is performed for general comparative purposes. The plots were prepared from data in the sources indicated on each of the figures. The detailed cost data and descriptive factors are included in each of the sources and the user should refer to them before using the data for more detailed analyses.

VI.10.6.3. Costs affected by site-specific factors

The data arrays can be seen to exhibit large variations in the coefficient of determination (R^2) values. Examples of site-specific factors include: the contaminants being treated and properties of each; characteristics of the as-found matrix for the wastes; concentration of contaminants; distribution of contaminants in the matrix; type and properties of the soil; hydrogeology of the site.

In the case of bioremediation (Fig. VI.10.11), very little correlation of cost with amount treated is observed. Most of the data are gathered between 1000 and 10,000 yd^3 (i.e. 765 and 7650 m^3). In this case, there are significant differences between *in situ* and *ex situ* applications. Applications included for the data were for BTEX, VOCs, PAHs and chlorinated VOCs contaminants.

The unit costs for bioventing (Fig. VI.10.12), decrease from about $10 to $20/cu. yd for 10,000 yd^3 of soils treated to less than $5/$yd^3$ for large quantities (i.e. from about US $13 to US $27/$m^3$ for 7650 m^3 of soils treated to less than US $6.5/$m^3$ for large quantities; 1 $yd^3 = 9.7646\ m^3$).

In Figure VI.10.13, thermal desorption shows an economy of scale from about $200/ $300 per ton at 10,000–20,000 ton treated to less than $50 per ton at the higher amounts, but the R^2 value is only about 5%.

The R^2 value for SVE projects is about 70% (see Figure VI.10.14). In this case, the cost per pound of contaminant removed is very telling. Cost per pound removed for several projects range from several hundred dollars for a few thousand pounds removed to about

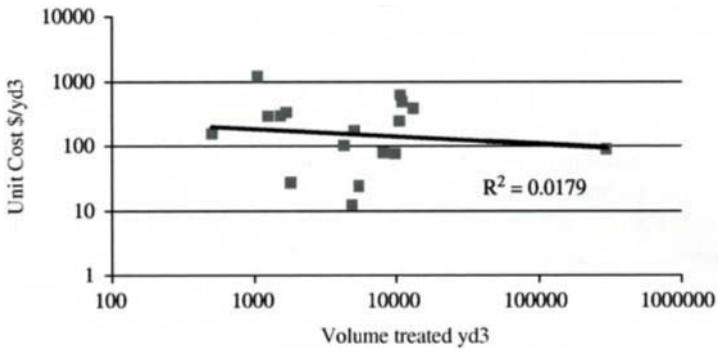


Figure VI.10.11. Costs for bioremediation projects. *Sources*: (1) FRTR – Federal Remediation Technology Roundtable case studies (Vol. 1 (1995), Vol. 5 (1997) and Vol. 7 (1998b) and CDROM (2000)). Available at: http://www.frtr.gov/cost. (2) US Army Corps of Engineers (USACE): *Cost Data for Innovative Treatment Technologies*, Internal Draft, July 1997. *Note*: US units used; 1 yd^3 = 1 cu. yd = 0.7646 m^3.

$20,000/lb when the amount removed is less than 100 lb (i.e. to about US $44,000/kg when the amount removed is less than 45 kg; 1 lb = 0.45359 kg). The cost per pound R^2 value is over 90%.

Five of the on-site incineration projects involved soil, sludge, sediment and debris and two involved liquids and fumes. All were included in the analysis for Figure VI.10.15. There are too few data points for a definitive assessment, but they are useful for a general range determination of cost ranges.

There are many pump and treat applications in existence. Clearly, the unit cost for operations over the life of the system cannot be determined because many, if not most, are

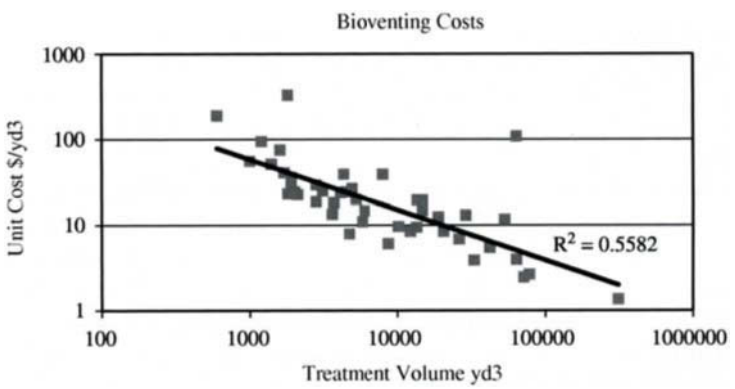


Figure VI.10.12. Cost summary for 47 bioventing projects. *Source*: AFCEE Technology Transfer Division: *Bioventing Performance and Cost Results from Multiple Air Force Test Sites, Technology Demonstration*, Final Technical Memorandum, June 1966. *Note*: US units used: 1 yd^3 = 1 cu. yd = 0.7646 m^3.

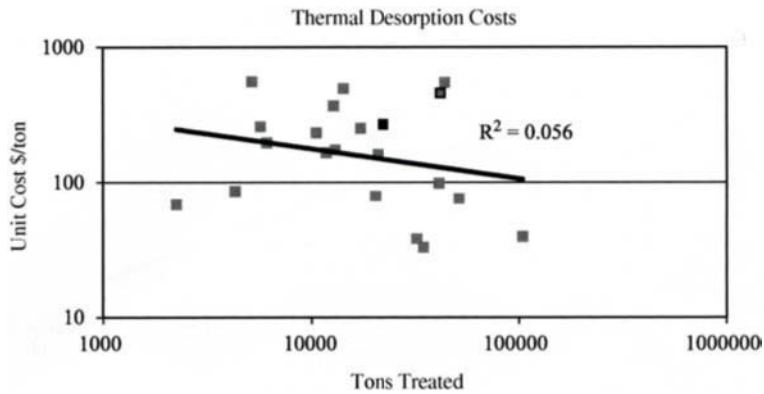


Figure VI.10.13. Cost summary for 21 thermal desorption projects. *Sources*: (1) FRTR case studies (Vol. 1 (1995), Vol. 5 (1997) and Vol. 7 (1998b) and CDROM (2000)). Available at: http://www.frtr.gov/cost. (2) LANL: *A Compendium of Cost Data for Environmental Remediation Technologies*. LA-UR-96-2205, August 1996. Available at: http://www.lanl.gov/orgs/d/d4/enviro/etcap. (3) USACE: *Cost Data for Innovative Treatment Technologies*, Internal draft, July 1997. *Note*: US units used; 1 US ton (short) = 0.90718 ton.

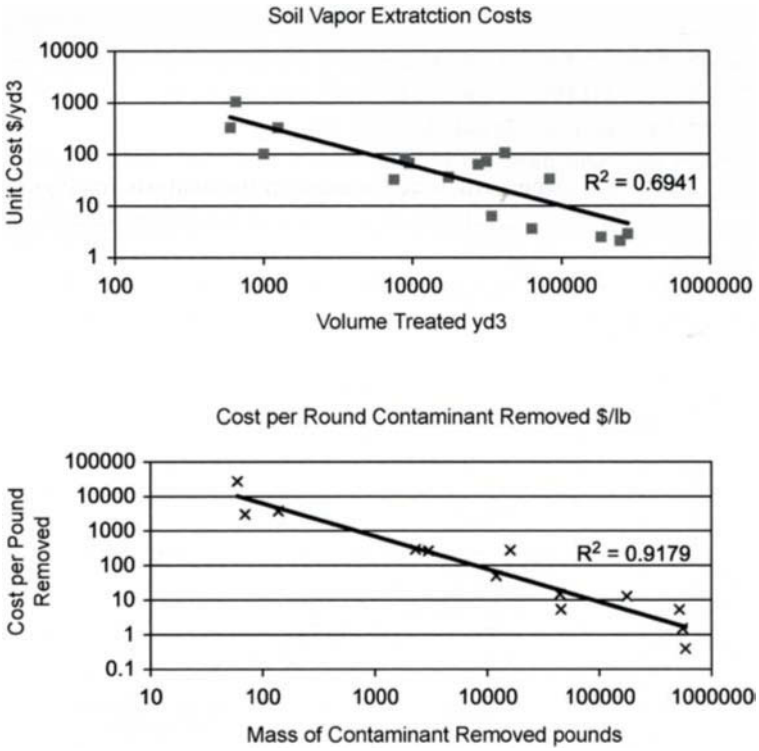


Figure VI.10.14. Cost summary for 22 SVE projects. *Sources*: (1) FRTR case studies (Vol. 1 (1995), Vol. 5 (1997) and Vol. 7 (1998b) and CDROM (2000)). Available at: http://www.frtr.gov/cost. (2) LANL: *A Compendium of Cost Data for Environmental Remediation Technologies*. LA-UR-96-2205, August 1996. Available at: http://www.lanl.gov/orgs/d/d4/enviro/etcap. (3) USACE: *Cost Data for Innovative Treatment Technologies*. Internal draft, July 1997. *Note*: US units used: 1 yd^3 = 1 cu. yd = 0.7646 m^3; 1 lb = 0.45359 kg.

