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The Role of Ecological Chemistry in Pollution Research and Sustainable Development

Edited by
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Gheorghe Duca

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The Role of Ecological Chemistry in Pollution Research and Sustainable Development

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Series C: Environmental Security

The Role of Ecological Chemistry in Pollution Research and Sustainable Development

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PREFACE

Sustainable Development has become the leading concept of the 21 century. It describes a development, which agrees with the needs of the present generation but does not endanger the chances of the coming generations to satisfy also their needs. “Sustainable development” has become an important general goal for all fields of life like economy, ecology and social balance. The development and shaping of our future has been discussed internationally like on the summits of the Conferences in Rio and in Johannesburg. But this is also a topic on national base in various countries. Leading authorities in various fields of economy and politics have also accepted this concept.

Although the concept of sustainable development has been generally accepted, there are still problems how to achieve and evaluate these general goals. It is clear that the definitions about the prime needs vary from man to man, from country to country and from continent to continent. **But pollution does not respect national borders.** Therefore, it is necessary to develop the politics of economy, ecology and social demands by a synergistic way that they are strengthened by each other. If it is not possible to stop tendencies, which threaten the future quality of life, the cost demands of societies will dramatically increase and negative tendencies will become irreversible.

The European policy agrees to go a common way of sustainable development and to establish the general conditions for this. The coming years will show how well the defined model can be realized. This is the main task for politics. But other subjects like NGOs, associations of research institutions and the industry as well as organizations for the protection of nature play also an important part to develop the model of sustainable development.

The Commission of the German Parliament proposed the following ecological rules for a sustainable development:

- The rate of the use of renewable resources should not exceed the rate of their regeneration. This corresponds to demanding the sustainability of ecological performance, i.e., (at least) a sustainability of an ecological capital defined by its functions.
- Emissions to the environment should not exceed the capacity of individual ecosystems.
- The timeframe of anthropogenic impacts on the environment must be in a balance to the timeframe of the reaction ability of relevant natural processes in the environment.
- Dangers and risks for human health resulting from anthropogenic activities must be minimized.

Research and innovation are preconditions for the transformation of economic and social processes in favor of a sustainable development. Chemistry, the science and practice of the transformation of matter, is of central importance thereby.

NATO Advanced Research Workshop on ***The Role of Ecological Chemistry in Pollution Research and Sustainable Development*** aimed to bring together scientists from different fields of Ecological Chemistry and Sustainability from Eastern, Western and Southern Countries in order to present their recent research findings and to exchange ideas how to overcome the problems of environmental pollution and how to move towards a sustainable new world. This workshop was co-organized by Braunschweig University of Technology from Germany and the Academy of Sciences of Moldova, being supported by NATO Science for Peace and Security Programme. Thirty-four prominent scientists and specialists in Ecological Chemistry from thirteen countries contributed with oral and poster presentations.

The workshop was the continuation of a series of international events on Ecological Chemistry held in Chisinau, Moldova in 1995, 2002 and 2005. During the last International Conference in 2005, it was concluded to strengthen the interactions between the scientists in the field of environmental chemistry from Western and Eastern Europe, USA, Arab and NIS Countries to promote the exchange of the latest experience and closer involvement of scientists in international cooperation. The event was proposed to be held in Moldova in order to involve as many scientists as possible from the NIS countries and hence to strengthen the links from both parts of the political world.

The objective of this NATO Advanced Research Workshop was to present examples of the state-of-the-art of pollution research in the NIS, Middle East and Western European Countries on Soil and Water Pollution and then to discuss on promising approaches and strategies for environmentally friendly technologies towards a sustainable development incl. capacity building by education. It was aimed.

- To review a set of ecological chemistry issues from pollution research to sustainable development relevant to regional and international cooperation.
- To explore ways of strengthening the role of researchers in environmentally friendly policies and decision making in the national and regional contexts.
- To enhance the role of ecological chemistry in society and the building of knowledge societies based on a peaceful development in Western and Eastern Europe, USA, Arab and NIS countries.

As responsible co-directors of this workshop and editors of this book we hope that the scientific contributions and outcomes of intensive discussions attach great importance to this event.

Acknowledgements

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Scientific Content

The NATO ARW Meeting entitled **The Role of Ecological Chemistry in Pollution Research and Sustainable Development** was scheduled in **six sessions** dealing with **(1)** Organic Pollutants and POPs in the Environment, **(2)** Water Pollution and Wastewater Treatment, **(3)** Soil Pollution and Prevention, **(4)** Waste Management, **(5)** Risk Assessment, Mitigation Measures and Environmental Awareness, and **(6)** General Discussion, Conclusions and Recommendations.

In the **Session 1**, an overview of **POPs Management in Moldova, Ukraine and Turkey** was given as an example. All these three countries already approved the POPs convention of Stockholm and are presently making efforts to take an inventory and to manage the POPs stockpiles. In each case they established POPs teams which are working on this subject. Besides POPs, they are also working on the problem of obsolete pesticides which are partly listed up within the POPs. The overall goals include developing a National Implementation Plan NIP, to inform and make aware public and the stakeholders for participation, and to work on legal frameworks which are in agreement with the EU directives. Besides this planning work, POPs have to be registered, the stockpiled substances partly repacked in suitable containers, and transported to destruction facilities. What is lacking of is the partly non-availability of sufficient capacities of such plants for POPs destruction in these countries likely resulting in the problems of trans-boundary transportation of hazardous wastes across Europe. Further topics in this session dealt with the problems of **brominated flame retardants** and their solution, **pharmaceuticals and personal care products** and their behaviour in wastewater treatment plants, and occurrence of **chlorinated dioxins and furans in Venice Lagoon**.

The **Session 2** gave first an **Overview of Water Research and Managemen**t exemplified at the case of Moldova and continued with two sets of presentations showing the main aspects in water research: (i) **Fundamental Research** on Phys.-Chem. Processes occurring in natural and technological waters and study of the reaction mechanisms and intermediate products, and (ii) the **Applied Aspects** of Wastewater and Sludge Treatment and Reuse, with the recovery of specific elements from it. As a conclusion, one may note that many key fundamental and applied issues of water pollution and wastewater treatment were discussed at the workshop. The presentations and discussions have demonstrated that the scientists have in general a close approach in studying and explaining the natural processes in waters, and elaboration and application of water treatment, supply and reuse. The presentations have elucidated the various sides of the same paramount problem, which is faced by the mankind nowadays – research of the phenomena occurring in natural and wastewaters, with the scope to provide the sustainable management of waters and protect the water resources. Only such approach would enable to develop and implement the model of sustainable development that has no alternative. Although the presentations contained the information, experience and data directly related to the original research and problems in the specific countries, however, their importance cannot be limited only by these respective countries. In a broader sense, the results presented can be used by the research community and water systems managers worldwide.

The presentations in the **Session 3** can be concluded as follows: Soil pollution and degradation brought about by chemicals for plant protection, irrigation water with an increased degree of mineral content, oil products, exhaust gases, industrial wastes, organic wastes from animal manures, and humus losses by soil erosion. In order to preserve the soil fertility erosion should be prevented; optimal doses of organic fertilizers, compost or natural organic matters should be applied. Natural organic matter, especially humic substances exert important protective effects in soils for plants, surface and ground waters. The use of organic amendments in soil will not only has positive effects on soil fertility and agricultural production, but also contributes to protect soil and related environment from organic pollution. Soil amendment polymers like hydrogels also improve soil fertility especially in degraded soil in semi-arid climates and desert areas. Veterinary medicinal products VMP and biocides for disinfection in stables enter manure and following the agricultural soils depending on the persistence of these substances. Development of Technical Guidance for laboratory testing on degradation of VMP and biocides in manures and degradation and sorption in soils thus may sustainably contribute to more sophisticated prediction the fate of these bioactive substances before application.

Session 4 dealt with the **overall** as well as **particular aspects of waste management**. According to the existing management scheme, the wastes produced in the households are collected commingled and transported to landfills or dumping places by the municipalities. These need to be improved in most countries. Investigations are performed in order to re-structure the waste management in legal and technological aspects, according to the rules of sustainable waste management. Wastes contain hazardous constituents but can also be considered as a valuable resource for recycling. It is possible to gain money and save significant amount of resources by implementing the right collection, recycling, and treatment options and technologies. In low income country the first step of a suitable waste management is separation at source. The produced waste can be separated into wet and dry fractions in order to make the further processing of the recoverable material more easy. Drop-off centers for paper and glass can be also installed. In order to increase the amount of recoverable material it is essential to incorporate the informal sector (street collectors) into the existing system. The biochemical stabilization of waste before land filling is supported by the humification of organic matter. Industrial hazardous wastes need a special attention. This was demonstrated for phosphate sludges which could be successfully solidified in Turkey. Further options are recycling in the automotive industry and the production of phosphate fertilizers that are an increasingly limited resource for agriculture. Winery wastes contain highly valuable natural compounds like tartaric acid that can be isolated in industrial processes. Pathogens and chlorinated organic substances can be treated through gamma-irradiation and/or via environmentally-friendly heterogenic chemical catalysts.

As an important issue, **Risk Assessment, Mitigation Measures and Environmental Awareness** were dealt with in **Session 5**. For the purpose of risk assessment monitoring with biosensors are developed and used successfully. The knowledge and awareness of public groups for environmental problems were investigated comparatively in two different countries for school pupils, students, and adults. Younger people proved to have more knowledge on these issues than the older ones, since these subjects are introduced into the curricula just recently. It is, therefore, important to teach different aspects of environmental protection and sustainability at each level of education, beginning at primary and secondary schools, continued at higher education, and finally also taught in vocational and further education. **Teaching sustainability** for students of chemistry as future experts for hazardous substances and having enormous influence on production processes and emissions is of obvious importance. An internet based laboratory course for organic chemistry was demonstrated which does consider environmental safety as well as of sustainability. This course material is already translated into several languages and is available for free also in developing countries. Such approaches will help to disseminate the outcomes of scientific investigations and hopefully make people and public authorities aware of environmental protection and sustainability.

In the last **Session 6**, the participants discussed on all presentations given in each session and acknowledged the outcomes of this workshop. They identified urgent subjects that should be further treated in **Topical Networks**. Herewith, the workshop participants will sustain the links to international colleagues they made during this workshop. These **Networks** are (i) POPs Management and Mitigation, (ii) Brominated Flame Retardants and Alternatives, (ii) Water Management, (iv) Waste Management, (v) Soil Sciences and Humics, (vi) Sensors for Environmental Monitoring and Control, and (vii) Environmental Education. Each network will be chaired by an elected expert who is responsible for future cooperation of network partners. It was recommended to organize a follow up meeting in 2010 in Turkey and to report on the achievements obtained in the meantime.

Achievements

The workshop deliverable was the draft document with conclusions and recommendations that was further discussed and modified considering participants' comments. During the closing session it was decided to create collaboration networks on workshop topics in order to sustain the links between the participants also in future.

The participants further agreed on the organization of a follow-up workshop or symposium in Ecological Chemistry in Konya, Turkey in 2010.

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CONTENTS

PART I. ORGANIC POLLUTANTS AND POPS IN THE ENVIRONMENT – OCCURENCE, FATE AND PREVENTION MEASURES

BROMINATED FLAME RETARDANTS IN THE ENVIRONMENT

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Abstract. Environmental contamination by brominated flame retardants (BFRs) has received a lot of attention in the scientific literature since the late 1990s. A number of BFRs, such as penta- and octabromodiphenyl ethers (penta- and octaBDE's) and hexabromocyclododecane were identified as bioaccumulating and potentially toxic compounds. For others the databases are still incomplete. This chapter gives an overview of recent trends of BFR concentrations in the environment, with some attention to the analytical methods and difficulties, and their toxicology. The European ban on penta- and octaBDE's has already initiated decreasing trends in their environmental levels in Europe. However, the concentrations of these BFRs in the USA are considerably higher than in Europe and decreasing trend have not been observed yet. In sediments, much higher decaBDE concentrations have been found as compared to pentaBDE concentrations, both in Europe and the USA. DecaBDE was recently banned in Europe for use in electric circuit boards, but applications in textile and furniture are still allowed. Endocrine disruption, often through the thyroid gland is the most worrying effect of several BFRs.

Keywords: brominated flame retardants, polybromodiphenyl ethers, hexabromocyclododecane, decabromodiphenylethane, environment, analysis, risk.

1. Introduction

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) have been found in the environment and in food since the 1960s [24, 43]. Although most of these chemicals have been phased out, residues are still being found, emphasizing the persistent character of these POPs [10]. On top of that, chemical contaminants that remained undiscovered in food and the environment for many years have recently been identified. One such category is the group of brominated flame retardants (BFRs). About 75 commercially available BFRs are currently being used worldwide to flameproof electronic

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equipment such as personal computers and televisions, but also in upholstery textile, building materials, planes, cars, etc. [13]. The amounts in which they are added to the plastics or fibers range from 1% to more than 10% by weight. Some BFRs, tetrabromobisphenol-A (TBBP-A) for example, are chemically bound to the materials to be flame proofed, while others, for example pentabrominated diphenylethers (PBDE's) and hexabromocyclododecane (HBCD), are applied as additives. During production, impregnation and after use (end-of-life disposal) both types of chemicals "escape" to the environment and can accumulate in sediments and organisms. Fish and meat, as well as human milk are now known to contain these chemicals at the level of micrograms per kilogram. The important issue is the dose-response relationship: Do the present environmental levels of BFRs cause toxic effects or not and, if not, what are the margins of safety? Since 1998, many studies on BFR exposure have been carried out. PBDE concentrations in North America are ca. 10-fold higher than those in Europe [43], most likely caused by the more stringent fire safety regulations in the USA.

Apart from the well-known polybrominated diphenylethers (PBDE's), other BFRs have been discovered in food and environmental samples. One of them is HBCD, a highly bioaccumulative BFR. TBBP-A is another BFR, which is produced in high volumes. However, this BFR is of a more polar character, and, therefore, does not bioaccumulate as much as most PBDE's and HBCD. Other BFRs, produced in lower volumes, have also been found in the environment today. Examples are pentabromotoluene (PBT) [23] decabromodiphenylethane (DBDPE) [27], 2,4,6-tribromotoluene (TBT) and 2,4,6-tribromoanisole (TBA) [35].

Toxicological information on BFRs came slower than reports on exposure data, partly due to the relatively long time needed for *in vivo* studies. Clearly, the toxic effects of BFRs are different from those caused by chlorinated dibenzo-*p*-dioxins and dibenzofurans and PCBs, as they elicit a much lower response at the Ah receptor or do not activate this receptor at all. Over the last years, increasing evidence has become available that many BFRs are endocrine disruptors [17]. A large European study ("FIRE") on the possible endocrine effects of BFRs has provided evidence for some of these effects [21, 48]. Based on the current knowledge, health risks due to BFR-contaminated food items seem to be limited [31]. However, margins of safety in the USA may be small for some BFRs, and a more precise assessment of those margins is urgently needed.

Following scientific publications on the occurrence of PBDE's in the European environment and a risk assessment was carried out by the European Union, *Pentamix* (technical pentabromodiphenyl ether mixture) and *Octamix* (technical octabrominated diphenylether mixture) production and use was banned in Europe in 2004, recently followed by a ban on *Decamix* (technical decabrominated diphenyl mixture) per 1 July 2008 for use in electric and electronic instruments [49]. DecaBDE may still be used in textiles and furniture, providing that further research on environmental concentrations and fate of this BFR will show that effects are minimal. After the discovery the much higher PBDE concentrations in North America, as compared to Europe, a voluntary production stop of the

Pentamix was seen in Canada and the USA in 2004. However, HBCD, TBBP-A and DecaBDE are still being produced until today. This is understandable as the termination of the *Pentamix* and part of the *DecaBDE* production must have caused a serious demand for alternatives. Non-brominated alternatives, such as phosphorous-based FRs (PFRs) may become available in higher quantities, but the environmental safety of those FRs has not convincingly been demonstrated. Some reports on the presence of PFRs in environmental matrices have seen already in the literature. The outlook for this field is therefore mainly on a search for alternatives for the banned PBDE's and on a demonstration of their environmental acceptability, fire safety and production feasibility. In 2009 a new European research project called "ENFIRO" will start to study the environmental safety of a number of alternative flame-retardants, based on phosphorous, metals, or nanotechnology. This project will include complete life-cycle assessments to ensure the safety of these chemicals throughout their existence, from mining until disposal ("from cradle to grave").

This overview is a summary of the main developments seen recently in the field of environmental issues around BFRs. It certainly does not claim to be complete, as it is almost not possible to keep track of the multitude of studies on BFRs that appear in the literature. A number of good reviews on environmental levels of BFRs have appeared recently. As this paper was presented at a NATO Workshop in Chisinau, Moldova, under the "Science for Peace" Program, this paper also means to be of some help for Eastern-Europe research on BFRs. Trends in environmental levels of BFRs are discussed with reference to recent papers and reviews. Some attention will be paid to the analytical difficulties associated with the determination of BFRs in environmental matrices, and to potential toxic effects of BFRs.

2. Environmental levels of BFRs

BFRs were detected to be present in the environment in 1981 [1]. During the 1980s, not much attention was paid to these compounds, as most of the research in this field was focussed on PCBs and chlorinated dioxins and furans. Only after the reports on PBDE's in stranded sperm whales in the Netherlands [12], and on exponentially increasing trends of PBDE's in Swedish mothers milk [37] many research groups from all over the world started to analyse BFRs in various environmental matrices. Very soon it became clear that in addition to the pentabromodiphenyl ethers (pentaBDE's), represented by the tetraBDE 47 (2,4,2′,4′-tetraBDE) and the pentaBDE 99 (2,4,5,2′,4′-pentaBDE), the decaBDE (BDE209) was by far the highest in concentrations in sediments. The steep increase of decaBDE concentrations in sediments since the late 1970s was convincingly shown by Zegers et al. [50] who determined a suite of BDE's including decaBDE in sediment cores from various places in the world (Fig. 2.1).

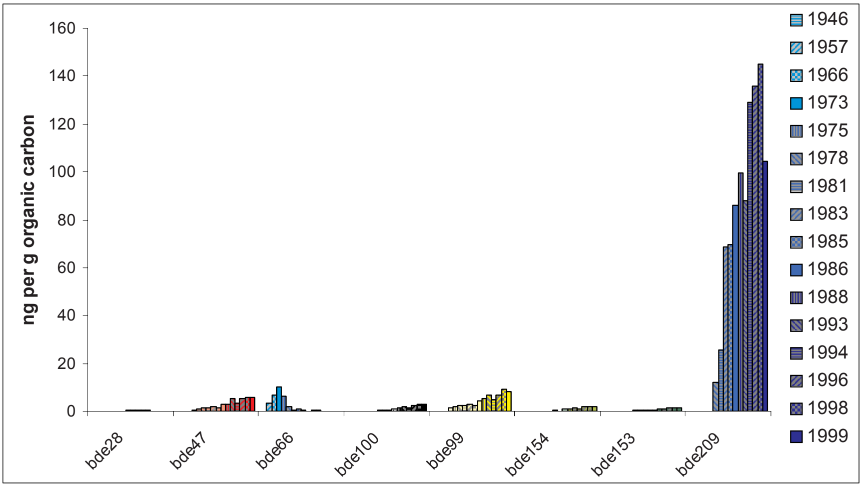

Fig. 2.1. Strong increase of DecaBDE in sediments from the Drammenfjord/Oslofjord, Norway [51].

However, bioaccumulation of decaBDE is limited, possibly due to the extremely low water solubility that makes it difficult for this compound to be transferred from sediments and suspended particulate matter via the water to organisms. The large size of the molecule is also not facilitating bioaccumulation. DecaBDE was, however, found in peregrine falcon eggs from Sweden [34]. This could be explained by exposure of terrestrial birds to soil directly, or indirectly through their preys. Aquatic birds seem to contain less decaBDE, because the fish they consume has also low decaBDE concentrations. This was confirmed by Chen et al. [7] who reported higher BDE levels in terrestrial birds. Following the first bird studies, it was shown that decaBDE and other BDE’s could be present in dust, due to use of it in furniture and possibly electronic instrumentation (TV, computers, etc.). This observation resulted in a different view on human exposure: different from PCBs, BDE’s can be taken up from dust and indoor air. This would imply an extra risk for children. This was made even clearer by Dye et al. [18] who showed a correlation between the occurrence and increase of feline hyperthyroidism (FH) and BDE levels in cats. They proposed cats to serve as sentinels for humans with regard to effects of indoor PBDE contamination. Takigami et al. [45] found substantial levels of BFRs in dust inside TV cabinets. In the most recent review of Law et al. [32] the BDE contamination of dust is emphasised. Harrad and Diamond [22] discuss the contamination of indoor environments through dust. This may represent an important exposure route, which distinguishes the PBDE contamination from that by PCBs, which come mainly though our food. The review on BFR concentrations in the European and Asian environment by Law et al. [32] shows the most recent developments in environmental BFR levels. It covers more than 100 studies on PBDE’s and HBCD in the environment from the period 2005–2007. Together with an earlier review from the same authors [31] it is a comprehensive dataset, which shows global environmental trends in BFR concentrations during the last decade. Generally, trends for PBDE's in Europe and Asia are levelling off, while HBCD concentrations increase at most locations. DecaBDE concentrations also increase in Asia. The authors call for more research into BFR contamination of local populations that are exposed to e-waste recycling activities [20]. Julander et al. [25] reported BDE concentrations in indoor air from an electronics recycling facility in Sweden. Law et al. [32, 36] report a paucity of data on PBDE's, although production is ongoing in Asia and consumption of fish that contains PBDE's is relatively high in some areas such as Hong Kong. Polder et al. [40] and Borghesi et al. [6] presented further evidence of the global distribution of BFRs by their reports on BFR levels in birds and fish from the southern hemisphere, South Africa and Antarctica, respectively. A multitude of data is meanwhile available on PBDE contamination of North America [e.g., 43, 44, 46].

A specific review on HBCD was made by Covaci et al. [9]. The bioaccumulative properties of HBCD are highlighted in this review. Interesting is the predominance of α-HBCD whereas the technical HBCD mixture mainly consists of γ-HBCD. This change in composition is presumably caused by a selective uptake, (partly) caused by the better water solubility of the α diastereomer. Transfer of γ into α-HBCD inside organisms is unlikely, as atoms should change place. During impregnation processes a conversion of γ into α-HBCD may also take place as process temperatures rise to above 160 ºC. This change of diastereomer composition would enable the identification of sources of HBCD pollution: producers when γ-HBCD would be high in water or sediments and users, when α-HBCD would be high. However, due to the complication of the transfer in biota this research has not been successful until today [38]. The further development of the BDE trend in Swedish human milk was shown by Fängström et al. [19], but now including HBCD data (Fig. 2.2).

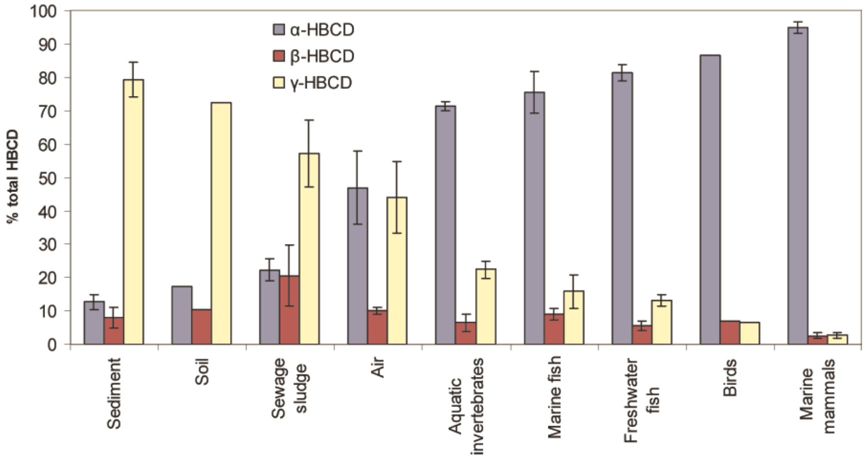

Fig. 2.2. HBCD patterns in biotic and a-biotic matrices [39].

Kierkegaard et al. [26] identified and quantified decabromodiphenylethane (DBDPE) in sediment from the river Western Scheldt, the Netherlands, and in various sewage sludge samples from Sweden. In the Western Scheldt sediment a concentration of 24 ng/g dry weight (dw) was found. Maximum decaBDE concentrations in Swedish sewage sludge were 100 ng/g dw.

3. Analytical issues of BFRs

Lower brominated BDE's are relatively easy to determine [8, 14, 15]. The required methods are basically the same as those used for the determination of polychlorinated biphenyls (PCBs). A Soxhlet extraction with a mixture of polar and non-polar solvents, e.g., *n*-pentane and dichloromethane or *n*-hexane and acetone, or an accelerated solvent extraction (ASE) is followed by a lipid removal step, e.g., on alumina or florisil columns or by gel permeation chromatography (GPC). A further fractionation is normally necessary to isolate the BDE's and a sulphuric acid treatment may be needed in case of dirty samples, to ensure a clean extract. The sulphuric acid may also be combined with a silica gel column. Lipids can also be removed simultaneously with the extraction when using ASE by adding a fat remover to the extraction cell [3–5]. The BDE's are normally determined by gas chromatography in combination with mass spectrometry (GC/MS) [11]. Electron capture negative ion (ECNI) is a sensitive technique for most of the BDE's. However, a drawback is that ^{13}C labeled internal standards cannot be used as the spectra normally only show the bromine cluster, m/z 79/81. Electron impact would be the alternative and allows the use of ^{13}C labeled standards but often lacks the required sensitivity. High resolution (HR) MS is the ultimate, but obviously expensive solution. Interesting results were obtained by comprehensive multi-dimensional GC in combination with ECD or time-of-flight (ToF) MS [28, 29]. The two-dimensional chromatogram makes the use of an MS often redundant.

The analysis of decaBDE is, however, of a different degree of difficulty [16]. Until now, results of interlaboratory studies on decaBDE have been relatively poor, for a number of reasons. These include:

- Possible degradation under influence of daylight
- Poor solubility, also in organic solvents
- High background concentrations, e.g. in dust
- Very low concentrations in biota (if present at all)
- Thermal degradation during the GC analysis
- Degradation in aqueous samples

The fully brominated molecule is instable and may easily loose bromine atoms. DecaBDE may disappear from organic solutions when placed on laboratory benches and in direct sunlight. The use of UV filters at laboratory windows and at fluorescent lightings is, therefore, highly recommended. The solubility of decaBDE in organic solvents used should be checked before preparing stock solutions or highly concentrated extracts. Dust normally contains high concentrations of decaBDE [23]. The laboratory should therefore be kept as clean as possible. Introduction of packing materials in the laboratory should be avoided. Blank analyses should be carried out more frequently than usually. The treatment of the blanks should be identical to that of the samples. When blanks have a shorter residence time at the bench than the sample extracts, deca BDE may remain on the (contaminated) glass wall, whereas it will migrate into the blank when stored for longer periods. This results in unrealistically low blank values. Thermal degradation in the injector of the GC or at the GC column [30] should be checked and minimized by using short and narrow, thin film GC columns, moderate injector and column temperatures (<270°C), and short injector residence times, or cold injectors. A short residence time can be achieved by using a pressure-pulse splitless injection. Longer residence times will cause degradation problems, not only for decaBDE, but also for other higher brominated BDEs. Fortunately, the use of ^{13}C-labeled internal standards is possible for decaBDE as the m/z 486.4 and 488.4 can be used for quantification with GC/ECNI-MS.