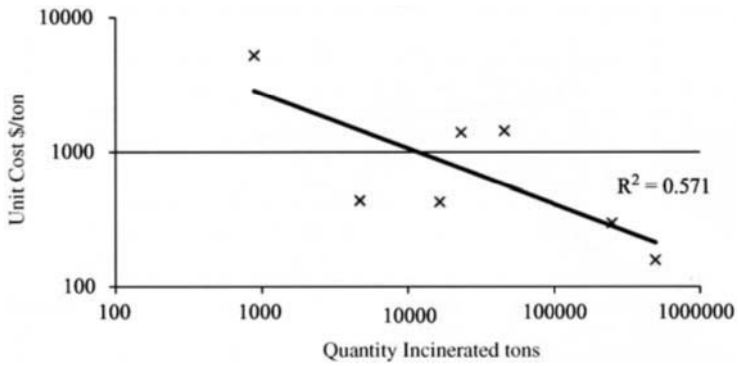


Figure VI.10.15. Cost summary for on-site incineration. *Source*: FRTR – Federal Remedial Technology Roundtable case studies (Vol. 12 (1998c) and CDROM (2000)). Available at: http://www.frtr.gov/cost. *Note*: US units used; 1 US ton (short) = 0.90718 ton.

still in operation. Figure VI.10.16 summarizes unit capital cost per 1000 gal capacity per year data for 32 projects. Figure VI.10.17 illustrates the average annual operating cost per 1000 gal groundwater treated. It is not clear how the amortized capital cost is managed in the annual cost picture. One difficulty in amortizing capital cost for P&T projects and for all projects that are in progress is the uncertainty about the length of the project. Duration of treatment is presumably dependent upon the quality of the treated effluent in the case of P&T applications.

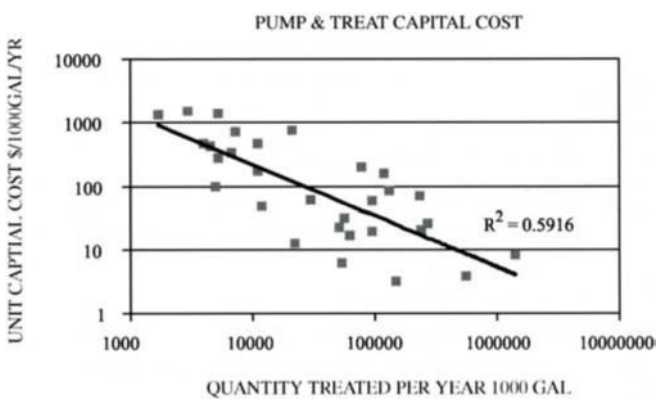


Figure VI.10.16. Summary of Pump and Treat (P&T) capital costs for 32 projects. *Source*: USEPA Office of Solid Waste and Emergency Response, *Cost Analysis for Selected Groundwater Cleanup Projects: Pump and Treat and Permeable Reactive Barriers*, EPA 542-R-00-013. December 2000. *Note*: US units used; 1 US gal = 3.78533 l.

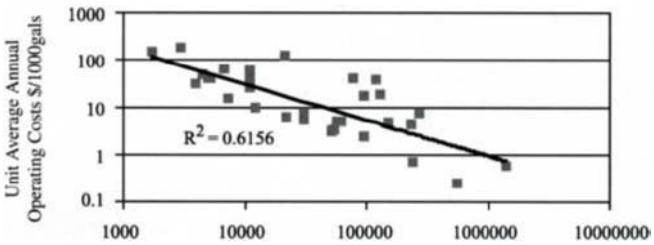


Figure VI.10.17. Summary of Pump and Treat (P&T) operating costs for 32 projects. *Source*: USEPA Office of Solid Waste and Emergency Response, *Cost Analysis for Selected Groundwater Cleanup Projects: Pump and Treat and Permeable Reactive Barriers*, EPA 542-R-00-013. December 2000. *Note*: US units used; 1 US gal = 3.78533 l.

VI.10.7. Concluding remark

A simplified logic approach to step-by-step selection of the most appropriate remediation strategies aimed at efficient and possibly cost-effective meeting the cleanup objectives for the contaminated sites is considered to be an important tool in the optimal implementation of a vast number of routine and innovative technologies, which are available for hazardous waste site remediation. Though comparative cost analysis of proper hazardous waste management vs. remediation has not been carried out here, from the discussed data on remediation costs based on several tenths case studies, it is clear that the costs of cleaning up past mistakes are much higher than the costs of adequate waste management controls.

References

AFCEE – Air Force CEE, Technology Transfer Division, 1996. Bioventing Performance and Cost Results from Multiple Air Force Test Sites, Technology Demonstration, Final Technical Memorandum. June 1996, available at http://www.afcee.brooks.af.mil/er/ert/costperf.htm.

BFSS – Bioremediation in the Field Search System, Version 2.1 (USEPA database), available at http://www.clu-in.org/PRODUCTS/MOREINFO/Bfss.htm.

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US EPA: http://www.epa.gov.

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VI.11

Innovative soil and groundwater remediation: the SITE program experience

Annette M. Gatchett and Robert A. Olexsey

VI.11.1. Site program introduction: history and goals

Superfund was initially focused on existing pollution problems, seeking to abate immediate threats or releases of hazardous substances, and most importantly, to clean up past releases. In 1980 when the Superfund law was signed, there were few choices available for cleaning up sites. Removing contaminants to secure chemical landfills and incineration were the accepted alternatives.

Each of those alternatives had problems of their own: landfills leak, and incinerators produce air emissions and ash that need to be controlled and handled. These problems led to public rejection of the cleanup alternatives, and general suspicion of the effectiveness of Superfund, as well as continuing liability for the waste generators.

The Superfund Amendments and Reauthorization Act (SARA) of 1986 attempted to address these problems. Destruction of contaminants was to be preferred over containment. More remediation options were to be identified, tested and developed. The Superfund Innovative Technology Evaluation (SITE) program was established to accomplish the latter task of adding more tools to the remediation "toolbox".

Historically, one of the greatest factors inhibiting the development and use of innovative cleanup technologies has been the lack of credible cost and performance data during technology development at the commercial scale. By addressing this need, SITE has aided in the first time field use of many technologies, contributing to wider acceptance of a particular technology.

The SITE program begins by soliciting those responsible for hazardous waste cleanup to apply to the program. When hazardous waste site owners approach the SITE program during the solicitation period, they may already have a particular technology vendor or technology in mind for their particular waste problem, or they may decide to solicit a variety of technologies. The SITE program and waste site owner will evaluate the technologies together and choose the one with the best potential to solve the problem. This type of solicitation allows the SITE program to better assess and deal with the actual problems of the user community. Also, with this approach, multiple demonstrations per site are possible.

With the SITE program acting as a third-party evaluator, the potential for biased data collection and reporting is negligible. Furthermore, National Risk Management Research

Laboratory NRMRL's Quality Assurance Office also reviews planning documents and performs audits of sample collection and analysis procedures to verify that the data collected are appropriate to their intended purpose. Thus, the SITE program is founded on the program's objectivity as a third-party evaluator and on the credibility and quality of the data.

VI.11.2. How site encourages innovative technologies

Technology vendors are a central part of the SITE program, because they provide remediation services for sites requiring cleanup. Vendors experience various benefits by participating in the SITE program, namely, increased exposure, market share, technical acceptance and recognition.

How does SITE help developers of innovative environmental remediation technologies? First, by understanding how ideas develop into usable technology. The classic view is that there are six steps from inventor's brainstorm to market:

1. idea;
2. proof of concept on the bench scale;
3. pilot scale;
4. prototype on the field scale;
5. field demonstration;
6. sales.

SITE provides assistance in this process during steps 4 and 5: prototype on the field scale and field demonstration.

If a technology is ready for field demonstration, the SITE program can help in several ways. Field demonstrations take place on Superfund sites or other contaminated ground. Permission to use actual contaminated sites is the first benefit of the program. Access to the site in the form of roads and test pads is the second benefit of the program. SITE provides credibility to the demonstration by taking samples and providing independent analysis of pre- and post-treatment contamination. The extensive quality control/quality assurance that all demonstration plans must pass also adds to the credibility of the results. The results of demonstrations are reported widely, and are included in the evaluation of the economic data. The combination of credible technical and economic data can help the developer over step 6, toward market acceptance and sales.

A demonstration can begin in a few months once a site and vendor have been selected. Field tests can be as short as a few days or weeks for some *ex situ* thermal and chemical treatments, or as long as a few years for *in situ* thermal, chemical or biological treatment. The tasks of a demonstration are divided between EPA and the technology developer (Table VI.11.1), with the developer setting up, running and dismantling the equipment, and EPA leading the planning, sampling, monitoring, analysis and reporting of results.

EPA spends an average of US $400,000–600,000 to facilitate, support, take samples, provide analysis and report the results of a field demonstration. Each developer spends an average of about US $250,000 to set up, run and break down the demonstration equipment and process.

Table VI.11.1. Demonstration activities.