Since 2000, the analysis of HBCD has been carried out in a relatively small number of laboratories. Initially, total HBCD was analyzed by GC, together with the PBDEs. However, the three diastereomers (α-, β- and γ-HBCD) are normally not separated. This problem is compounded at GC temperatures >160 ºC, at which the isomers tautomerize [39]. As the diastereomers have different response factors, a reliable total-HBCD concentration cannot be determined by GC. Also, the broad HBCD peak causes CV values higher than those of the BDEs. The solution to this problem was offered by Morris et al. [38], who developed an isomer-specific HPLC method for HBCD. In addition to the three HBCD diastereomers, TBBP-A can be determined in the same analytical run. The identification and quantification of the three HBCD isomers is important because the isomeric patterns differ under different production conditions, and also differ between biota and sediments. The sensitivity of the HPLC method is nowadays comparable to that of the GC-ECNI-MS method, which makes it less suitable for analyzing samples with extremely low HBCD concentrations. A prerequisite is the use of a triple quadrupole (QQQ) MS detector. Meanwhile, showed that there are also a number of enantiomers of HBCD that can be separated and determined by HPLC using chiral columns.

In spite of its high production figures (highest of all BFRs), TBBP-A is not frequently analyzed in environmental laboratories. One reason may be its lower bioaccumulation potential, since environmental concentrations are generally lower than those of the PBDEs and HBCD. However, TBBP-A, being a phenolic compound, may have a greater adverse effect on humans and wildlife. Also, more complicated clean up methods are needed for a proper determination of TBBP-A and that may further deter analysts from measuring it. Direct injection into the

GC without derivatization is not a viable option. Acidification is required after extraction prior to HPLC determination. These steps normally introduce additional errors and/or losses. The use of ^{13}C-labeled TBBP-A may help to reduce the effects of such errors. At present, the determination of TBBP-A by HPLC, together with the HBCD diastereomers, seems to be the simplest, most attractive option [39]. Until more data are produced in interlaboratory studies, TBBP-A results appearing in the literature should be carefully scrutinized for appropriate internal quality assurance (QA).

The analysis of DBDPE was reviewed by Kierkegaard [28]. This compound has a great similarity with decaBDE, being fully brominated as well. The difference is the ethane in the center of the molecule instead of the oxygen atom. It is presumable used as an alternative for decaBDE.

4. Toxicology and risk assessment

Different from PCBs BFRs constitute a diverse group of compounds that all have their specific characteristics. Consequently, it is not possible to generalize the toxic effects of BFRs. Until now most effects found in toxicological studies on BFRs point to potential endocrine disrupting effects. A review on endocrine disrupting effects was recently made by Legler [33]. *In vivo* studies have found effects of various BFRs on thyroid hormone, estrogen and androgen pathways. Neurodevelopmental effects have also been found. However, in many studies a wide margin of safety between effect concentrations in rodent studies and environmental and human concentrations has been found. Nevertheless, and in particular for the higher levels in the USA for most BFRs, health risks due to chronic exposure cannot be excluded. Further chronic studies are necessary, which should definitely include metabolites as they may be more potent than the mother compounds of several BFRs. Kuiper et al. [30] emphasize the high sensitivity of the zebra fish reproduction assay and found a statistically significantly reduced larval survival and *non-significant* indications for decreased egg production at internal levels that were more than 55 times the highest environmental recordings. Those results indicate limited risk for endocrine or reproductive effects of current environmental PBDE contamination in fish [31]. Rattfelt Nyholm et al. [41] have studied the maternal transfer of BFRs with zebra fish, finding higher BFR concentrations in the fish eggs.

Bakker et al. [2] recommend further monitoring of BDE's in Dutch food although the concentrations of, e.g., BDE99 are well below the human exposure threshold level. The HBCD intake in the Netherlands from fish is estimated at 0.12 ng/kg bodyweight/day [48].

5. Conclusions

A number of BFRs are widespread in the global environment. Also, they occur in food and feed from all continents. There is generally agreement among scientists, and between scientists, authorities and the industry about the undesirable properties of the Penta- and Octamix, and HBCD. These compounds will no doubt be phased out in the near future. Debate is ongoing on decaBDE. For other BFRs, there is little information available. Concentrations of DBDPE have been reported in biota and sediments. TBBP-A is only found at relatively low concentrations in biota but due to the limited amount of information on the possible effects of this compound it remains unclear if effects occur at these relatively low environmental levels. Even less is known about pentabromotoluene and other BFRs. This clearly calls for more studies on exposure and toxicity of BFRs. Future up-to-date information on BFRs and environmental contamination will no doubt be available through the BFR symposia that are organized every 3 years, with the next one in 2010 in Kyoto, Japan, through the annual International Symposium Dioxin, with the next one in 2009 in Beijing, China, and though the annual Canadian/American BFR workshops, the next one being organized in 2009 in Ottawa, Canada.

BFRs will not be the last group of chemicals that we will see occurring in our food and the environment. The vast number of chemicals that we produce and need in our modern society for all sorts of purposes from fire safety to pharmaceutical applications will continue to contribute to the spectrum of chemical residues present in our food and in the environment. Knowledge on existing classes of chemicals and modern analytical and toxicological techniques will help us make an inventory of the associated risks in an early stage, long before those residues reach levels of concern.

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FATE OF PERSISTENT ORGANIC POLLUTANTS IN THE VENICE LAGOON: FROM THE ENVIRONMENT TO HUMAN BEINGS THROUGH BIOLOGICAL EXPLOITATION?

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Abstract. The Lagoon of Venice has been receiving discharges of many classes of persistent organic pollutants (POPs) that have been accumulating in sediments and marine organisms and might represent an indirect threat to human health. In particular, the intensive harvesting of Manila Clam (*Tapes philippinarum*) and other traditional fishing activities carried out in the lagoon represent the highest direct source of risk for human health. This paper presents an overview of sources and fates of dioxins, polychlorinated biphenyls and hexachlorobenzene in the Lagoon of Venice. Pollution data of environmental matrices (atmospheric depositions, water and sediments) and biota (clams) of the lagoon are presented for describing the environmental and biological contamination. Evidences on possible human contamination are derived from recent data of POPs in mother milk and blood serum of Venetians with different work exposure and food habits. This overview evidences a critical environmental state for some areas of the Venice Lagoon and confirms a non-negligible human health risk for regular shellfish and fish consumers. The overview supports the need for keeping some lagoon areas restricted to fishing and for maintaining the current situation under monitoring.

Keywords: POPs, dioxins, polychlorinated biphenyls, hexachlorobenzene, monitoring.

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1. Introduction

Despite regulations and monitoring programs coastal areas are inevitably receiving organic pollutants that are waste products of industrial and other human activities in the mainland. In particular, the persistent organic pollutants (POPs), that are characterized by low degradation rates and high affinity to lipids and organic matter, accumulate in coastal sediments. Therefore, POPs might be available directly to benthic species and then indirectly transferred to other organisms of the food web even several years after their discharge to the environment. Human beings, through the exploitation of coastal resources, are the top predators of marine coastal food web and thus, other than the producers, are the final receptor of these pollutants [15]. In degraded situations the fishery exploitation and consumption of seafood might enhance human health risks that need to be considered as a further critical effect of POPs and included in the ecosystem health assessments [12].

In this work the case of the Lagoon of Venice (Italy) is presented that has been receiving discharges of many classes of pollutants, including POPs [3]. This ecosystem is also providing several services to local population, including traditional fishing activities and intensive exploitation of Manila Clam (*Tapes philippinarum*). Despite the many possible fates of POPs in this system, these exploitation activities might represent the highest direct source of risk for human health. Here, an overview of sources and fates of dioxins, polychlorinated biphenyls and hexachlorobenzene in the Lagoon of Venice are presented, using the data regarding contamination of environmental, biological and human matrices.

2. The Lagoon of Venice

The Lagoon of Venice (Adriatic Sea, Italy), is the largest lagoon in the Mediterranean Sea. It covers an area of about 500 km^2 and has an average depth of 0.7 m. The lagoon is characterized by large shallow areas divided by a network of deeper channels connected to the Adriatic Sea by three narrow inlets that allow seawater circulation. Thus, these features result in a complex geomorphological, hydrodynamic, and ecological system.

In the last century an industrial pole on the lagoon shores has been developed into one of largest industrial areas in Europe: the Industrial Zone of Porto Marghera. Here, a very broad range of activities and processes like non-ferrous metal production, chemical industry, municipal, hospital and hazardous waste incineration have been important sources of dioxins and dioxin-like compounds as well as other classes of pollutants that were released into the environment [3,4]. Moreover, discharges from urban areas (mainly cities of Venice, Chioggia and Mestre), diffuse pollution in the watershed basin, sewage treatment plants, leakage, and incomplete fuel combustion from boats represent secondary sources of POPs to the lagoon.

The Lagoon of Venice is also an ecologically important saltmarsh environment being a wintering site for seabirds [1] and nursery area for many fish species [13]. Natural resources of this productive ecosystem are exploited since centuries by traditional fishing and farming activities producing between 3,000–6,000 t year^{-1} of fish in the last decades. Moreover, the benthic bivalve Manila Clam (*Tapes philippinarum*) was introduced in the 1980s and subsequently a mechanical clam harvesting activity was developed, exploiting the entire central part of the lagoon and providing the fish market with up to 40,000 t year^{-1} of clam, i.e., more than 50% of the Italian clam production [6]. Despite that the clam harvesting is not allowed nearby the Industrial Zone, the contaminated clams are illegally caught in this highly polluted area, and fish indirectly contaminated by food web accumulation [2] might reach the consumers and represent a direct source of risk for human health.

3. Environmental contamination

Monitoring of POPs in several sampling stations in the Lagoon of Venice have been carried out in the last decade for evaluating the contamination of different environmental matrices, thus including the fall out, water column, and sediments (see Fig. 3.1).

3.1. Atmospheric depositions

In a study conducted in 2002–2003, 58 samples of atmospheric depositions were collected using bulk samplers placed in seven stations located in different areas of the lagoon [14]. Average daily depositions of PCB, PCDD/F and HCB in stations around the industrial area resulted in 13,669, 278 and 2,297 pg m^{-2} d^{-1}, respectively, and toxicity equivalent to 6.5 pg I-TE m^{-2} d^{-1}. For comparison, daily depositions in the city of Venice were on average 1,348, 35 and 247 for PCB, PCDD/F and HCB, respectively, and toxicity equivalent to 0.9 pg I-TE m^{-2} d^{-1}. In general, depositions of POPs in industrial area were one order of magnitude higher than in other stations.

The comparison of the results of the study conducted in 2002–2003 with fallout estimated for 1998–1999 evidenced a decrease of PCB and HCB depositions but toxicity remained high because of important contribution from PCDD/F. In fact, toxicity of PCB and PCDD/F deposition was calculated as 233 and 280 mg I-TE yr^{-1} for 1998–1999 and 2002–2003 samples, respectively [14]. The results showed that the industrial area is still an important source of atmospheric depositions containing POPs. These findings were confirmed by the new data collected in 2004 [5].

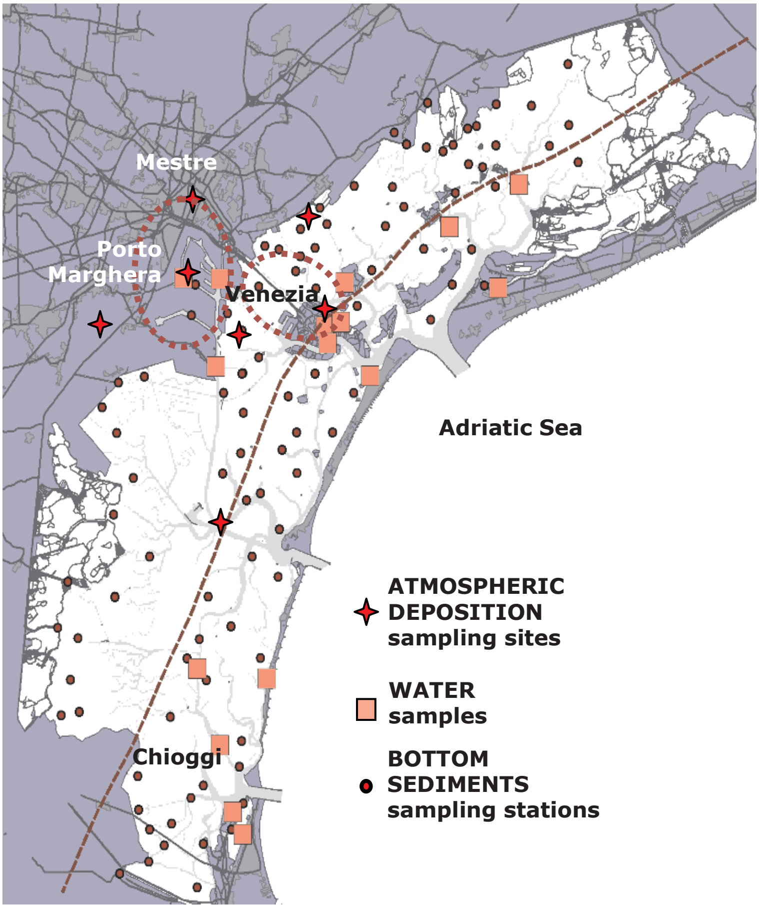

Fig. 3.1. Sampling stations for POPs' monitoring in the Lagoon of Venice.

3.2. Water column

In a study conducted in 2001, water samples were collected monthly in 16 stations of the lagoon [7]. Average concentrations in lagoon waters of PCB, PCDD/F and HCB were reported as 0.3 ng l^{-1}, 2 pg l^{-1} and 0.03 ng l^{-1}, respectively. Water of industrial channels resulted in having concentrations one order of magnitude higher, i.e., 2.1 ng l^{-1}, 17 pg l^{-1} and 0.27 ng l^{-1} for PCB, PCDD/F and HCB, respectively. However, also the water of canals in the city of Venice showed high concentrations 2.6 ng l^{-1}, 12 pg l^{-1} and 0.09 ng l^{-1}, respectively, providing evidence of non-negligeable secondary sources of these pollutants from urban area. In terms of toxicity, in fact, the industrial area was the most important source (0.36, 0.26, 0.05 pg I-TE l^{-1} for industrial channels, city canals, and lagoon, respectively).