Activities	Responsible organization
Predemonstration	
Site selection	SITE program
Waste characterization	SITE program
Treatability testing	SITE program and technology vendor
Demonstration plan preparation	SITE program
Site preparation	Site owner
Equipment mobilization	Technology vendor
Demonstration	
Equipment operation	Technology vendor
Process monitoring and measurement	SITE program and technology vendor
Sample collection and photo documentation	SITE program
Quality assurance field audits	SITE program
Visitor's day and community relations	Site owner, EPA regions, state agencies
Post-demonstration	
Equipment demobilization	Technology vendor
Site restoration	Site owner
Laboratory analysis	SITE program
Quality assurance laboratory audit	SITE program
Technology and cost evaluation	SITE program
Technology transfer-bulletins, reports, videotape and conferences	SITE program

VI.11.3. How well does the site program work?

The success of the SITE program can be measured by the number of demonstrations, projects and related reports produced. The SITE program is working cooperatively with a total of 152 technologies. By September 2003, 136 technologies were field evaluated. Approximately 6–8 field demonstrations are completed each year. An additional 5–6 new projects are accepted into the program annually.

Demonstration evaluation documents and other information are distributed through electronic sources, CD ROM and hard copy annually. For each demonstration, a two-page bulletin is produced to give a quick explanation of the technology. A larger Innovative Technical Evaluation Report, along with a Capsule report, provide data for those who are interested in study details. Document requesters include consultants, industry, universities, media, state and local governments and other US agencies such as the Department of Defense (DOD) and the Department of Energy (DOE). Developers and EPA staff are encouraged to publish results in journals, and to participate in forums and conferences to ensure the widest dissemination of information on successful innovative technologies.

Since 1993, the use of innovative technologies has outpaced that of established technologies, resulting in dramatic cost savings. The SITE program has shown that innovative technology usage has resulted in significant cost savings compared to conventional technologies. The SITE program conducts an annual analysis of technology costs from EPA regional offices. Cleanup of contaminated sites through the use of innovative technologies has resulted in a total inflated cost savings of over US $2.1 billion adjusted for inflation with an average savings per site of 70%. Innovative technology use has increased in both public and private sector cleanups. While SITE is only one contributing factor in technology selection, the program played a significant role. Innovative technologies were considered in less than 20% of the cleanup decisions prior to 1986; now alternative treatments are considered in almost every Superfund decision (Gatchett and Edwards, 1998).

Figure VI.11.1 shows a breakdown of savings by technology type. Soil vapor extraction (SVE) showed the highest savings of over US $1.0 billion, followed by US $500 million for bioremediation. Since SVE was one of the initial technologies accepted into the SITE program (in the late 1980s), large savings would therefore be expected from this technology. Solvent extraction, thermal desorption and vitrification each account for over US $100 million in savings. Phytoremediation is a newer technology that is beginning to be chosen in Superfund Records of Decisions, with four sites showing a total cost savings of US $17 million when compared to conventional technologies. The number of sites and associated cost savings for phytoremediation and treatment barriers are expected to increase rapidly in coming years (Superfund Annual Report to Congress, 2000).

One goal of the SITE program is to evaluate and encourage technologies with marketable futures. Some technologies in the program have passed the innovative stage and are now accepted as standards. As mentioned above, SVE is now considered a standard option for removal of volatile organic compounds (VOCs) from the unsaturated zone. The first system was demonstrated in SITE by Terra Vac Inc. SVE uses readily available equipment, including extraction wells, a vapor liquid separator and a vacuum pump.

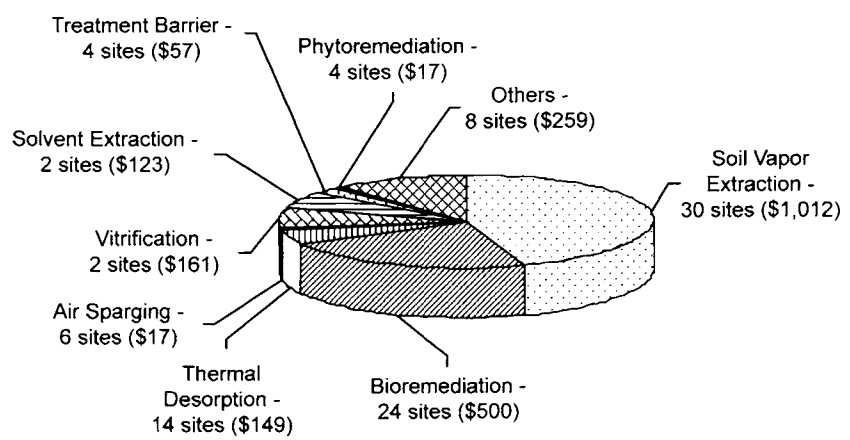


Figure VI.11.1. Cost savings for innovative technology use (Superfund annual report to Congress, Dec. 2000).

The vacuum pump draws the subsurface contaminants from the extraction wells to the liquid vapor separator. The vapor phase contaminants are then treated with an activated carbon adsorption filter or a catalytic oxidizer before the gases are discharged to the atmosphere. The technology is effective in most hydrogeological settings, and can reduce soil contamination levels from saturation to non-detection. The Terra Vac system was demonstrated in 1987–1988 at the Groveland Wells Superfund site in Groveland, MA, and at a Superfund site in Puerto Rico. Terra Vac has since applied the technology at 15 additional Superfund sites, and at more than 4000 other waste sites worldwide.

Many other companies have since developed and are marketing SVE technologies. Some companies with enhancements to the basic SVE system (such as hot air injection combined with groundwater extraction) have become SITE participants.

Private-sector developers continue to show strong interest in the SITE program and many of those who used the program have indicated favorable results. An example of a company that has benefited by its association with SITE is the Terra-Kleen Response Group.

Terra-Kleen is a solvent extraction process, aimed at removing PCBs from soil. The technology was demonstrated between May 16 and June 11, 1994 at the North Island Naval Air Station (NAS) in San Diego, CA. The demonstration showed that the solvent extraction was effective in successfully reducing PCB concentrations from 144 ppm to less than 2 ppm.

As a result of the information provided in the demonstration, the US Navy Environmental Leadership Program (NELP) at NAS has reconsidered cleanup for three sites contaminated with PCBs. NELP selected the Terra-Kleen system because "...it meets all the selection criteria, it is new and innovative, it can be completed in a relatively short time period, and it removes and isolates PCBs from the three sites." The decision also saves about $3.5 million compared to solidification/stabilization, the previous choice.

Since the demonstration, Terra-Kleen has received many other inquiries from states and countries regarding use of their technology. The founder of Terra-Kleen stated in a July 1994 letter to President Clinton, "These individuals connected with the EPA's SITE program have been of untold assistance in allowing this technology to be demonstrated so that it can now be used in full scale at other sites. Currently, we are removing DDT from soil at the Naval Communication Station, Stockton, saving the Navy considerable cost over incineration destruction of the soil. Again, none of this would have been possible without the ever-present help and assistance of the EPA's SITE program."

Some types of technologies have been sufficiently accepted by the market, so that the SITE program is no longer interested in developing or demonstrating them further. For example, solidification/stabilization technologies for metals-contaminated soil are well proven in the laboratory, field and marketplace. SITE has conducted 12 demonstrations of solidification, stabilization, fixation or vitrification processes; many of these technologies have been selected for site cleanups.

VI.11.4. Future directions

The science of site investigation has advanced dramatically in the past 20 years. Advancements in field detection equipment and laboratory analyses have revealed new

information about the problems at waste sites. These advancements, coupled with the experience gained from the numerous sites under investigation, have generated a need for new, innovative technologies.

One of the critical needs for remediation technology is for methods to accelerate aquifer cleanup. By nature, groundwater is a slow-moving, slow-to-change medium. Groundwater contamination may consist of multi-phase contaminant plumes, light non-aqueous phase liquids (LNAPLs) and dense non-aqueous phase liquids (DNAPLs), which can potentially move in different directions. As the complexity of the geological formation increases so does the need for innovative technologies to treat or detect DNAPL. New technologies are needed to control and remediate this diverse problem.

The search for effective remediation technologies for metals in soils, treatment of recalcitrant compounds and the general need for *in situ* treatment remain SITE program priorities. Because of technical difficulties related to sediment remediation, this is another area where the remediation community would benefit from new processes, approaches or less-expensive methods for treatment. *In situ* treatment, sampling and containment are technology areas of interest that will be addressed in the future (Table VI.11.2).

More recently, there have been significant technology breakthroughs in chemical conversion methodologies. Technologies that rely on chemical conversion of the contaminant species (oxidative/reductive) rather than destruction or stabilization will convert contaminants to environmentally harmless compounds. Metal-enhanced dechlorination or treatment barriers fall into this category. The technology is a groundwater treatment technique that degrades chlorinated volatile organics (VOCs) using an electrochemical process that oxidizes iron while chlorinated VOCs are reduces. Two methods of *in situ* metal-enhanced dechlorination are used: a permeable treatment wall or a funnel and gate configuration. The permeable wall can be used above ground in a reactor (*ex situ*) setting. In the future, material other than iron will be assessed for effectiveness on VOCs and other groundwater contaminants.

The SITE program emphasizes the need for technologies capable of *in situ* remediation of DNAPLs in difficult geological formations. This continues to be a theme through the remediation community as a whole. The program continues to evaluate *in situ* thermal and chemical oxidation type technologies under a broad array of geological conditions. In addition, effective remediation technologies for metals in soils, treatment of recalcitrant compounds and the general need for *in situ* treatment remain high on the priority list (Fig. VI.11.2).

The SITE program also emphasizes the need for technologies that focus more on types of contaminated sites rather than single contaminants (i.e. wood preserving sites,

Table VI.11.2. Contaminant emphasis areas for 2000–2006.

Surface water/groundwater	Soils/sediments
DNAPL/chlorinated solvents	Pesticides
PCBs	PCBs
Arsenic, mercury or other heavy metals	PAHs
	Arsenic, mercury or other heavy metals

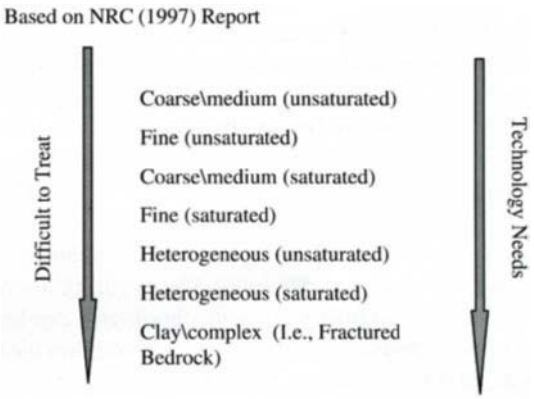


Figure VI.11.2. NRC chart. Future research areas: DNAPL roadmap (NRC, 1997).

manufactured gas plant sites). Most sites are not contaminated with a single contaminant, but with mixtures including by-products formed from normal degradation. Recent applications have led the SITE program to move in this direction. Based on the multi-agency review board, a list of new areas is:

- mining issues/acid mine drainage;
- manufactured gas plants;
- wood treating/preserving;
- pesticide manufacturers/formulators.

VI.11.5. Technologies on the horizon

As a result of innovative remediation technology field demonstrations each year, the SITE program maintains a unique position in the hazardous waste remediation marketplace. Together with a stakeholder group including representation from a number of other federal and state environmental agencies, the SITE program ensures that the most pressing issues are prioritized and addressed.

A number of promising technologies based on sound scientific principles, but lacking engineering and performance documentation, are appearing on the horizon. Some of these, described below, are being researched and developed under the SITE program, and by the US DOE, US DOD and others. It is likely that field demonstrations may occur within the next few years for these technologies or for second-generation improvements of these techniques.

VI.11.5.1. Bioremediation

Various bioremediation technologies have entered the SITE program. In some instances, biodegradation is used with other technologies to accomplish a greater total removal efficiency of organic contaminants. Difficulties associated with biodegradation include: determining which microorganisms can break down specific organic compounds, culturing the microorganism in a favorable environment that provides nutrients and

promotes growth, and the length of time required to completely degrade an organic compound to acceptable levels. Enhancements under investigation include: hydrogen peroxide and other electron acceptors, co-metabolic processes and consortia, nitrate enhancement, and anaerobic or sequential aerobic/anaerobic degradation.

VI.11.5.2. Phytotechnology

Phytotechnology is a set of technologies using plants to remediate or contain contaminants in soil, groundwater, surface water or sediments. Plants can be used to remediate, treat, stabilize and control contaminated media. These technologies can be implemented either *in situ* or *ex situ*. The specific phytotechnology chosen is based on the type of contaminant, media that are affected and the remediation goals. Remediation goals include areas such as phytotechnology containment, stabilization, sequestration, assimilation, reduction, detoxification, degradation, metabolization and/or mineralization. To achieve these goals, the proper phytotechnology system must be designed, developed and implemented, using detailed knowledge of the site layout, soil characteristics, hydrology, climate conditions, analytical needs, operations and maintenance requirements. Other factors that need to be taken into consideration are the economics, public perception and regulatory environment.

Plants naturally remove man-made contaminants through several mechanisms. Some plants degrade organic pollutants directly or indirectly by supporting microbial communities. Other plants take up inorganic contaminants from soil or water and concentrate them in the plant tissue where the contaminant can be removed and disposed of separately, leaving the soil clean.

Phytoremediation can reduce concentrations of hydrocarbons from spills and leaking underground storage tanks; PCBs from transformers; PCP and creosote from wood preserving sites; and nitrates, pesticides and herbicides from agricultural runoff. Some plants can extract heavy metals such as lead, chromium and uranium. Phytoremediation is best suited for cleanups over a wide area, with contaminants in low to medium concentrations.

Wetlands constructed with reeds and cattails are used to prevent acid mine drainage from polluting streams; poplar and willow trees are planted as interceptor barriers to remediate groundwater contamination. Common crop plants like mustard are used for extraction, and alfalfa and ryegrass are used for *in situ* soil remediation. Planted areas can be used in conjunction with other technologies, for example, following a removal action of high-concentration hot spots.

Using plants to remediate, contain, stabilize or provide hydraulic control has the potential to be much less expensive than conventional cleanup options. The cleanup time can be longer than with some physical or chemical processes, but the installation and maintenance costs are typically very low. Public acceptance of the phytotechnology can be very high, in part because of the added benefits of park-like esthetics, including bird and wildlife habitat.

Well proven at the greenhouse and pilot scale, phytoremediation is too new to have widespread acceptance among site managers, owners and responsible parties. US EPA National Risk Management Research Laboratory tested and evaluated the technology's efficacy and cost in the field at sites in Oregon, Utah and Ohio. More demonstrations and

applications of the technology will verify and disseminate information on this technology (Interstate Technology and Regulatory Cooperation, 2001).

VI.11.5.3. Electroremediation techniques

Techniques such as electro-osmosis, electromigration, and electrophoresis through electrokinetics, and electrochemical oxidation are used *in situ* to treat contaminated soils, sediments and aqueous media. In electrokinetics, direct current flowing from positive to negative electrodes in combination with pore-conditioning fluids circulating in the soil provide *in situ* removal of contaminants. The contaminants are directly deposited on the electrodes or removed from the conditioning fluid through a purification process. Electrokinetics can effectively increase the flow of fluids and/or gases within formations where intrinsic permeability is very low. In electrochemical oxidation, electrodes are used to generate hydrogen peroxide from contaminated groundwater. The hydrogen peroxide catalytically decomposes on iron particles to form hydroxyl radicals, which then react with organic contaminants. This technology performs chemical conversion, thereby destroying the contaminants.

VI.11.5.4. Advanced physical/chemical treatment

Many new technologies are under development in the area of physical and/or chemical treatment of contaminated matrices. Many of these technologies remain unproven or are in developmental phases. Using these technologies can expand *in situ* cleanup opportunities to medium- and low-permeability soils, semivolatile organic compounds (SVOCs), VOCs, in addition to metals and areas where excavation costs are prohibitive or excavation is infeasible. These advanced physical/chemical treatment technologies include:

- *In situ chemical oxidation* involves the use of various oxidants and delivery techniques in various combinations to destroy heavy organic compounds. The method involves thoroughly permeating the contaminated zone with sufficient quantities of chemical oxidants so that the chemical can contact and fully react with contaminants. Oxidants used in the systems include hydrogen peroxide, ozone, potassium and sodium permanganate (Interstate Technology and Regulatory Cooperation, 2000).
- *In situ extraction techniques* are used to mobilize heavy organic-based contaminants such as DNAPLs. These techniques are designed to effect rapid mass transfer from the immobile contaminant phase into a mobile fluid phase, either a liquid or a gas. The subsurface may be heated by either resistive heating techniques or steam. Another technique is the subsurface injection of co-solvents or surfactants in order to lower the interfacial tension between the contaminant and soil while increasing contaminant solubility in water.
- *In situ delivery systems* such as directional drilling to place wells under surface structures or in horizontal positions for increased injection or sparging efficiency will be important in areas where buildings or structures cannot be removed.
- *New materials used in permeable reactive barrier (PRB) designs* may reduce costs, and enhance barrier longevity or contaminant treatment. PRBs are an *in situ* treatment technique where contaminated groundwater flows through a reactive zone.

The contaminants are either immobilized or chemically transformed to a more desirable state. The PRB serves as a barrier to the contaminants, but not to the groundwater flow. There are currently four types of barrier designs: (1) funnel and gate, (2) continuous wall, (3) injection well configuration and (4) passive collection with reactor cells.

- *Soil amendment techniques* are designed to reduce both bioavailability and leachability of inorganic contaminants by changing geochemical form. By the addition of amendments such as phosphates and sulfites, contaminants are bound by forming insoluble metal species. These insoluble species reduce the bioavailability of the compound if ingested. Delivery systems such as pressure injection are important in delivering amendments to the subsurface uniformly (Interstate Technology and Regulatory Cooperation, 1999).

VI.11.5.5. Treatment trains and combination technologies

A treatment train is a sequential combination of technologies or unit processes that treat recalcitrant waste matrices more effectively than any single technology could. Treatment trains of innovative technologies can be less costly and more effective in achieving treatment goals than conventional technologies. The "Lasagna" process is an example of several innovative technologies used in concert to treat contaminants *in situ* in less permeable soils including clays and silts. Electro-osmosis first drives contaminants out of soil pores and into treatment zones created by hydrofracturing, pneumatic fracturing or trenching. Contaminants are then treated in treatment zones by biodegradation, catalytic dechlorination or adsorption. Electrodes for the electro-osmosis system can be placed by sheet piling, hydrofracturing or horizontal drilling. Much of the development of this process has proceeded under a Cooperative Research and Development Agreement with Monsanto Company, DuPont, General Electric and EPA.