3.3. Sediment contamination

In spite of water circulation, the lagoon sediments represented the main sink for POPs and today constitute the main burden of PCDD/F, PCB, and other persistent organic pollutants. Since 1997 several studies have been carried out for measuring concentrations of POPs in superficial sediments (0–15 cm) at different sites of the lagoon (see Fig. 3.1). Average values of POPs concentrations in sediments of homogeneous areas of the lagoon have been compared with background concentrations measured in core samples. In sediments of industrial channels, results evidenced concentrations of 810, 14 and 260 μg kg^{-1} dw for PCB, PCDD/F and HCB, respectively (dw = dry weight). Outer lagoon was much less contaminated with concentrations of 5, 0.3 and 0.2 μg kg^{-1} dw, respectively. However, the comparison is even more critical when background pre-industrial levels are used, i.e., 0.001, 0.03 and 0.1 μg kg^{-1} dw. Although the sediment contamination of Venice canals was quite high (PCB = 600 μg kg^{-1} dw; PCDD/F = 0.5 μg kg^{-1} dw), the results evidenced the industrial area as the primary source of POPs discharges in the Lagoon of Venice ecosystem. Moreover, the sediments of the industrial channels presented the toxicity three orders of magnitude higher than background values and two orders higher than outer parts of the lagoon [5].

These data represent a quite robust description of the POPs contamination of the lagoon and evidenced the maxima of concentrations in the channels around the industrial area. In particular, the superficial sediment concentrations of POPs with a toxicity higher than 2,500 ng I-TEQ kg^{-1} dw can be found in the channels of the industrial area. Moreover, the integrated enrichment factors, calculated on the basis of ratio between the actual and background concentrations of POPs, clearly evidenced the hot spots of pollution in the inner-central part of the lagoon around the industrial area of Porto Marghera [5].

Moreover, the PCDD/F fingerprints in the sediments of different areas were compared with those of the industrial and urban wastes (sewage treatment plant), showing clearly that these hot spots are related with the discharges and wastes from the production of dichloroethylene (DCE) and vinyl chloride (VCM) for PVC production.

4. Contamination of biota

The high contamination of lagoon sediments in certain areas is a source of serious concern for the possible bioavailability of POPs to the benthic community and their entering into the lagoon trophic chain [2]. In particular, due to its intense exploitation and its strict benthic ecological properties, Manila Clam (*Tapes philippinarum*) is the most studied species in terms of contamination with POPs [8–11].

4.1. Contamination of Manila Clam

Several POPs data for both sediments and Manila Clam evidenced that sediments are the major direct source of contamination for this benthic bivalve. Moreover, dioxin fingerprints for both sediments and clam flesh highlight the main source of POPs for different areas of the lagoon [5].

The ranges and the average values of the toxicity equivalent in the clam flesh in the three monitoring area in the northern, southern and central part of the lagoon has been compared with those concerning the clam sampled nearby the industrial area [11]. PCDD/F and PCB concentrations expressed in toxicity equivalents were quite similar in the three fishing areas (0.2 pg WHO-TE g^{-1} ww; ww = wet weight) and were approximately an order of magnitude lower than those found in the canals of the industrial zone (2 pg WHO-TE g^{-1} ww), where the fishing is forbidden. However, it is worth noting that concentrations up to 9 pg WHO-TE g^{-1} we have been found in flesh of clams collected in the industrial channels [11].

The relative concentrations of the main dioxin congeners in both sediment and clams strongly suggest that the sources of contamination in the three monitored areas are different. In fact, the fingerprint concerning both the sediment and the clams nearby the industrial area was characterized by the highest percentage of OCDF. The percentage of OCDF was lower in the other three areas and reached its minimum in the South Lagoon, where the fingerprint was characterized by the highest percentage of OCDD, which is usually found in the discharges of urban waste water treatment plants and can be released into the environment also by combustion processes and boats engine [11].

This finding indicated that the central and north lagoon was affected by both urban wastewater and industrial pollution. However, the higher OCDF percentages with respect to OCDD in the industrial area suggest that the contamination is related, directly or indirectly, to industrial activities. Interestingly, the dioxin fingerprints for clam and sediment pertaining to the same area were remarkably similar: This finding supports the hypothesis that the sediment is still the main source of contamination for clam and suggests the presence of a quantitative relationships between the equivalent toxicities in the abiotic and biotic compartment.

In this framework a regression model between sediment and clam's toxicity has been identified as a valuable tool for health risk assessment [8]. In fact, the regression between the logarithms of the WHO-TE in clam flesh and sediment was found to be statistically significant for both PCDD/F and PCB.

This prompted the development of experiments consisting in the displacement of clam from a polluted to a cleaner area for allowing natural detoxification from POPs [8,10]. The results evidenced the high detoxification rates, and a bioaccumulation model provided basis for estimating the capabilities of clam to detoxify [10]. The findings all concur in evidencing that clams contaminated by industrial pollution underwent a very rapid decline of TE when the specimens were harvested and transplanted into the areas with low contaminated sediments. This culture-based fishery regime might represent a possible solution for avoiding an incidental direct human exposure to dioxins and PCB through contaminated clams reaching the fish market.

5. Human contamination

Although the overview of environmental and biological POPs contamination might evidence the possible sources of these pollutants to human beings through air, water and food, it is difficult to evaluate and control these sources. Direct and indirect sources of POPs were assessed in order to test the possible human contamination, and recent data on mother milk and on blood serum of Venetians with different work exposure and food habits were compared with other sources.

5.1. Blood serum

In a recent work, two datasets on POPs concentrations in serum referred to Italian men with different exposure histories were presented and compared [8–10]. One dataset, collected in 1998 and particularly focusing on dietary exposures, regarded the determination of PCB and PCDD/F in blood serum of 41 selected volunteers, was divided into two groups: 22 consumers eating large amounts of locally caught fish and shellfish, and 19 people consuming very little fish of any kind. The second dataset represents the concentrations of PCB, PCDD/F and HCB in serum samples collected in 2007 and refers to 16 Italian volunteers with diverse exposure histories: Six individuals have been employed for several years in chemical plants of Porto Marghera Industrial Zone, whereas for the other ten people no particular concerns regarding their exposure life histories are known [9]. The results obtained are compared in Figs. 5.1.1–5.1.3 for PCDD/F, PCB and HCB respectively.

Results for PCDD/F (Fig. 5.1.1) show an average toxicity of 13.91 and 19.33 pg TE g^{-1} lipid for low ($n = 19$) and high fish consumers ($n = 22$), respectively; whereas values of 16.08 and 9.41 pg TE g^{-1} lipid were found for individuals subjected to occupational exposure ($n = 6$) and for the others with unknown exposure life-histories ($n = 10$), respectively.

The results for PCB concentrations in blood serum (Fig. 5.1.2) show a significant difference between low and high fish consumers with averages of 9.30 and 30.68 pg TE g^{-1} lipid, respectively; whereas the average values of 22.00 and 6.77 pg TE g^{-1} lipid were found for occupational exposed and the others, respectively. On the basis of these results [9] concluded that total PCB TE values are significantly different either between the groups with different dietary habits (low and high fish consumers) and between the groups distinguished on the basis of occupational or general exposure. Moreover, PCBs TE values for high fish consumers in Venetian population are comparable with the values of the group of people subjected to workplace exposure. The data for HCB concentrations (Fig. 5.1.3) evidenced the sensible difference between the concentration in blood serum of males subjected to workplace exposure (0.073 µg HCB g^{-1} lipid) and to general exposure (0.023 µg HCB g^{-1} lipid).

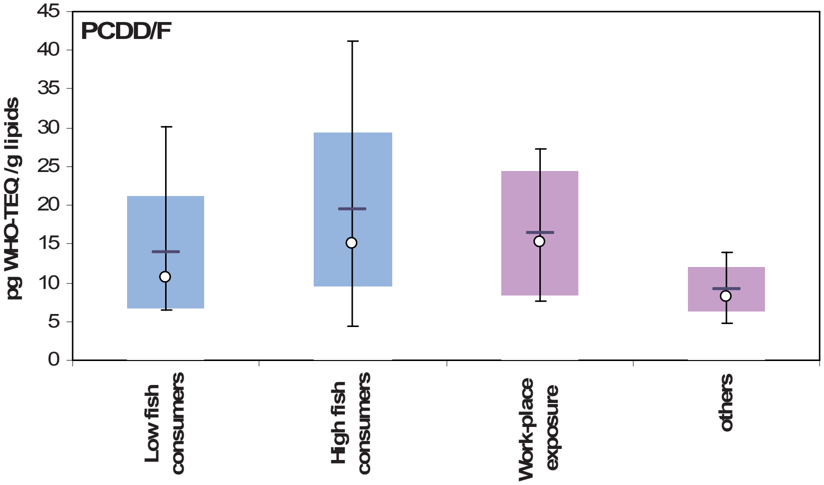

Fig. 5.1.1. PCDD concentrations in blood serum.

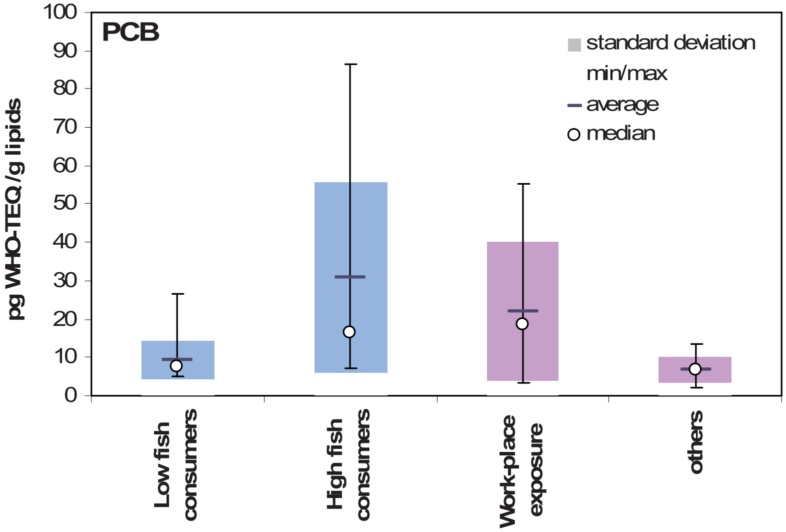

Fig. 5.1.2. PCB concentrations in blood serum.

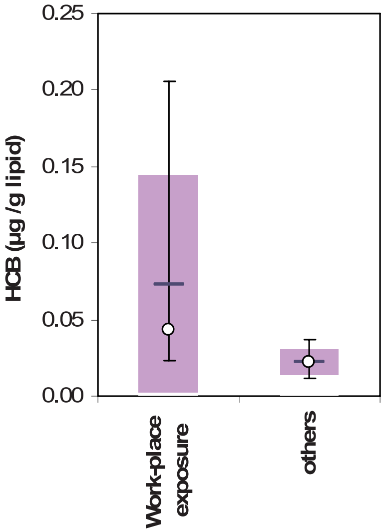

Fig. 5.1.3. HCB concentrations in blood serum.

Precaution is recommended considering these evidences because of the limited number of the samples. Nevertheless, these results support the concerns regarding the human exposure to dioxins and claim for further epidemiological studies in order to provide a deep insight into the exposure levels for the Italian population.

5.2. Breast milk

New data of POPs in the breast milk were measured in 2008 of 3 mothers living in Venice. The averages were resulted in 5.2 ± 1.7 pg WHO-TE g^{-1} lipids for PCDD/F and 6.7 ± 1.3 pg WHO-TE g^{-1} lipids for PCB. Total toxicity of PCDD/F + PCB was, therefore, 11.9 pg WHO-TE g^{-1} lipids. Analogous analyses conducted in 2000 for Venice and Rome resulted in 30.7 and 20.4 pg WHO-TE g^{-1} lipids in average, respectively.

Therefore, the results obtained in 2008 for WHO-TE are lower than those measured in 2000 but some caution is required in giving any conclusion because of the small number of 2008 data (three cases). In fact, the comparison with the data available in literature [15] shows that the collected data are in the upper part of the variability range presented in literature, and the comparison with the similar data collected in 2000 shows the higher contamination in the breast milk of mothers from Venice than at the mothers from Rome.

6. Conclusions

The fall-out, water and sediment data show very high concentrations of POPs, mainly in the industrial area of Porto Marghera and its surroundings. Thus, the industrial sources appear clearly as the main POPs sources in the Lagoon of Venice whereas the city of Venice and other urban areas appear to be of secondary importance.

The direct discharges continue to be a major POPs source to the environment, and atmospheric fall-out can be a secondary source. In particular, the data show a decrease of POPs in atmospheric depositions but the fall-out continues to play a substantial role to the inputs of POPs in the lagoon.

POPs are clearly accumulated in the sediments of the lagoon, with concentrations in industrial channels that are three orders of magnitude higher than the background values, while the other parts of the lagoon show concentrations, which are 5–10 times above the pre-industrial levels. The dioxin fingerprints evidenced that sediment is the main source of contamination of clams by the industrial-derived dioxins. There are high concentrations of POPs in the clams fished in the industrial channels.

A little enrichment (although not significant) of PCDD/F human blood serum could be linked to the fish consumption and occupational exposures of Venetian volunteers. On the contrary, considering total PCBs toxicity, the higher values for Venetians are clearly associated with the high fish consumers and the workers of chemical plants of the Venice Lagoon. The preliminary studies on human contamination presented here, although based on a limited number of samples, are supporting the concerns regarding the human exposure to dioxins and claim for further epidemiological studies in order to provide a deep insight into the exposure levels for Venetian and Italian population. Moreover, the higher levels of PCDD/F and PCB are found in the breast milk of Venetian mothers compared with the Roman ones in 2000. Although the toxicity levels in the breast milk in 2008 are lower than those measured in 2000, drawing more robust conclusions ask for a larger number of investigated cases.

There is a clear need for a constant monitoring of POPs in the Venice Lagoon in order to let this fragile ecosystem to heal gradually its wounds, and to safeguard it from further pollution. The environmental monitoring is indispensable for giving information about ecological risks.