VI.11.6. Conclusion

The SITE program of the United States Environmental Protection Agency (EPA) has been bringing together the private sector, EPA, and other federal and state agencies to successfully address complex hazardous waste problems.

The SITE program is a key element in EPA's efforts to increase the availability and use of innovative technologies for remediation of the nation's hazardous waste sites. For more than 15 years, the SITE program has successfully promoted the development, commercialization and implementation of innovative treatment technologies. The program provides environmental decision-makers with relevant data on new, viable remediation technologies that may have performance or cost advantages compared to conventional treatment technologies. The SITE program technology evaluations are used by the remediation community to choose cleanup technology options, and that data are credible because of the rigorous quality assurance and careful planning of the demonstrations. To date, the program has completed 136 field demonstrations and is currently working with an additional 16 projects. Some technologies once considered innovative such as SVE, *ex situ* thermal desorption and *ex situ* solvent extraction have been accepted as standard in part because of this program. Superfund site managers, who in 1986 had the choice of incineration or

landfill, can now find many other tools in the "remediation toolbox". SITE continues to look to the future for innovative solutions to solve the cleanup challenges of the past. General information, full reports and technology profiles on the SITE program are accessible through http://www.epa.gov/ORD/SITE.

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PART VII

New developments in solid waste information and environmental control strategies

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VII.1

The clean, green net: environmental computer resources under construction

William B. DeVille

VII.1.1. Introduction

The Internet is a worldwide linkage of computers that use standardized data transfer protocols allowing relatively rapid, relatively inexpensive transfers of information across the network. It is a set of information management technologies that will as surely transform the world as did written languages, printing, industrialization, mass transport and mass communications.

Vannevar Bush, Director of the U.S. Office of Scientific Research and Development during World War II, conceived new technologies for managing and presenting information that would have an impact far beyond merely facilitating easier and faster access to data. His vision was that the result would be new ways of relating data and, ultimately, new ways of publishing information in ways that incorporate these relational links.

The title of Dr. Bush's (1945) article[1] in *The Atlantic Monthly*, "As We May Think", emphasized his belief that future information technologies could result in radical changes in the way humans assimilate, comprehend and use information. He called the encyclopedic array of data made available by advanced information technologies, the "memex". A person viewing the memex might establish new pointers, or links relating data in new ways, that could then be published as a contribution to the memex.

This somewhat philosophical introduction may assist the reader to grasp the underlying construction of the World Wide Web (WWW). The web is a large and growing set of data (web pages, text blocks, graphics, sounds, movies, etc.) among which links may be established using the hypertext markup language (HTML) and uniform resource locators (URLs, the addresses of sites or objects on the web).

Objective and a caution. The objective of this chapter is to give an overview – with particular illustrations – of some of the environmental science and engineering resources on the Internet. I also hope to give the reader a feel for potentially useful ancillary

[1] If the reader has access to the WWW on the Internet, it would be worthwhile to perform a search for the term "Vannevar Bush" and then select a hypertext link to an electronic version of the article. The web address (known as a URL for "uniform resource locator") for the Lycos web searcher is http://lycos.com (copy the address precisely as printed, and enter it into the *open location* or *open dialogue box* in your web browser).

resources, from environmental law and regulation databases to Internet communications lists ranging from professional peer discussion groups, to environmental sites for the general public. Emphasis will be given to the WWW because of the richness and power of the user interface (with graphical interface browser software such as Netscape Navigator or Microsoft Explorer) and the intuitive ease of use of the web's hypertext links.

A cautionary note is due to the continuing rapid evolution of everything on and associated with the Internet, from the software protocols and languages to the implementing and viewing of computer hardware and software. Above all, the scope and content of information resources and the techniques used to present them are constantly growing and changing.

There is a kind of tension in writing about computer information resources within the medium of a book chapter. Books – even those written on topical, time-related subject matter – have a kind of permanency that is lacking in the rapidly evolving world of computer information networks.

Ten years after this book has been published, I would expect to be able to go into a library, locate it through the card catalog (most likely, a computerized one), pick it up, and read it just as it was published. That assumption will not hold for many of the computerized information resources that are available today. The technological media for accessing the information (including the computer hardware, operating systems, network protocols, search engines and software readers) will have changed in 10 years. The databases available today on the Internet's WWW will likely be unusable on the hardware/software systems that will be in use 10 years in the future – just as they would have been impossible to use in today's form, 10 years ago.

A number of examples of information resources on the web are provided in this chapter, including their current web site addresses. Please be cautioned that the Internet addresses of sites listed may change rapidly, even over the next 2 or 3 months. But this is not as much a problem as it might first seem, because the Internet also provides search engines working with continually updated databases of resources that allow the user to find addresses on any topic. It is also very common to see "under construction" labels on web pages, indicating that changes are being made literally on a day-to-day basis.

VII.1.2. An overview of the World Wide Web

The initial conception and development of the web was done at the European CERN laboratories. The web has been called the "killer application" of the Internet, because the use of HTML for formatting and linking files allowed simple and intuitive navigation around the Internet. Web viewers do not have to master the complex commands of the UNIX computer operating system. Furthermore, HTML richened the appearance and formatting of documents by contrast to the plain, unformatted screens to which Internet users had been accustomed. Although HTML-formatted documents are actually plain text with added formatting tags, browsing software (such as Netscape or Explorer) allowed superimposition of a graphical interface and "point and click" navigation among documents and web sites. This ease of navigation is undoubtedly the reason for rapid growth of Internet use, and reminds one of Vannevar Bush's visions of the electronic library.

HTML formatting also allows electronic publication of documents that are essentially platform-independent. That is, a document prepared and stored on a UNIX computer may be accessed and viewed by computers using Macintosh or Windows operating systems, and appear essentially the same on all three types of computers, including complex features such as graphics, sounds, animations and so on. The list of new features available is constantly growing as HTML and its associated browsing software evolve.

As is typically the case on the Internet, committees[2] exist that attempt to establish standardized features of the HTML language. As is also typically the case on the Internet, some software developers do not adhere strictly to the recommended standards. This means that some documents may appear differently, or have features that are not consistent between different browsers. Many web pages now provide downloadable documents in the Adobe Acrobat page description format (PDF). This provides greater control of the document formatting and appearance than does HTML, and is especially suitable for long documents.

One of the more exciting developments is the use of an extension of HTML formatting called XML (extended markup language). XML can permit far better control of document formatting and definition of data elements within web pages than does HTML. Imagine, e.g., the difficulties that researchers encounter in compiling and evaluating data that is spread among many host computers on the Internet. XML is already allowing chemists to share information through use of XML data definitions that support agreed-on specifications for the data.

VII.1.3. An overview of web resources

There are already millions of sites on the web, holding billions of published items. It would be wise for web "surfers" to recognize that it is in some ways a new and strange environment, lacking many of the traditional institutional contexts that we use to judge the validity of information.

Caveat emptor. Web sites range from home pages created by individuals to those maintained by professional societies, environmental organizations, publishers, universities, governmental agencies and companies. Their quality (from any point of view ranging from aesthetics to trustworthiness of content) extends over a broad spectrum. Most of them offer free access. Some restrict access by requiring passwords, and limit themselves to paying subscribers, organizational membership or some other access criterion. The Internet exercises no control on the type or quality of information on the web. It remains a fact that it is much cheaper and easier to publish electronically on the Net, than to publish through a recognized scientific or engineering publishing firm or a peer-reviewed journal such as *Science* or *Nature*.

This means that the burden of validation of information obtained from the web rests squarely on the user, who must take into account the reliability of the source of the information. There are, however, some fairly conventional indicators of the probable veracity and quality of information based on sources. For example, scientific and engineering professional societies, major university academic departments and governmental agencies

[2] http://www.w3.org/.

tend to review the content quality of web sites associated with them. Authorship by a person of known credentials can be a good quality indicator (although cases of falsely ascribed authorship have already cropped up on the Internet).

Familiar academic trappings in a new wrapping. Many peer-reviewed scientific journals have already appeared on the Net, and this will become more common in the near future. One of the first is the *Journal of Molecular Modeling*,[3] which is available in electronic form on the Internet or on CD-ROM as well as in paper form. This journal's web site advertises itself as "The first fully electronic journal in chemistry – the advanced way of publishing." Abstracts and papers may be downloaded to the viewer's computer in one of the two ways, as HTML files formatted for viewing by a web browser or as PDF (portable document files) viewable by Adobe's Acrobat Reader software. In either case, the papers are well formatted, can include pictures and graphics and generally look much like similar papers printed in contemporary scientific journals. The HTML formatting language allows additional elements such as movie clips with sound, rotating three-dimensional model presentations, and high-quality color images. Ancillary files, such as raw data sets, could easily be attached to the "paper" for downloading by the viewer. It will be interesting to see how such features, which go beyond the capabilities of the printed page, may influence the techniques used by scientists to present their research.

VII.1.4. Finding information on the web

Web search engines. An obvious question is, "How do I find the information that I'm interested in?" One possibility is to use a web searcher. Several are:

Google	http://www.google.com/
Lycos	http://lycos.com
WebCrawler	http://webcrawler.com/
Altavista	http://www.altavista.com/
Amazon	http://www.amazon.com/
Scirus	http://www.scirus.com

Of these web searchers, Scirus is a specialty search engine that targets *scientific information only* in earth and planetary sciences, and environmental sciences and covers over 100 million science-related pages.

These and several other search engines provide free access for relatively simple types of keyword searches.

Caution: No web search engine will find all information that is out on the web. Of the current 5 billion or so web pages, the search engines "know" about less than 10% – and they may not be very selective in choosing the search "hits" presented to

[3] http://www.ccc.uni-erlangen.de/jmolmod/index.html.

the user. For this reason, it is advisable to become knowledgeable about potential sources of information on the web, such as university, professional society or governmental web sites and to examine such web sites as supplements to searches made with web search engines.

One example is a search I conducted for the term "pollution prevention" using the Google search engine. Although by no means a comprehensive listing of sites with pertinent information, and although many of the items found were either of no interest or of dubious quality, some of the search hits were very useful. Google found about 515,000 relevant web links for this simple search. Fortunately, I found what I was looking for in the first page of search results.

VII.1.5. Google search results for "pollution prevention"

Results: About 515,000 *Search time*: 0.07 s.

Although I have recently sifted through more than a thousand web sites on the topics of solid waste, hazardous waste and pollution prevention, I had neither the time nor the patience to look at all the 515,000 "hits" provided by Google. Fortunately, Google (like many other search engines) tries to provide relevant "hits" on the first few pages of the search results, i.e. it tries to prioritize the results. The term "pollution prevention" keyed a "canned" response based on someone's understanding of the context of the terms, and resulted in an intelligently selected set of hits. In this case, the search provided URLs to several sites with useful information on the topic. Even better, several of those sites provided still more links to the topic.

In this case, I was really interested in finding references on pollution prevention for leather tanning. Simply by changing the Google search term to "pollution prevention leather tanning", the number of references found by Google dropped dramatically, and were far more relevant to my immediate interest.

Results: About 2260 *Search time*: 0.20 s.

"Web worms" and indexing. Several organizations index the web by means of automated programs ("web worms") that seek out web sites and send back indexes of their contents to their home computer. This allows web services such as Yahoo[4] to compile lists of "significant" web sites. In this sense, Yahoo is somewhat more sophisticated than some of the other web search services, which rely entirely on automated, non-contextual indexing of the contents of sites.

The problem is that most current indexing is non-contextual, which can result in surprising and often very irrelevant responses to search queries. Efforts are being made to give more intelligence to the web worms and automated indexing. Gary Taubes (1995) wrote an interesting article on this subject.[5]

CERN's WWW virtual library indexes.[6] Another approach to identifying and organizing topical content guides to the web was initiated by CERN, the European

[4] The acronym stands for "Yet Another Hierarchical Officious Oracle". The URL is http://www.yahoo.com/.

[5] Indexing the internet. Science 269, September 1995, pp. 1354–1356.

[6] http://www.vlib.org/.

Organization for Nuclear Research. This effort was described as "using amateurs to index the web until we can get librarians to do it right." Volunteers from around the world were enlisted to help categorize web information resources and provide useful links to them. Over the past several years, some of the host organizations, URLs and the focus of several of the index lists have changed. Nevertheless, they remain useful.

Bio Sciences	http://mcb.harvard.edu/BioLinks.html
Biotechnology	http://www.cato.com/biotech/
Chemistry	http://www.liv.ac.uk/Chemistry/Links/links.html
Earth Science	http://www.geo.ucalgary.ca/VLEarthSciences.html
Energy	http://www.crest.org/gem.html
Engineering	http://www.vlib.org/Engineering.html
Epidemiology	http://www.epibiostat.ucsf.edu/epidem/epidem.html
Statistics	http://www.stat.ufl.edu/vlib/statistics.html
Technology transfer	http://www.nttc.edu/gov/other/tech.html
US Federal Government	http://www.lib.lsu.edu/gov/fedgov.html
US Government Info.	http://iridium.nttc.edu/gov_res.html
United Nations	http://www.undcp.org/unlinks.html

These indexes typically link to other pages or web sites, so that an ever-expanding set of possible sites of interest is the norm.

The deadly lure of hypertext links (how to lose focus on your topic). Hypertext links are so easy to click on and follow that the most likely outcome will be that the web user tracks information threads that are totally unrelated to the original topic of interest. The result can be serendipitous enlightenment or wasted time and effort.

Suppose the desired information is about solid waste landfill design in Denmark. If the search term provided to the Google[7] search engine is "solid waste landfill design", the results of such a search will be

Results: About 77,400 *Search time*: 0.42 s.

Although many of the 77,400 reference links may be interesting, it would be fruitless to try to find information about Danish landfill design in this way.

A straightforward solution to avoid information overload is to refine the search term, thus "solid waste landfill design Denmark". A recent Google search using this request provided these results:

Results: About 2760 *Search time*: 0.42 s.

Within the first 20 Google results was a link to the technical guidelines for siting and designing landfills in Denmark (as of 1995).

[7] http://www.google.com.

VII.1.6. Examples of a few web pages that I have found useful

Chemical Information Sources from Indiana University.[8] A concise, useful "Bibliography on Chemical Hazards"[9] is also found there, as is a related "chemical safety or toxicology information" page. Educators may be interested in the "chemistry courses on the Internet" and "clearinghouse for chemical information instructional materials" pages. The page titled "chemical information sources (major tools or databases)" is a good reference tool.

Hazardous Substances Research Centers.[10] The US EPA has funded regional academic research centers that focus on problem aspects of hazardous substances. The regional center for the south and southwest portion of the US involves three universities, Louisiana State University, Georgia Tech and Rice University. Much of this research at these regional centers focuses on contaminated sediments. Through the "research briefs" link, I was able to find a useful summary of the research objectives on studies of sediments at Bayou D'Inde in Louisiana. The sediment contamination had resulted from hazardous wastes, and I have worked on the problems at this particular site.

Enviroene.[11] This web site is a joint project of the US EPA, Department of Defense and Department of Energy. Aside from providing useful links to a variety of US governmental web sites, there are some extremely interesting special topic pages. One that provided me with some particularly useful information is the link to the "solvent substitution data systems (SSDS)" page. This allows queries of the solvent alternatives guide (SAGE), the hazardous solvent substitution data system (HSSDS) and the Department of Defense Pollution Prevention Technical Library. These tools can be important to persons seeking alternatives to hazardous solvents.

Thomas.[12] This provides searchable and downloadable access to US Congressional legislative bills. As a governmental bureaucrat, I find it very important to keep apprised of the current status of environmental legislation. Similar web resources are becoming available to track legislation in other countries.

The US EPA Office of Solid Waste Home Page.[13] This provides links to solid and hazardous waste regulations, technical requirements, case histories and technical resources. This page also provides a link to information on waste minimization issues, resources and technologies.

VII.1.7. Some evaluations and conclusions

The state of the art. The web is now useful for many purposes, and surely it will continue to develop. One of the major limiting factors at this time is the bandwidth of communication lines for data transfers. Ten years ago, a 1200 baud modem seemed fast – and was quite

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[8] http://www.indiana.edu:80/~cheminfo/.
[9] http://www.indiana.edu:80/~cheminfo/12-01.html.
[10] http://www.hsrc.org/hsrc/html/ssw/.
[11] http://es.epa.gov/.
[12] http://thomas.loc.gov.
[13] http://www.epa.gov/osw/.

usable for transmission of simple text files. But a 14.4 modem is about the bare minimum for hooking up to the web and at this speed, transfer of large graphics files is not feasible. Even the fastest phone line modems available are much slower than the Ethernet connection I have to a web server, which itself is hooked up to a high speed data connection to the outside world – and I am often dissatisfied with the speed of communications.

The rapid growth of the number of people using the Net, together with continuing enhancements to the HTML language will make the bandwidth problem even more critical. Several promising technologies already exist and are being further developed to help solve this problem. Some examples are faster data transmissions over existing copper phone lines, optical fibers or use of cable TV connections. It is, therefore, likely that greater communication bandwidths will become widely available in the near future. When that happens, the current level of information technology will begin to seem primitive and Dr Bush's vision of changes in the way people think may come closer to reality. Dr Bush was an optimist about the impact of such things on society. I hope he was right.

Rapid improvement over a short term. Candidly, I did not myself find the WWW to be a very useful information-gathering tool before about 1994. One reason was that I had been using a text-based web browser called Lynx, which provides a far more primitive interface than do current graphical browsers. The primary reason, however, was that most of the material that I now find useful was not on the web until quite recently. Even a couple of years ago, a great many web sites that I routinely use were not yet published or contained little information of interest.

Some of the electronic journals and discussion lists that were formerly available only via email are now available at web sites, but with the added advantages of better formatting and far better facilities for searching the archives of back issues. Even the concept of discussion lists is moving over to some web sites, with improved interfaces such as better thread management (i.e. the ability to follow discussions about a selected topic more easily).