This overview evidences a critical environmental state for some areas of the Venice Lagoon and confirms a non-negligible human health risk for regular shellfish and fish consumers. In general, this overview supports the need for keeping some lagoon areas restricted for fishing and for maintaining the current situation under the monitoring.

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PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN THE ENVIRONMENT

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Abstract. Various problems concerning the pharmaceutical and personal care products (PPCPs) in the environment of the Eastern European countries are described. The main classes of PPCPs in the environment, as well as major occurrence pathways and PPCPs fate, are depicted. The influence of specifics of the regional pharmaceutical market, medication consumption culture and pharmaceutical waste disposal techniques on environmental pollution with PPCPs, are discussed. Examples of wrong drugs prescription, drugs misuse, drugs overconsumption, and poor pharmaceutical waste management are presented. The necessity in research and management of PPCPs with emphasize on the local specifics and practices are concluded.

Keywords: PPCPs, pharmaceuticals, personal care products, drugs overconsumption, drugs prescription, pharmaceutical waste.

Abbreviations:

AA – 4-aminoantipyrine
AAA – 4-acetylaminoantipyrine
CAFOs – confined animal feeding operations
CNS – central nervous system
FAA – formylaminoantipyrine
NSAID – non-steroidal anti-inflammatory drug
PPPCs – pharmaceutical and personal care products
STP – sewage treatment plant

A.M. Bahadir and G. Duca (eds.), *The Role of Ecological Chemistry in Pollution Research and Sustainable Development*,

1. Introduction

Pharmaceuticals and personal care products represent a group of environmental micro-pollutants that could be detected recently due to development of new sensitive analytical methods. Their fate in natural ecosystems is poorly understood and their effects on different organisms are largely unknown. While large studies concerning PPCPs in the environment problems have been performed in the US and Western European countries [1–3], a little is known about their occurrence and fate in the Eastern European and other developing countries. Therefore, it is necessary to determine and to analyze the major problems that can influence PPCPs presence in the environment taking in consideration all the regional aspects.

2. Analysis and discussion

PPCPs have been present in the environment since their industrial production and mass application started. Development of the more sensitive analytical methods made it possible to detect their presence in residual concentrations. Recently, standard methods of PPCPs determination in water, soil, sediment, and biosolids, have been developed [4, 5].

Though, the individual environmental concentrations of the PPCPs are very low, effects of their mixture on the living organism are largely unknown and, therefore, unpredictable. Besides, their constantly increasing inflow lets assign them to the group of persistent organic pollutants and makes it necessary to study their influence on the living organisms.

There are several important questions that need to be solved regarding the presence of PPCPs in the environment:

- Assessment of PPCPs' origins concerning the specifics of the area/community using them and development of the new effective strategies of their release prevention
- Determination of fate and trends of the most environmentally occurring, persistent PPCPs
- Determination of the influence of their low and ultra low individual concentrations and multi-component mixtures on the non-target organisms that might be affected

Main classes of PPCPs detected in the environment are: antidepressants, antiepileptics, antihypertensives, antimicrobials, antineoplastics, antiseptics, β_2-sympathomimetics, contraceptives, hypnotic agents, lipid regulators, musks, painkillers/NSAIDs, CNS stimulants, sunscreen agents, X-ray agents [6].

The main routes of their penetration in the environment are described in the picture below (Fig. 2.1) [7].

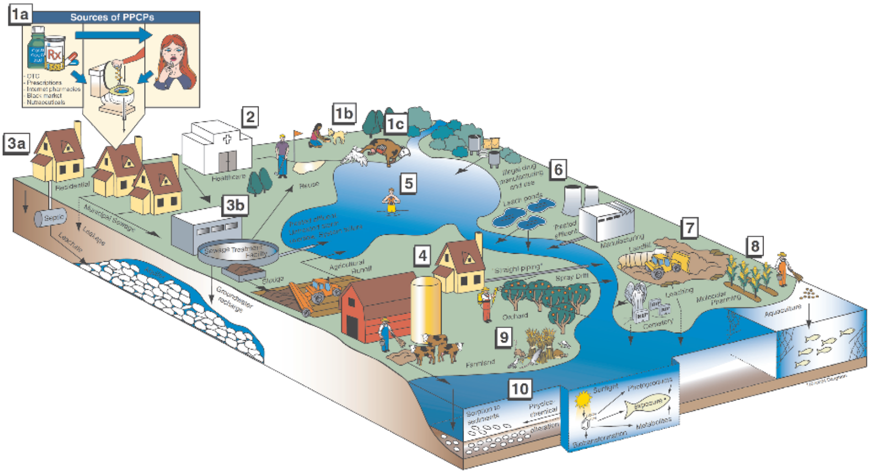

Fig. 2.1. Origins and fate of PPCPs in the environment.

Thus, the PPCPs enter in the environment as a result of:

1. Usage by individuals (1a) and pets (1b): metabolic excretion (non-metabolized parent drug, parent-drug conjugates, and bioactive metabolites); sweat and vomits, excretion exacerbated by disease and slow-dissolving medications; disposal of unused/outdated medication to sewage systems; underground leakage from sewage system infrastructure; disposal of euthanized/medicated animal carcasses serving as food for scavengers (1c)
2. Release of treated/untreated hospital wastes to domestic sewage systems (weighted toward acutely toxic drugs and diagnostic agents, as opposed to long-term medications); also disposal by pharmacies, physicians, humanitarian drug surplus
3. Release to private septic/leach fields (3a); treated effluent from domestic sewage treatment plants discharged to surface waters, re-injected into aquifers (recharge), recycled/reused (irrigation or domestic uses) (3b); overflow of untreated sewage from storm events and system failures directly to surface waters (3b)
4. Transfer of sewage sludge to land (e.g., soil amendment/fertilization); "straight-piping" from homes (untreated sewage discharged directly to surface waters); release from agriculture: spray drift from tree crops (e.g., antibiotics); dung use from medicated domestic animals (e.g., feed) – CAFOs
5. Direct release to open waters via washing/bathing/swimming
6. Discharge of regulated/controlled industrial manufacturing waste streams; disposal/release from clandestine drug labs and illicit drug usage
7. Disposal to landfills via domestic refuse, medical wastes and other hazardous wastes; leaching from defective (poorly engineered) landfills and cemeteries

8. Release to open waters from aquaculture (medicated feed and resulting excreta); future potential for release from molecular farming (production of therapeutics in crops)
9. Release of drugs that serve double duty as pest control agents: examples: certain antibiotics used for orchard pathogens; warfarin (anticoagulant) – rat poison; acetaminophen (analgesic) – brown tree snake control; caffeine (stimulant) – *coqui* frog control
10. Ultimate environmental transport and fate of PPCPs. Most PPCPs are eventually transported from terrestrial domain to aqueous domain where they undergo different transformations: photo-transformation (both direct and indirect reactions via UV light); physicochemical alteration, degradation, and ultimate mineralization; volatilization (mainly certain anesthetics, fragrances); some uptake by plants; respirable particulates containing sorbed drugs (e.g., medicated-feed dusts)

All the main routes can be considered the same from country to country, region to region with the prevalence of one or another. However, there can be found apparent differences in amounts and kinds of PPCPs occurring in the environment of different states. These depend on the peculiarities of their production, marketing, usage and disposal techniques.

Thus, among the most prescribed and used pharmaceuticals in the Eastern European (including former USSR states) are those not that widely represented or even prohibited in the USA and Western European countries. These are arbidol hydrochloride (1-methyl-2-(phenylthio)methyl)-3-carbethoxy-4-((dimethyl-amino)methyl)-5-hydroxy-6-bromindole hydrochloride (**1**), drotaverine hydrochloride ((1*Z*)-1-[3,4-dietoxyphenyl)methylidene]-6,7-diethoxy-3,4-dihydro-2*H*-isoquinoline hydrochloride (**2**), metamizole sodium (sodium [(2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl)methylamino] methanesulfonate) (**3**), phenylpiracetam (2-(4-phenyl-2-oxopyrrolidin-1-yl)acetamide) (**4**), rimantadine hydrochloride (1-(1-adamantyl)ethanamine hydrochloride (**5**) (Fig. 2.2).

Arbidol hydrochloride (**1**) (arbidol) and rimantadine hydrochloride (**5**) (rimantadine) are very popular anti-flu drugs that can be often bought without any prescription needed.

Arbidol pharmacokinetics supposes that large amounts of drug are passing organism without any changes. Bioavalability of the drug after oral administration is about 100%. About 40% of oral dose is excreted as unchanged form, the rest is composed of about 17 different metabolites. The biotransformation of arbidol leads to the loss of dimethylaminomethyl substituent in position 4 and sulfooxidation with formation of N-demethylarbidol, N-demethylsulfonylarbidol, sulfonylarbidol, sulfinylarbidol and N-demethylsulfinylarbidol. During the 2nd phase of the metabolism, conjugation at hydroxyl group occurs with formation of glucuronides and sulfates. The major arbidol metabolites are glucuronide arbidol and glucuronide sulfinylarbidol [8, 9].

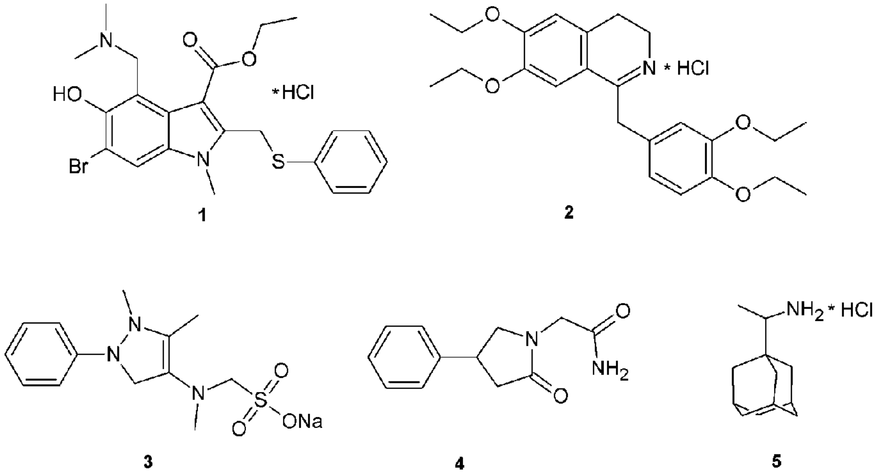

Fig. 2.2. Chemical structures of arbidol hydrochloride (**1**), drotaverine hydrochloride (**2**), metamizole sodium (**3**), phenylpiracetam (**4**), rimantadine hydrochloride (**5**).

Rimantadine (**5**) is metabolized in liver in a higher percentage than arbidol, with only 15–20% of the administrated dose being excreted as initial drug. The main rimantaidne metabolites are 2-, 3-, and 4-hydroxyrimantadine. From these, 2-hydroxyrimantaidne shows the same level of antiviral activity as rimantadine, while 3- and 4-hydroxyderivatives posses a lower anti-flu activity [10].

Drotaverine hydrochloride (**2**) is a chemical analogue of papaverine that is frequently used as antispasmodic drug. The main mechanism of its pharmacological action is based on selective inhibition of phosphodiesterase 4. The oral bioavalability of drotaverine ranges form 25% to 91% [11]. Drotaverine undergoes hepatic biotransformations that include mainly oxidation with formation of monophenolic metabolites and their consequent conjugation with glucuronic acid. Its metabolites are excreted with urine at the level of about 20–25% and with faeces at about 60–65% of the administered dose [12].

Metamizole sodium (**3**) (metamizole) is a NSAID, commonly used as painkiller and antipyretic. It has been prohibited in the US and many European countries as of risk of agranulocytosis it can cause, but it is still in a wide use as an over-the-counter medicine in many countries including Brazil, Bulgaria, India, Romania, Russia, Spain, Turkey and Mexico.

After oral or intravenous administration metamizole undergoes rapid metabolism with formation of 4-methylaminoantipyrine that is further transformed in 4-formylaminoantipyrine (FAA) and 4-aminoantipyrine (AA), which is acetylated to 4-acetylaminoantipyrine (AAA). These 4 major metabolites account ~60 % of the administered dose excreted from the organism [13, 14].

The occurrence and fate of metamizole metabolites were studied in investigations of sewage effluents from a military hospital, municipal sewers and a sewage treatment plant (STP) in Berlin, Germany [15]. This study showed that during the sewage treatment an average decrease of AA/AAA was 26% of the loads, whereas no changes were observed for FAA. The measured concentrations of metamizole residues in the STP effluents were up to 7 μg/l.

Phenylpiracetam (carphedon) is a derivative of a well-known nootropic drug piracetam. Recently, it has become an often prescribed general stimulant and nootropic medicine in Russia. Phenylpiracetame does not undergo any biotransformations in humane organism. Approximately 40% of the drug administered is excreted with urine and about 60% with bile and transpiration [16].

Another particularity concerning the PPCPs in the Eastern European countries is their use in uncontrolled and imprudent manner. A greater concern represents abusive self-medication and inappropriate disposal of high active drugs like antibiotics and antipsychotic drugs. Thus, the study performed in Russia showed that antibiotics were widely stocked among the general population. The most common preparations in home medicine cabinets were trimethoprim-sulfamethoxazole (46.3%), ampicillin (45.1%), chloramphenicol (32.7%), erythromycin (25.5%), and tetracycline (21.8%). The major indications for automedication with antibiotics were acute viral respiratory infections (12.3% of total indications), cough (11.8%), intestinal disorders (11.3%), fever (9%), and sore throat (6.8%) [17]. Similar results of antibiotic misuse were obtained for Poland [18].

Very often, antibiotics are incorrectly prescribed by doctors. A study assessing prescribers' indications for drugs in childhood showed that incorrect antibiotic indications accounted from 24.1% of the total antibiotics prescribed in Tenerife (Spain) to 67.4% in Slovakia. Incorrect indication of first-choice antibiotics prescribed in acute otitis media and tonsillitis ranged from 28.9% of total antibiotics use in Russia to 75.4% in Tenerife (Spain) [19].