As of now, a number of web sites exist with further communications and research in the environmental science and technology disciplines. I recommend them to the reader.

References

Bush, V., 1945. As we may think. The Atlantic Monthly (available in http://lycos.com).
Taubes, G., 1995. Indexing the Internet. Science, 269, 1354–1356.

Uniform Resource Locators (URLs) – the web sites

Information sources

Hazardous Substances Regional Academic Research Center (Louisiana State University, Georgia Technical University, Rice University: http://www.hsrc.org/hsrc/html/ssw/
Indiana University – chemical information: http://www.indiana.edu:80/~cheminfo/
Indiana University – Bibliography on Chemical Hazards: http://www.indiana.edu:80/~cheminfo/1201.html
US Congressional Legislative Bills – Thomas web site: http://thomas.loc.gov
US EPA – Department of Defense and Department of Energy, Enviroene web site: http://es.epa.gov/

US EPA Office of Solid Waste Home Page: http://www.epa.gov/osw/
Journal of Molecular Modeling: http://www.ccc.uni-erlangen.de/jmolmod/index.html
W3C World Wide Web Consortium: http://www.w3.org/

Web search engines (web searchers)

Google: http://www.google.com/; Lycos: http://lycos.com
WebCrawler: http://webcrawler.com/
Altavista: http://www.altavista.com/
Amazon: http://www.amazon.com/
Scirus: http://www.scirus.com

"Web worms" programs and indexing services

Yahoo – Yet Another Hierarchical Officious Oracle: http://www.yahoo.com/

WWW virtual library indexes

CERN, the European Organization for Nuclear Research: http://www.vlib.org/
Bio Sciences: http://mcb.harvard.edu/BioLinks.html
Biotechnology: http://www.cato.com/biotech/
Chemistry: http://www.liv.ac.uk/Chemistry/Links/links.html
Earth Science: http://www.geo.ucalgary.ca/VL-EarthSciences.html
Energy: http://www.crest.org/gem.html
Engineering: http://www.vlib.org/Engineering.html
Epidemiology: http://www.epibiostat.ucsf.edu/epidem/epidem.html
Statistics: http://www.stat.ufl.edu/vlib/statistics.html
Technology transfer: http://enviro.nfesc.navy.mil/erb/rel_sites.htm#a
US Federal Government: http://www.lib.lsu.edu/gov/fedgov.html
US Government Info.: http://www.nttc.edu/resources/goverment/govresources.asp
United Nations: http://www.unep.org/Documents.Multilingual/Default.asp?DocumentID=293

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VII.2
Solid waste management policies for the 21st century

John H. Skinner

VII.2.1. Introduction

Solid waste management has moved to the forefront of the environmental agenda. Actions to reduce the environmental risks of solid waste treatment and disposal operations have reached unprecedented levels. Nations are considering restrictions on packaging and controls on products in order to reduce solid waste generation rates. Local and regional governments are requiring wastes to be separated for recycling, and some have even established mandatory recycling targets. Incinerators and waste-to-energy plants have been equipped with state-of-the-art air pollution controls. Landfills are being designed with liners, impervious caps and liquid collection systems, and gas and groundwater are being routinely monitored.

Previously considered a local issue, it is now clear that solid waste management has international and global implications. Concern about transboundary shipment of hazardous waste has led to the adoption of the Basel Convention by the United Nations. Recognizing the inter-relationship between solid waste standards and economic development, the European Community is moving forward to harmonize waste disposal requirements in member countries. Solid waste management in countries with developing economies poses a special set of problems. In these countries quite often financing is not available for the construction of waste treatment facilities, and there is a lack of trained personnel to operate waste management systems. Also, there are generally no regulations or control systems, no administrative body responsible for solid waste control and no obligation for industry to dispose of wastes properly.

More than ever before, solid waste management policy makers worldwide need sound and reliable information on the technical performance, environmental impact and costs of solid waste collection, recycling, treatment and disposal systems.

VII.2.2. Integrated solid waste management

Most solid waste management professionals recognize that there is no single, simple solution to solid waste problems. Instead an integrated approach is necessary combining the elements of several techniques. Integrated solid waste management is a comprehensive strategy involving four key elements applied in an integrated manner:

1. reducing the volume and toxicity of the solid waste that is generated,
2. recycling or reusing wastes to the extent feasible,
3. recovering energy from the remaining waste through combustion systems equipped with the best available pollution control technology, and
4. utilizing landfills with adequate environmental controls.

In the following sections each of the elements of this strategy will be discussed in turn.

VII.2.2.1. Waste reduction

Waste reduction activities are important to halt or slow down the increasing rate of waste generation per-capita.

Waste reduction has several aspects, all of which should be addressed. One is toxicity reduction, in which the nature of the waste is changed by reducing manufacturer's use of toxic materials in consumer products. Another is volume reduction – cutting the amount of waste generated by using less material in the first place. Waste reduction also includes encouraging the production of products that can be recycled more easily, such as shifting from multi-material to one-material packaging. Other options to reduce wastes include the redesign of products, material use changes, and restrictions on specific product types.

The approach to reducing waste must be broadly based incorporating actions that can be taken by industries, individuals, commercial enterprises and governmental agencies. Industry can reduce waste through raw material substitution and redesign or products and processes. Individuals, commercial enterprises and agencies can use their purchasing power to create a demand for low waste products or items produced from recycled materials. Governments should investigate the use of economic and other incentives to encourage waste reduction. Waste reduction efforts also need to focus on consumer behavior. Education and information dissemination programs can be effective means of causing desired behavioral and attitudinal changes.

There are many cases of successful reduction of wastes produced by industrial processes. Experience has shown that modifications to industrial processes that reduce waste also result in lower raw material, energy and waste disposal costs. Productivity is often enhanced and liabilities related to release of hazardous substances are reduced.

VII.2.2.2. Recycling

Recycling involves separating recyclable materials from the waste stream and transporting these materials to recycling markets.

Prior separation of recyclable materials has the advantage that the materials are not contaminated by other wastes. However, this requires the waste generator to separate the wastes correctly and store them in separated form. Also, the generator needs to transport the separated material to recycling centers or separate or compartmentalized collection vehicles need to be used. Key factors in success of pre-separation efforts are

the cooperation and willingness of the generator to participate in the program over the long term, and the additional collection and transport costs that may be required.

Mixed solid waste or mixed recyclables can be separated for recycling at processing centers or materials recovery facilities. These facilities can be designed to separate mixtures of glass bottles, paper and cardboard, aluminum cans and steel cans and plastics. The success of these plants depends on the processing costs and the quality of the recyclable material produced.

A major recycling impediment is the question of continued viability and availability of secondary materials markets. It is important to understand that separation of materials from the solid waste stream in itself does not constitute recycling. Recycling only occurs when these materials are incorporated into products that enter commerce. Therefore, requirements to separate certain fractions of materials from waste may produce a supply of materials, but these requirements in themselves will not ensure recycling. In fact, if markets for these materials are not found, the materials are subsequently disposed of, and all of the costs of recycling are experienced with none of the benefits. Similarly, requirements to incorporate separated waste materials in products will not result in recycling unless these products are of a quality and price that they successfully compete in the marketplace.

VII.2.2.3. Combustion with energy recovery

Waste-to-energy facilities employ the controlled combustion of solid waste for the purposes of reducing its volume. Municipal waste-to-energy facilities produce a number of benefits to a waste management system. Combustion can destroy bacteria and viruses in wastes as well as harmful organic compounds. Combustion can reduce the volume of solid waste by up to 90% thereby conserving landfill space. It also offers the possibility of recovery of energy in the form of steam or electricity. Modern solid waste-to-energy facilities burn wastes at high temperatures with residence times necessary for efficient combustion. There are several decades of experience with this technology and research and technological developments have significantly advanced the state of the art and practice. There are hundreds of examples of well-designed and operated municipal waste combustion systems around the world.

Environmental management of municipal waste combustion facilities includes the control of air emissions and the management of ash residues. Standards for control of air emissions incorporate good combustion practices, emission monitoring and highly efficient air pollution control systems to control organic emissions (dioxin and furans), metals, acid gases and other pollutants.

With respect to management of ash from municipal waste combustion facilities, technologies are available to safely dispose of these residues. These include specially designed landfills for ash disposal and technologies to chemically extract metals or to solidify and stabilize the ash. The added costs of these techniques can be offset if the ash is treated to the extent that it can be used safely as an aggregate or building material.

VII.2.2.4. Sanitary landfills

The disposal of waste on the land continues to be a predominant method used worldwide. It is important here to distinguish between sanitary landfill and uncontrolled open dumping. The open dumping of waste on the land without adequate controls can result in serious public health, and safety problems and severe adverse environmental impacts. However, a sanitary landfill is an engineered structure that is designed and operated to protect public health and the environment.

Sanitary landfill technology has advanced very rapidly over the past decade. Today's state-of-the-art landfills are equipped with leachate collection systems, liner systems, systems for control of landfill gas, groundwater monitoring, closure and post-closure care. The objective is to ensure that landfilling is performed in a manner that greatly reduces the chance of release of contaminants to the environment – and also, to assure that any release that does occur is quickly detected and corrected. Since land disposal of solid waste is practiced on such a wide-scale basis it is important that the best available technologies be used.