Besides, the increase in misuse of prescription drugs is rapidly increasing, and according to some studies, may soon exceed that of illicit narcotics. According the studies performed in 2001–2005 the global consumption buprenorphine, an analgesic prescribed for substitution treatment of drug dependency, more than tripled from 420 million daily doses to 1.5 billion daily doses. Illicit preparations of buprenorphine have been found to be misused in Iran, Pakistan, the United Arab Emirates, the Czech Republic, Finland, Georgia, and Mauritius, among other countries. The same study showed that misuse of fentanyl through pharmacy theft, fraudulent prescriptions, and illicit distribution by patients, doctors, and pharmacists is also a growing problem in North America, Europe and Russia, where it is sold by traffickers as an imitation of illicit drugs such as heroin.

The misuse of prescription drugs is exacerbated by the higher volumes of drugs in the unregulated market and the rapid growth of internet pharmacies, which in some countries are not subject to national drug control regulations. And, despite the closure of thousands of illegal internet pharmacies, there is an increasing number of such internet sites selling medicines containing opioids and stimulants without prescription [20].

Other major problems are pharmaceutical waste management schemes and treatment technologies implemented in the Eastern European countries. Though, many countries from the region have a very good legislation in the field, it is not being implemented. A good study in this field has been performed by Croatian researchers [21, 22]. It disclosed the evidence of improper practices from the point of waste production to final disposal, while landfilling appeared to be the main route of pharmaceutical waste disposal in Croatia. Moreover, information on quantities, type and flow of medical waste were found to be inadequate. A similar situation can be found in other Eastern European countries too [23, 24].

Still, a very small number of studies were performed in the field of PPCPs in the Eastern European environment. Most of them detected the presence of certain groups of PPCPs in the STPs effluents and rivers: caffeine, galaxolide, carbamazepine and triclosan in the Somes river, Romania [25, 26]; anthropogenic gadolinium and estrogens in hydrologic basin of Prague, Czech Republic [27, 28]; ibuprofen, naproxen, ketoprofen, diclofenac, bezafibrate and clofibric acid in the Warta River, Poland [29] and other common anti-bacterial, anti-convulsant, anti-hallucinatory, anti-inflammatory, and analgesic formulations in the rivers of the South Poland [30] in the range of 1–10 ng/l.

3. Conclusion

The region of the Eastern European (including the former USSR states) can be characterized as a rapidly growing pharmaceutical market with very popular indigenous drugs and not that well established rules and culture of medicinal consumption. Besides, the local practices of pharmaceutical waste release and disposal as well as practices of untreated sewage release and poor technologies of its treatment are of big concern. Thus, there is a need of research and information in the field of PPCPs in the environment in these states considering all the local specifics and practices.

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MONITORING AND MEASURES ON POPS IN TURKEY

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Abstract. Turkey signed the Stockholm Convention on May 23, 2001, with the objective of protecting human health and environment, focusing on eliminating or reducing releases of 12 POPs, the "Dirty Dozen". Turkey has developed its National Implementation Plan (NIP) as a Party to the Stockholm Convention. The NIP sets out how the Stockholm Convention is being implemented in Turkey and outlines the next steps to be taken in the management of POPs. A number of experts, representative of the institutions, ministries, universities, Scientific and Technical Research Council of Turkey – Marmara Research Center, and non-governmental organizations took part in preparing the inventory and preparation of the NIP.

Keywords: POPs, HCB, PCBs, POPS regulation.

1. Introduction

The United Nations Environment Programme (UNEP) Stockholm Convention on POPs (http://chm.pops.int/) is a global agreement that came into effect on May 17, 2004. The objective of this Convention is to protect human health and the environment from Persistent Organic Pollutants. As a Party to the Convention, Turkey has an obligation under Article 7 to develop and implement a National Implementation Plan (NIP).

The purpose of the NIP is to inform the Conference of the Parties and the public regarding Turkey's initiatives current and projected, to meet the requirements of the Stockholm Convention. These initiatives include legislation, regulations, voluntary programs and standards, policies, programs and other related measures including action by Turkish authorities and public stipulate that the NIP for reducing unintentionally produced POPs, including dioxins and furans, hexachlorobenzene (HCB) and PCBs.

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The twelve POPs defined within the Convention have been classified into in three groups in the Convention text for proposes of control measures (Table 1.1).

Table 1.1. The 12 POPs "Dirty Dozen".

Annex A: Substances Subject to Elimination	Aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, and toxaphene Polychlorinated biphenyls (PCBs)
Annex B: Substances Subject to Restricted Use	DDT
Annex C: Unintentionally Produced Substances	Dioxins and furans (PCDDs/PCDFs) Hexachlorobenzene (HCB); and Polychlorinated biphenyls (PCBs)

2. POPs

2.1. Brief description of POPs

Persistent Organic Pollutants (POPs) are organic compounds of natural or anthropogenic origin with a particular combination of physical and chemical properties that were once released into the environment; they remain intact for exceptionally long periods of time as they resist photolytic, chemical and biological degradation. They include industrial chemicals such as PCBs, pesticides such as DDT and by-products such as dioxins and furans. They characterized by low water solubility and high lipid solubility. POPs bio-accumulate in fatty tissues of living organisms, including humans, and are found at higher concentrations at higher trophic levels in the food chain. This way, humans, wildlife and other organisms are exposed to POPs, in many cases for extended periods of time spanning generations, resulting in both acute and chronic toxic effects. In addition, they are introduced to humans through the food chain and passed on from mother to child and are known to have significant immunological, neurological and reproductive health effects and suspected for cancer.

2.2. POPs are global issue

POPS are semi-volatile chemicals, which evaporate from the regions in which they are used and are then transported over long distances in the atmosphere. They are also discharged directly or by atmospheric deposition into waterways and are transported by current of fresh and marine waters, even through the ground waters. This result shows the widespread distribution of POPs across the globe, including the regions where they have never been used, such as the inhabited and remote areas.

POPs occur at low levels in air and water, so human concerns arise from their ability to bio-accumulate in organisms rather than from direct exposure. POPs have a tendency to accumulate in fatty tissue of organisms and be transferred along terrestrial and aquatic food chains.

POPs are a global issue for the environment and human health. They can cause birth defects, various cancers, effect the immune system, cause the dysfunction and reproductive problems in mammals. In addition, the weight of evidence indicates that high levels of exposure over the long term may contribute to increasing rates of birth defects, fertility problems, greater susceptibility to disease, diminished intelligence disrupting endocrine systems and some types of cancers in humans. The major concern for human health is the effect of exposure to POPs on developing fetus. POPs have been detected in the breast milk of women throughout the world.

3. Assessment of the POPs issue in the country

On May 22–23, 2001, 125 countries including Turkey signed the Stockholm Convention, a global agreement under the United Nations Environment Programme (UNEP) that will reduce or eliminate emissions of POPs. The Convention:

- Sets out obligations for countries covering the production, use, import, export, release, and disposal of POPs.
- Requires countries to promote, and in some cases require, the use of the best available techniques (BAT) and best environmental practices (BEP) to reduce and/or eliminate emissions of unintentionally produced POPs from certain combustion and chemical processes.
- Includes provisions aimed at preventing the introduction of new POPs and for adding other POPs to the Convention in the future.

With the ratification by 50 countries, the convention entered into force on May 17, 2004. Because of the Convention includes obligations related to hazardous wastes and their transboundary movements, it is closely linked with the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (www.basel.int) and the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (www.pic.int).

The quantitative basis of the issue would typically be established by the development of inventories of the POPs covered by the Convention.

3.1. Assessment with respect to Annex A part 1 chemicals (POPs pesticides)

The authorization for the use of any pesticide is aligned with international rules. When the use of a pesticide is banned in the world, it will also be banned in Turkey. Registration Committee of Ministry of Agriculture and Rural Affairs (MARA) register agricultural pesticides after studying the chemical and physical properties, biological activity, residues, toxicological and eco-toxicological properties with internationally approved analytical methods and techniques. MARA monitors registered pesticides from their production or import to their consumption. Provincial and County Directorates of MARA responsible for market control constantly control pesticide retailers. Unsatisfactory product standards for the samples taken during market control necessitate punitive actions.

Pesticide use per hectare as active ingredient is 0.63 kg for Turkey, whereas it is 17.5 kg for Netherlands, 3.5 kg for USA, 4.4 kg for Germany and France, 7.6 kg for Italy and 6 kg for Greece. It is clear that when compared with developed countries, pesticide use levels are very low in Turkey. Thus, agricultural sector in Turkey is not an environment-polluting sector, rather affected by the pollution.

According to the reports of MARA, there is only an approximate of 2,700 tons of HCB present in the stocks.

Monitoring studies were carried out for various foodstuffs after POPs pesticides were registered and after they were banned by Plant Protection Research Institute of MARA.

3.1.1. Past, Present and Projected Future Production and Use of POPs Pesticides

According to the statistics, the total use of pesticides in Turkey was declining from 36,662 tons in 1985 to 30,792 tons in 2002. It can be observed that, over the 17-year period, use of pesticides decreased. These quantities represent the registered pesticides (Table 3.1.1.1).

Table 3.1.1.1. Annual amounts of authorized pesticides use in Turkey.

Year	Amount of pesticide use (tons)
1985	36,662
1997	33,713
1998	35,487
1999	32,230
2000	33,548
2001	29,798
2002	30,792

A total of 1231 commercial pesticides had been registered in 1995; though the picture changed in 2004 as 485 active ingredient and 3006 commercial pesticides were registered in Turkey. However, due to various reasons only 252 active ingredients containing registered pesticides are commercially available.

POPs pesticides ban was started in Turkey by 1970s, and their use, production, import, and export are prohibited by law.

Dieldrin was banned in 1971, aldrin, chlordane, heptachlor, endrin were banned in 1979 and toxaphene was banned in 1989. In addition, registrations of plant protection products containing these active ingredients were cancelled. Mirex and its formulations have never been registered in Turkey. There is no record of production of POPs pesticides in Turkey since their ban. After registration, plant protection products were being prepared by using imported active ingredients. Production of those active substances in Turkey has never been an issue. Records from Under secretariat of Foreign Trade and Under secretariat of Customs show the fact that POPs substances have not been imported or exported after they have been banned.

Starting from 1968 the use of aldrin, dieldrin, heptachlor, DDT, chlordane and toxaphene was restricted. Application of soil with aldrin and heptachlor was forbidden, but use for seed treatment was allowed.

3.1.2. Identified Obsolete Stockpiles and Wastes of POPs Pesticides

According to the official statements, there are only stocks of HCB and DDT. After POPs pesticides had been banned, as a precaution MARA collected the data of the stocks of retailers and firms. As a result, 2,700 tons of HCB (hexachlorobenzene) and 10,930 kg of DDT were found in the stocks in Turkey. Because of harmful effects on human health and environment, the Plant Protection and Agriculture Quarantine Law banned HCB in1985. The DDT stock was found in the storage of Ankara Central Service Directorate of MARA.

3.2. Assessment with respect to PCBs (Annex A, Part II Chemicals)

Polychlorinated Biphenyls (PCBs) are organic compounds, which were used in electrical machinery and equipment insulation. They have been used as insulators in transformer and in capacitors for years and some of the transformers and capacitors in start-up power stations in Turkey contain PCBs. PCBs also appear as by-products of organochlorine productions like PVC and unintentionally during waste incineration.

There are two regulations related to PCBs in Turkey:

1. “Regulation for Dangerous Chemicals”, 11.07.1993 dated, Official Gazette No: 21637
2. “Regulation for The Control of Hazardous Wastes”, 14.03.2005 dated, Official Gazette No: 25755

According to Article 41 of "Regulation for Dangerous Chemicals", products and equipments containing polyhalogenated biphenyls and terphenyls and their combination cannot be used as of January 1, 1996. According to Article 42 of the same regulation the use of such materials in

- Closed system electrical devices (transformer, resistor, inductor)
- Large densers (total weight of 1 kg and more)
- Small densers (whose chlorine content is not more than 43% and does not contain more than 3.5 penta and more chlorine biphenyl containing polychlorine biphenyl)
- Heat transfer liquids which are used in closed system heat appliances (except for processing food, medicine, feed and other veterinary products)
- Hydraulic liquids used with underground digging equipment and electrolyte aluminium production devices
- For conversion of other products as a first step or intermediate step are allowed until January 1, 1996

3.3. Assessment DDT (Annex B Chemicals)

DDT and its related products are very persistent in nature. Even after 10–15 years from its application more than 50% of them remain in the soil.

DDT has been used between 1957 and 1985. Since then, no use (import, export, use, stockpiles, etc.) of this active substance has been reported; moreover, these chemicals are sufficiently managed via a great number of legislations.

3.3.1. Past, Present and Projected Future Production and Use of DDT

According to the available data and records, there was no DDT production in Turkey in the past. Use of DDT was restricted in 1978 and banned in 1985 in Turkey. When they were registered, plant protection products were prepared using active ingredients imported from other countries.

Nationwide monitoring of organochlorine pesticide residues has been performed on agricultural products, soil, and rivers. No illegal use of DDT has been found.

3.3.2. Identified Stockpiles of DDT and DDT Waste

After the ban on POPs pesticides the stock records of retailers and firms were collected as one of the precautions taken by MARA. Turkey has 10,930 kg of DDT in the stocks. DDT stock is located in the facilities of Ankara Central Supply Directorate of MARA.

3.4. Assessment of releases from unintentional production of Annex C chemicals (PCDD/PCDF, HCB and PCBs)

This section intends to summarize the inventories of the emission of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs), Hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) which are unintentionally formed in a wide range of thermal and industrial chemical processes. These are the chemical substances covered by Annex C of the Stockholm Convention.

Potential sources are

- Thermal processes: waste incineration, uncontrolled waste burning, metal smelting, and refining processes, thermal power generation, cement kilns, wood and other biomass burning, and gasoline combustion.
- Industrial chemical processes: production of pulp and paper when bleaching with elemental chlorine is used.

Development of national inventory made by the Toolkit prepared by UNEP Chemicals, which is an effective methodology for identifying the relevant industrial and non-industrial processes releasing PCDD and PCDF.

A detailed database of emission factors, which provides suitable default data, was applied as representative of the class into which the processes are grouped. The main source categories for PCDDs/PCDFs emissions in the Toolkit are identified as

- Waste incineration
- Ferrous and non-ferrous metal production
- Power generation and heating
- Production of mineral products
- Transport
- Uncontrolled combustion processes
- Production of chemicals and consumer goods
- Miscellaneous
- Disposal
- Hot spots

Persistent Organic Pollutants, which may have similar effects, are found in all environmental compartments, are persistent and, being fat soluble, tend to accumulate in higher animals, including humans. Their resistance to degradation and semi-volatility means that they may be distributed over long distances and give rise to trans-national exchanges of pollutants. In addition, POPs released into the environment many years ago continue to contribute to contemporary exposure. Due to high persistence of POPs, concentrations in soils and sediments decrease very slowly, following any reduction in releases to air and water. Concentrations in air are more responsible to emission reductions, so the POPs emissions can be decreased rapidly in air than in soil or water.

It is possible to state that once released into the environment, all POPs follow a range of similar routes. In the atmosphere they exist in both the gaseous phase and bound to particles, depending upon the environmental conditions, and are deposited on soil, vegetation and water bodies by wet and dry deposition or in mist. Dioxins have been measured in areas with no local sources and it can, thus, be deduced that they are available for long-range transport over a scale of thousands of kilometres.

Table 3.4.1. Dioxin and furan emissions in Turkey.

	Source Categories	Annual Releases (g TEQ/a)				
Cat.		Air	Water	Land	Products	Residue
1	Waste Incineration	19.883	0.000	0.000	0.000	0.6
2	Ferrous and Non-Ferrous Metal Production	113.854	0.000	0.000	0.000	195.7
3	Power Generation and Heating	15.772	0.000	0.000	0.000	0.0
4	Production of Mineral Products	25.088	0.000	0.000	0.000	3.3
5	Transportation	3.063	0.000	0.000	0.000	0.0
6	Uncontrolled Combustion Processes	5.000	0.000	4.000	0.000	0.0
7	Production of Chemicals and Consumer Goods	0.000	0.000	0.000	21.589	0.0
8	Miscellaneous	0.010	0.000	0.000	0.000	0.0
9	Diposal/ Landfilling	0.000	0.000	0.000	0.001	0.0
10	Identification of Potential Hot-Spots					
1-9	Total	182.7	0.0	4.0	21.6	199.6

TEQ = international toxicity equivalencies.

The total emissions (air, water, soil, and product) of unintentionally produced POPs (dioxins and furans) in Turkey are given in Table 3.4.1. According to this table, the most important POPs producer sectors are ferrous and non-ferrous metal production, production of mineral products, waste incineration and power generation.

For PCBs emissions, Turkey has two main problems; lack of information and research on PCBs production, and insufficient laboratory facilities for PCBs analysis in different matrices, except for some governmental laboratories.

Besides being formed as unintentional by-products of manufacturing or disposal processes, PCDD/PCDF may also be introduced into processes as contaminants in raw materials. PCDD and PCDF releases arise from four types of sources.

The processes considered are as follows:

- Chemical production processes – for example the production of chlorinated phenols and the oxychlorination of mixed feeds to make certain chlorinated solvents, or the production of pulp and paper using elemental chlorine for chemical bleaching
- Thermal and combustion processes – including incineration of wastes, the combustion of solid and liquid fuels, and the thermal processing of metals
- Biogenic processes, which may form PCDD/PCDF from precursors such as pentachlorophenol. The last one is related to previous contamination
- Reservoir sources such as historic dumps of contaminated wastes and soils and sediments, which have accumulated PCDD/PCDF over extended periods

In January 2001, UNEP Chemicals within the framework of the IOMC (Inter-Organization Program for the Sound Management of Chemicals) released the "Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases" as a draft. This Toolkit is for the preparation of a release inventory for polychlorinated dibenz*o*-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) as requested in subparagraph (a) of the Article 5 in the Stockholm Convention on Persistent Organic Pollutants. It is aimed to cover all release vectors (air, water, land, products, residues) from industrial and domestic activities by identifying the sources and quantifying the releases for two classes of unintentionally generated POPs.

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CURRENT STATE IN THE FIELD OF PERSISTENT ORGANIC POLLUTANTS MANAGEMENT IN UKRAINE

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Abstract. The paper represents the results of an overall analysis and review of the current state in the field of persistent organic pollutants (POPs) management in Ukraine, as well as the experiences gained in realization of the recent activities aimed at collecting and processing the data on different sources of the wastes consisting of or contaminated with hazardous chlorine-containing substances, as a significant input to the development of a National Plan for implementation of the Stockholm Convention on POPs. It is summarized the last achievements in developing managerial tools and a methodological approach to developing the national inventories of available and potential POPs-containing wastes and contaminated sites.

Keywords: persistent organic pollutants, POPs, waste inventory, waste management.

Abbreviations:

BAT – best available techniques
BEP – best environmental practices
DDT – 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane, organochlorine pesticide
DDE – 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene, DDT derivative
DEPA – Danish Environmental Protection Agency
DANCEE – Danish Environmental Assistance to Eastern Europe
GEF – Global environment facility
HCB – hexaclorobenzene, organochlorine fungicide
HCH – 1,2,3,4,5,6-hexachlorocyclohexane, organochlorine insecticide
NIP – National Implementation Plan
OCPs – obsolete chlorinated pesticides
PCBs – polychlorinated biphenyls
POPs – persistent organic pollutants
UNEP – United Nations Environment Programme

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1. Introduction

Pollution of the environment with hazardous chemical substances and persistent organic pollutants in particular is one of principal factors of unfavorable ecological situation in Ukraine and in the whole world. Abilities of this group of substances to remain intact in the environment during long periods of time, as well as to spread over large distances from their sources cause the necessity to control their releases and manage their handling at the international level. The prognostication of ecological situation and development of measures for their improvement at the national level is possible only on the basis of the approved international system for POPs management that is specified in corresponding international documents [1–4].

Ukraine is considered as a country with an economy in transition. It signed the Stockholm Convention on POPs on 23 May 2001 and became the Party of this global treaty in December 2007. Besides that, Ukraine is a Party of the Basel Convention on Transboundary Movement of Hazardous Waste and the Rotterdam Convention on Prior Informed Consent, which also concern the POPs issues related to the provisions of the Stockholm Convention. The Stockholm Convention on POPs initially targets 12 chemicals for reduction and eventual elimination, among them are nine pesticides: aldrin, dieldrin, chlordane, DDT, endrin, heptachlor, hexacholorobenzene, mirex, toxaphene; two POPs are industrial chemicals: hexachlorobenzene, which is also used as a pesticide, and polychlorinated biphenyls; and two families of unintentionally produced chemicals: dioxins and furans [1]. Under the Convention, Parties are required to develop and implement a plan for the implementation of their obligations. These national implementation plans should include action plans designed to characterize and address the available or potential wastes consisting of, containing or contaminated with POPs, as well as releases of unintentionally produced POPs, promoting the use of the best available techniques and best environmental practices to manage the existing and new sources of POPs.

During recent years, certain background international activities, which allowed making the basis for an overall evaluation of the POPs problem in Ukraine, were realized. And among them the main were the projects carried out under the aegis of the Ministry of Environmental Protection of Ukraine jointly with the National Academy of Sciences leading specialists and the following international organizations and companies:

- Elimination of Risks Related to Stockpiled Obsolete Pesticides in Ukraine – DEPA-DANCEE and COWI consulting group, Denmark
- Assistance to the Ukrainian Environmental Authorities Management of Contaminated Sites - DEPA-DANCEE and COWI consulting group, Denmark
- Developing an Inventory of Polychlorinated Biphenyls and the Review of Technical and Economic Requirements for Environmentally Sound Technologies of Treatment /Destruction of PCBs – Canadian Trust Fund and UNEP Chemicals

And the Project “Enabling activities related to the implementation of the Stockholm Convention on Persistent Organic Pollutants in Ukraine” supported by the Global Environment Facility and UNEP was realized within the period 2003–2007 and currently resulted in the draft version of the NIP.

The Department of Environmental Safety of the Ministry of Environmental Protection was designated as the official focal point for the Stockholm Convention on POPs in Ukraine.

2. Legal framework and POPs status

The legal basis governing the environmental policy and regulations in the field of chemical safety in Ukraine is founded in the following main laws: “On Environmental Protection” (1991), “On Pesticides and Agricultural Chemicals” (1995), “On Wastes” (1998), and “On Ecological Expertise” (1996). These main laws cover the basic principles of environmental protection, the rational use of natural resources as well as ecological safety and form the foundation for further legislation and regulation. The current legislation in Ukraine is to govern the environmental impact assessment and approval of measures proposed for the management of chemicals. There exists a sufficiently clear hierarchic system of regulations developed in accordance with the force of the laws and divided into legislative and sub-legislative documents or into general and departmental ones.

The following laws, regulations and official administrative approvals related to POPs are currently in force in Ukraine [5]:

- Law of Ukraine “On Provision of Sanitary and Epidemiological Safety of Population” (1994)
- Law of Ukraine “On Plant Protection” (1999)
- Decree of the Cabinet of Ministers dated 17.11.2001 N 1520 “On Approval of Statement about the State Ecological Inspection
- Decree of the Cabinet of Ministers dated 13.07.2000 # 1120 “Regulation on the control of transboundary movements of hazardous wastes and their treatment”
- Decree of the Cabinet of Ministers dated 30.03.98 # 391 “On Approval of Statement about the State Monitoring System of the Environment”
- Decree of the Cabinet of Ministers of 27.03.1993 No 354 “On approving of the order of the removal and disposal of unfit or banned for use of pesticides and agricultural chemicals and their packaging”
- Decree of the Cabinet of Ministers of Ukraine N 440 from 20.06.1996 “Order of receiving permission on the production, storage, transportation, use, destruction and disposal of poisonous substances including toxic industrial waste, biotechnology products and other biological agents”

- "List of pesticides banned for use in agriculture"; Approved by the State Interdepartmental Commission on Testing and Registration of Plant Protection Products, Growth Regulators and Fertilizers, dated on 05.08.1997; Agreed with the Ministry of Health Care of Ukraine
- "List of Pesticides and Agricultural Chemicals allowed to use in Ukraine" (1999)

The most of POPs-pesticides under the Stockholm Convention were regulated by the Soviet legislation. The use of DDT, aldrin, endrin, heptachlor, toxaphene and their various preparations was banned till 1987. Definitely only mirex was never registered, as it is required under the Law "On Pesticides and Agricultural Chemicals". It means that it could not be imported, produced and used anywhere within the country.

In Ukraine the list of the banned OCPs (1997) includes aldrin, chlordane, dieldrin, endrin, heptachlor and its mixtures, HCB, toxaphene, DDT and its preparations, DDD, DDE and HCH. The complex inventory of sites for storage and disposal of the agro-chemicals, which are considered as obsolete or banned for use, was initiated by the so-called Order of Three Ministers (2001) and the Decree of the Cabinet of Ministers of Ukraine "On developing the infrastructure for elimination of the banned and obsolete pesticides" (2002). The initial data obtained by regional bodies of the Ministry of Agrarian Policy, the Ministry of Environmental Protection and the Ministry of Health in 2003 were renewed within the above-mentioned international projects and the latest search and analysis of the available information was carried out within the NIP project (GEF/UNEP) [5]. The overall results dated by 2006 reveal that about 22,000 tons of obsolete pesticides are stored in about 5,000 store-houses in agricultural facilities of all types of ownership. This total amount includes: about 18,000 tons of non-POPs or unidentified obsolete pesticides and the rest – POPs-pesticides, such as DDT, heptachlor, HCB and HCH. During the recent years a certain amount of the revealed obsolete pesticides is already disposed and the actual figures are not specified yet.

PCBs were never produced in Ukraine but like in other industrialized countries were used in a number of applications. The most part of PCB-containing equipment is used mainly in power generation and distribution systems in Ukraine while some uses in various industrial sectors (ferrous and non-ferrous metallurgy, food, chemical, and coal mining) are also recorded. According to the Ukrainian legislation now in force these substances are referred to the list of pollutants that must be controlled but there are no any special regulations concerning PCBs in Ukraine.

Being based on the general data on PCBs obtained in the Russian Federation (1999–2001), a rather different methodological approach to developing a PCBs inventory was elaborated in Ukraine within the UNEP Chemicals Project under the financial support provided by Canadian POPs Trust Fund (2002–2004). There was determined the amount and location of the PCBs-containing equipment and synthetic liquids, which were available at the largest enterprises of transportation, industrial, agrarian, energy and defence complexes of Ukraine. The data collected in a format of administrative reporting became a part of the information and analytical system, which was created to perform a comprehensive evaluation of types, number and location of the exposed equipment, and materials containing PCBs. The inventory covered more than 3,500 enterprises of all types of property and served as the base to advance for the further NIP development.

The current database on PCBs in Ukraine reflects the situation actual for 2003–2004 and reveals the availability and location of about 250 tons of pure PCBs liquids (sovtol, TCB, ascarel, hexol, delor, clophene, pyranol) and electrical equipment of Soviet and foreign production – about 1,000 PCBs transformers, about 100,000 units of PCBs capacitors, in use or phased out [6]. A lot of data concerns the unidentified electrical equipment, mainly, imported from the former CEE countries.

3. Methodological approach and tools

Realization of the activities aimed at inventorying of POPs sources, as well as the sites contaminated and potentially contaminated with obsolete pesticides and other hazardous substances, collecting and processing the data within the above-mentioned projects was based on an overall methodological approach with the following main components:

- Preparation of the data collection methodology, including the ranking system
- Design of a special software and preparation of databases and other computer tools to manage the information on contaminated sites, obsolete pesticides and POPs in Ukraine
- Training of the local administrations personal in inventorying procedures and computer skills

This approach was achieved through the implementing of the specially designed inventorying procedures for the establishment of an overview of POPs sources and in order to evaluate the amounts of the available wastes or potential contaminants and give priority to those sites, which may cause the potential harmful impact on the environment and human health. Such inventorying system might stipulate the progress of the existing analytical base and should be supported by development of the corresponding norms and regulations.