VII.2.3. Strategies for the future

Any discussion of solid waste management policies for the future must refer to Agenda 21, adopted at the United Nations Conference on Environment and Development in 1992. Agenda 21 addresses the pressing environmental problems of today and aims at preparing the world for the environmental challenges of the 21st century. Agenda 21 deals explicitly with solid waste management in two chapters: Chapter 20 on the environmentally sound management of hazardous waste, and Chapter 21 on the environmentally sound management of solid wastes. Agenda 21 holds out the hope that sustainable development, that integrates environmental protection and economic development, will lead to the fulfillment of basic needs, improved living standards for all, better protected and managed ecosystems and a safer, more prosperous future.

In order to be consistent with sustainable development, solid waste management systems must meet the needs of the present without compromising the ability of future generations to meet their needs. This involves efficient management of today's wastes while conserving resources and protecting the environment for current and future generations. Using Agenda 21 as a starting point, 10 principles or strategies for future solid waste management programs can be suggested.

VII.2.3.1. Waste prevention and toxic reduction as strategies of choice

Traditional waste management strategies have relied primarily on collection of wastes followed by treatment and disposal. A waste prevention strategy emphasizes not creating the waste in the first place, and reducing the use of toxic materials so that the wastes that are generated are less toxic or less hazardous. Waste prevention not only enhances environmental protection, it often involves economic benefits. Waste prevention is a very powerful concept that has significant potential for reconciling both environmental and

economic goals. Waste prevention should be the cornerstone of sustainable waste management policies.

VII.2.3.2. Economically sound recycling and recovery

Recycling and recovery of materials and energy from solid waste not only reduces the volume of waste for disposal but also conserves natural resources. However, in order for recycling to be consistent with sustainable development it must be economically feasible. Otherwise, resources are wasted not conserved.

In order to effectively carry out successful recycling programs, solid waste managers must operate in a business-like manner as raw material suppliers. They must treat the users of their materials as customers. This means they must produce recyclable materials meeting the customer's material quality requirements, and offer recyclable materials at a price competitive with other material supplies. They must operate their separation, collection and processing systems to produce competitively priced, quality materials at the lowest possible costs. The elements of success of a recycling operation are the same as for any successful business; staying close to the customer, understanding and meeting their quality needs and operating in a cost-effective manner to produce a competitively priced product.

VII.2.3.3. Product stewardship

It is important to understand that wastes are simply discarded products and the design and use of a product can have a significant impact on the nature of the waste that is produced. For example, waste prevention and toxic reduction can be accomplished by substituting raw materials, changing product designs, increasing process efficiencies, and extending product lifetimes. Recycling and reuse can be enhanced by designing products so that components and materials can be easily separated, by eliminating contaminating materials that inhibit recycling, and by using more recycled materials in the original product. Eliminating certain materials from products can also reduce the release of toxic materials to the environment during waste treatment and disposal.

Product stewardship involves taking responsibility for a product throughout its entire life cycle including responsibility of management of wastes after the product is discarded. While persons responsible for waste management can identify desirable changes in products from a solid waste management perspective, the responsibility for making such changes lies with product manufacturers.

Product stewardship will be encouraged when the full costs of managing the product as a waste, including all environmental costs, are reflected in the economic decisions of product manufacturers and consumers.

VII.2.3.4. Establishment of environmentally sound treatment and disposal facilities

Even with maximum feasible rates of waste reduction and recycling, there will still be a need for waste treatment and disposal facilities. The state-of-the-art waste treatment and disposal has advanced rapidly in recent years, primarily due to requirements of

environmental regulatory programs. Today, technologies are available to effectively treat and dispose of wastes in an environmentally sound manner.

It is important that new facilities employing these new technologies capable of meeting stringent regulatory standards are established and issued operating permits. Otherwise, older, less environmentally sound facilities will continue to be used resulting in adverse environmental impacts and higher long-term costs.

VII.2.3.5. Rigorous enforcement of environmental laws and standards

The establishment of a national regulatory control program with appropriate legislation, regulations, ordinances and licenses is an extremely important step in protecting human health and the environment from the mismanagement of solid wastes. Furthermore, in the absence of regulatory controls, adequate treatment and disposal facilities are not developed.

Environmental standards must be rigorously enforced in order to assure the public that our solid waste systems are operated in ways that protect human health and the environment. Enforcement must create an incentive for compliance with environmental standards. It must level the playing field so that violators are not at a competitive economic advantage to the good citizens that comply.

VII.2.3.6. Control of transboundary waste shipments and elimination of illegal international traffic

Agenda 21 points out that illegal traffic of hazardous wastes may cause serious threats to human health and the environment and impose a special burden on the countries that receive such shipments. The prevention of illegal traffic in hazardous waste will benefit the environment and public health in all countries, especially developing countries. The Basel Convention on the Control of Transboundary Movements of Hazardous Waste and their Disposal controls transboundary movements of hazardous wastes through a system of prior notification and written consent.

Recognizing that simple elimination of transport of wastes is not sufficient for environmental protection, the Basel Convention also encourages efforts to reduce waste generation, develop national self-sufficiency in hazardous waste disposal, and ensure environmentally sound treatment and disposal systems. Wide-scale ratification and implementation of the Basel Convention are essential to control international shipments of hazardous waste and assure their proper treatment and disposal.

VII.2.3.7. Building institutions and capacity development

Many countries lack the national capacity to handle and manage solid wastes, primarily due to inadequate infrastructure. This includes inadequate facilities, lack of trained personnel, lack of information and monitoring systems, inadequate regulatory programs and insufficient financing. Therefore, establishment of an effective waste management system involves building institutions, training, developing human resources and, in general, building the capacity to control and manage wastes.

Developing the capacity to carry out research and development programs is important to improve understanding of the environmental impacts of solid waste management systems and develop solutions. Research into the social and economic aspects of solid waste management is necessary to understand and better design economic incentives and information and education programs. The results of research programs must be transferred into the field as new and improved solid waste management systems are developed. Therefore, outreach efforts to apply the results of research are essential. Technology transfer to countries with developing economies is especially important.

VII.2.3.8. Full cost accounting consistent with the polluter pays principle

Often the true economic costs of solid waste management are hidden and far removed from producer and consumer decisions. For example, some solid waste management costs are paid out of general tax revenues and are not apparent to the tax-payer. Obviously this does not produce any incentive to reduce wastes. Improper disposal of wastes often requires future clean-up actions that are borne by other parties. Uncontrolled releases from solid waste management units can result in environmental damages with economic implications. All of these costs must be fully accounted for and paid for by the responsible parties. Economic and environmental efficiency depends upon the polluter paying for the costs of pollution and not subsidizing these costs in an indirect way through other parties.

While discussions of such issues tend to dote on economic theory, there are a number of practical approaches that begin to account for these costs and incorporate them into production, consumption and waste management decisions. Pay-as-you-throw programs, which charge waste generators for the amounts of waste discarded is one example that produces an economic incentive to reduce and recycle wastes. Liability standards for waste generators produce a very strong economic incentive for waste reduction and on-site waste treatment. Product labeling programs attempt to influence consumer purchases by identifying recyclable products or products made from recycled materials.

VII.2.3.9. Public participation and education

Providing data and information to those who make or influence decisions can lead to voluntary actions with significant environmental benefits. A good example is when various production facilities are required to inform the public of the release of certain toxic wastes to the environment. This can result in public demand for a reduction of such releases and encourage voluntary industry programs to reduce these wastes. Public information is a powerful tool that can stimulate real results and an informed public can be an effective force in environmental protection.

However, it is important to provide the public with accurate and scientifically sound information. Environmental education is very important and there is a need for: (1) support for curriculum development on solid waste management and environmental issues; (2) assistance for teacher training; (3) scholarships and fellowships for educational programs; and (4) incorporating environmental and solid waste management issues into curriculum for students of engineering, law, science, business, economics and other disciplines. It is very important to increase environmental literacy to build public support for programs to train future generations of solid waste management and environmental professionals.

VII.2.3.10. Integration of waste policies with other international and national policies

Many national and international policies can have a strong influence on solid waste management practices. Consider the effect of: (1) energy policy on the incentives for waste-to-energy facilities; (2) transportation policy on freight charges for recycled materials; and (3) agricultural policy on the uses of sludge as fertilizers or soil conditioners. Other examples include the effect of financial policy on investment into environmental technologies and military policy's effect on clean-up of defense installations. Solid waste management professionals must play a role assuring the solid waste management implications of these policies are assessed in national and international forum.

VII.2.4. Concluding remark

In summary, there remains a tremendous opportunity to improve waste management practices in the future. However, in order to accomplish this it will be necessary for solid waste professionals to augment their technical and engineering skills. Any vision for improvement of solid waste management practices, must include the development of a professional work force, in both the public and private sector, capable of dealing with issues such as waste and toxic reduction, product design, market development, public information and education, enforcement strategies, research and development, technology transfer, and economic incentives. National Solid Waste Associations of different countries, among them SWANA – The Solid Waste Association of North America, through its affiliation with the International Solid Waste Association can play an important role in defining solid waste management practices that are consistent with sustainable development, and in helping solid waste management professionals bring about continuous improvement in solid waste management worldwide.

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