The above components included:

- Analysis of the production and types and PCBs usage, as well as technical specifications for the electrical equipment containing PCBs;
- Elaboration of the corresponding guidance – separately, on revealing and identification of polychlorinated biphenyls in products and waste, and the sites contaminated and potentially contaminated with different hazardous substances (within different projects)
- Making a format of reports for and instructions on how to fill them

- Development of the software for processing the obtained data using computer technologies
- Approval and adoption of elaborated documents in due order
- Appointing persons responsible for the inventory in regions of Ukraine, formation of regional work teams
- Delivery of the reporting forms to enterprises, central and local administrations
- Collection of the filled forms by territorial administrations of the Ministry of Environmental Protection
- Generalization of the information, submission it to the National Center for Hazardous Waste Management
- Processing of the data, analysis of the results, in particular:
  - Processing of the data, developing the database on the types of the equipment and materials containing PCBs including also the information on their quantity and location; analysis of the obtained information related to types of application and storage of PCBs at enterprises in Ukraine depending on the territory and branch (type of activity)
  - Developing separate databases on the sites of obsolete pesticides storage and the sites contaminated and potentially contaminated with different hazardous substances, including POPs

The specially designed computer tools may serve as the national information system for the inventorying of the POPs sources, wastes and contaminated sites. The initial database system was developed for environmental management of information related to facilities of generation, processing, recycling and disposal of waste. The integrated information system might be used to register and provide the data and reporting on POPs waste generation, quantitative and qualitative composition, handling and reduction as well as exercising of control of impact on natural environment and public health.

4. Conclusions and expectations

It is evident that the problem of environmentally sound management of POPs and the wastes consisting of, containing or contaminated with POPs relates to industry, energy, transportation, agriculture, other economic sectors and different types of activity, and so, it can be solved only by mutual efforts of not only mentioned authorities but other central executive bodies, as well as expert teams from the research sector and civil society. Analysis of “the state of the art” showed that current legislation, as well as an overall system of chemicals management in Ukraine is to be updated according to the requirements of the related international conventions and initiatives.

The overall goal is to finalize developing the NIP for POPs issues and its realization with the assistance of international organizations so that Ukraine can effectively address the reduction and elimination of persistent organic pollutants consistent with the protection of human health and the environment from the effect thereof, and meet its obligations under the corresponding environmental treaties. Taking into account this overall goal, the following specific objectives might be indicated and considered as priority ones:

- To develop and enforce the harmonized regulatory measures required:
  - Streamlining and clarification of competences and of the permitting system
  - Formation and keeping the national inventories as a part of an overall regulation system for data collection and processing
  - Harmonization of definitions and waste lists with the European Union definitions and lists
  - Urgent prohibition of illegal dumping of wastes
  - Further development of the legal framework to follow the movement of PCBs and obsolete pesticides and to improve the prevention of contamination
  - Development or adoption of non-available hygienic norms and standards for the content of a number of priority POPs in different media
  - Revision and approval of regulations that provide for metrological specifications of measurement techniques in accordance with the international practice
- To provide effective information exchange and achieve a high level of awareness of the POPs issues and international obligations among the officials and institutions involved:
  - To pursue methodological support for measures on environmentally sound management of POPs based on international experience and national research activities
  - To establish national educational programs and the coordinating mechanism required
- To achieve a high level of public and stakeholder participation in the implementation of the NIP for the reduction or elimination of POPs:
  - To prepare the communication exchange system related to POPs issues
  - To develop specific programs to increase the awareness of all stakeholders and civil society
  - To arrange special trainings in the regions
- To assess the existing analytical base capacity in Ukraine, including determination, revision and certification of the most appropriate modern analytical techniques for their implementation in the field of environmental analysis in Ukraine
- To provide the basis for financing of the NIP implementation measures from different national and international sources

All these measures will be non-effective or even impracticable in case they will be not supported by scientific studies and developments. It is strongly expected that the international cooperation in the research sector should target the most urgent problems revealed in Ukraine and would give the necessary scientific and methodological basis for elimination of POPs and prevention of future environmental contamination with these substances.

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PART II. WATER POLLUTION AND WASTE WATER TREATMENT

WATER QUALITY MONITORING AND MANAGEMENT IN MOLDOVA

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Abstract. The water resources of the Republic of Moldova are quite limited and can assure only 54% of the necessities of national economy. For the rational usage of these water resources the Academy of Sciences of Moldova initiated the development of the National Program on Water Management. The Program development was based on the results of the study of problems faced by all sectors of the national economy in regards to water supply and usage. The study also focused on the monitoring of the main water sources in order to assess their current state. This paper reflects the results of monitoring of river Dniester considered while developing the National Program on Water Management as well as the Program main components.

Keywords: water quality, monitoring, self-purification, redox-state, barrage influence, management.

1. Introduction

The main sources of surface water in the Republic of Moldova are constituted of Dniester and Prut rivers, a small part of Danube river and internal water network consisting of small rivers, lakes and artificial water bodies.

The Dniester is a trans-boundary river crossing the countries of Moldova and Ukraine, discharging into the Black Sea. From its total length of 1,352 km 636 km flow through Moldova and its basin occupies 57% of the area of the Republic of Moldova. This river is the largest one in Moldova and is the main source of water supply for about two million people. The run-off water as well as the municipal effluents, industrial discharges, and economical activity contribute to the degradation of the quality of this water source.

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In 1981, a barrage was constructed in the middle part of the river by Ukraine, creating the Dniestrovsk Hydroelectric Power Station (HPS). The newly formed storage pond is 194 km long; the capacity of the reservoir is 3.0 km^3. The main purpose of the barrage construction is power supply and flood control. In 1985, another barrage was constructed at the border between Moldova and Ukraine downstream of the Dniestrovsk HPS in order to create a 20 km buffer storage. The main purpose of the second barrage construction was to regulate the water discharge from the first barrage and also to generate electric power.

Since the beginning of full-capacity operation of the Dniestrovsk HPS, dramatic changes in the water quality occurred in the river emerging from the buffer reservoir. The temperature regime of the river has been changed as follows: the mean temperature value decreased by 8–10°C and reached an average of 16–18°C during summer time; while the average air temperature is usually 30–32°C. This led to the severe changes in the aquatic ecosystem: the diversity of hydrobilogical species and fish stocks decreased considerably and an increased rate of mass fish kills were observed periodically. Ichthyologists have pointed out the negative effects of the dam on the ichthyo-fauna. Some fish species have stopped spawning, thus, leading to a reduction in fish stocks by 18–30 times. Certain studies revealed that 80% of the sturgeon sampled showed signs of spawn reabsorption [1, 2].

Besides of the unfavorable temperature regime, dam construction had an impact on the water redox state [1, 3]. The presence of reducing substances in the amounts exceeding quite often the contents of oxidizers provokes a disbalance in the ecological state of water system [4, 5]. It is known that the reductive, quasi-reductive and super oxidative state of natural waters creates destructive conditions for the development of hydro-bionets, including fish. Quasi-reductive conditions are considered toxic for certain bacteria such as infusoria as well as fish larvae.

The redox state of surface natural waters is a parameter that characterizes the ecological state of the water and its capacity to self-purification [6]. Biologically favorable fresh water is determined by the presence of hydrogen peroxide within the limits of 10^{-6} mol/l. In sea water, the amount of hydrogen peroxide is substantially lower then in fresh waters. In the biogeochemical cycle of oxygen in fresh water ecosystems the stationary concentrations of oxidative equivalents such as OH radicals constitute $3–5 \cdot 10^{-16}$ mol/l. The range of variation of their concentration should not vary by more than 10 times.

In surface natural waters, redox processes occur in the presence of dissolved oxygen and lead to the formation of intermediate active forms such as hydrogen peroxide, hydroxide and super-oxide radicals [1, 7, 8]. Chemical and photochemical processes of oxidation occur with the involvement of transitional metal ions and depend on the rates of free radical formation and destruction, and their steady-state concentrations. Among transitional metal the copper, iron and manganese ions take the most essential part for redox transformation of dissolved oxygen and hydrogen peroxide in aquatic environment [9, 10].

The purpose of current investigation was to asses the impact of the Dniestrovsk HPS on the formation of redox conditions in the lower section of water reservoir in dependence of seasonal and spatial aspects.

2. Material and methods

The water monitoring was performed by selecting six permanent sites spread out on a distance of 310 km along the river bank between Naslavcea and Dubasari dams.

The water samples were collected from the upper horizons (0.5–0.6 m). The measured indicators hydrochemical included hardness, mineralization and the content of major ions (Ca^{2+}, Mg^{2+}, Na^{+}+ K^{+}, HCO_3^{-}, SO_4^{2-}, Cl^{-}). The traditional hydrochemical parameters of water served as additional indicators of potential impact of the water reservoir on the water flow from the Dniestrovsk barrage. The following parameters were measured: temperature, dissolved oxygen, pH, Eh, rH_2, BOD, COD, NH_4^{+}, NO_3^{-}, NO_2^{-} PO_4^{3-}, Cu(II), Fe(III), H_2O_2, and OH radicals.

3. Results and discussions

The investigations carried out during 2005–2008 in the segment Naslavcea (below the barrage of the buffer reservoir) and Dubasari (below the barrage) led to figure out the following results.

It was identified that the water discharged in the buffer reservoir of the hydro-technical station at Dniestrovsk were characterized as hydrocarbonate, hydrocarbonate-sulphate types of calcium and magnesium group, in which the ratio of anions and cations most often could be presented as follows: $Cl^{-} > Na^{+} + Mg^{+}$. The mineralization determined throughout all the investigation period has varied between 257–417 mg/l, hardness from 3.5 to 4.8 mg·equiv./l, and the ion content was continuously unstable. The water discharged from the buffer reservoir in most cases determined the mineralization, hardness and instability of ion content of the investigated segment of the Dniester river. A strong correlation between the mineralization in samples collected at Naslavcea and all sites lower the barrage was observed.

The Dniester oxygen regime was characterized by the following peculiarities. The content of dissolved oxygen in the water samples at Naslavcea was always lower than in samples from other sections of the river. The normal saturation by oxygen of the Dniester water occurred only in spring. During summer and autumn the saturation of water by oxygen was permanently decreased, constituting an average of 70.5% in summer and 79.5% in autumn.

Lower Naslavcea, most part of the year the concentration of oxygen dissolved in water was close to normal saturation (95–110%), except in the cases of hypersaturation of water (158–177%) observed at Cosauti and Dubasari. In the Dubasari water reservoir a decrease of oxygen content usually appears at the end of summer season.

According to the measurement of rH_2 indicator, the Dniester water had instable state both in seasonal and spatial aspects. The ratio of oxidants and reducers of the water can be characterized as neutral at Naslavcea and Cosauti in summer and in spring, and at Bosernita and Dubasari in autumn and in spring. At Mereseuca and in the deep horizon of Dubasari reservoir this indicator was shifted most often towards the reducing processes.

Mineral forms of nitrogen and phosphorous were constantly present in the water samples. The content of ammonium ions was increasing from Naslavcea towards the lower part of the Dubasari barrage from 0.015–0.021 till 0.136 mg NH_4/l. The seasonal variation was manifested by the increasing of NH_4 in autumn and its practical absence in spring.

The average content of nitrates throughout the year constituted 5.5–7.42 mg NO_3/l. The seasonal dynamics of the nitrates was opposite to the dynamics of nitrogen in the form of ammonium. The concentration of nitrates from Mereseuca to the lower part of Dubasari reservoir was increased in spring and decreased in autumn. At Naslavcea the maximum content of nitrates was observed in summer season. The content of nitrites was varying from 0.027–0.058 mg NO_2/l in the investigated segment of the Dniester river and was permanent in all the point of sample collection of the water. The absence of nitrites was observed only early in spring above and below the Dubasari barrage. The seasonal variation of nitrites content was manifested by the concentration increase in summer and decrease in spring. The continuous presence of nitrites in the Dniester waters and the low content or total absence of ammonium nitrogen allow concluding that the oxidation state of the waters is unfavorable, that causes a decrease of the rate of oxidation from NO_2^- to NO_3^-.

The average content of phosphates was varying in the section lines in the range 0.11–3.22 mg PO_4^{3-}/l. The maximal content of phosphates was observed in the summer of 2006 at Cosauti and Bosernita sites and constituted 3.22 and 1.37 mg PO_4^{3-}/l respectively. The increase in the content of phosphates occurred in spring in the segment of the river Naslavcea–Mereseuca, and in summer from Cosauti to Dubasari.

The amount of organic substances according to the BOD indicator constituted in average 3.1–3.3 mg O_2/l in the segment Naslavcea–Cosauti, and 3.6–3.9 mg O_2/l at Dubasari water reservoir. The seasonal variation was manifested by the increase of the indicator in spring at Naslavcea and Dubasari water reservoir (Bosernita–lower section line), while at Mereseuca and Cosauti this increase occurred in summer.

The Dniester waters are characterized by seasonal variation of the redox state.

The general trend during autumn–spring was observed towards a decrease of the hydrogen peroxide concentration and the formation of an instable state close to a quasy-reducing state of waters.

During summer time the content of hydrogen peroxide was rising, so that in June 2006 the value of H_2O_2 was of the order 10^{-6} M. The increase, however, was registered only for the Naslavcea–Cosauti sector, while for the Bosernita–Dubasari (below the dam) the hydrogen peroxide was missing. The increase in June was followed by a decrease of one order in August 2006.

The diminishing of the hydrogen peroxide content in September and November, as well as from June to August, its absence in March can be explained on the one hand by the decrease of photosynthetic activity, when the dominant role in the formation of H_2O_2 in natural waters is determined by the solar radiation (influenced by solar light the superoxid O_2^{-}. anion radical is formed, which is precursor of H_2O_2). On the other hand, the water temperature is decreasing (in the case of autumn), therefore the influence of another important physical–chemical parameters that promotes the redox catalytic processes are diminished.

The values of H_2O_2 concentration were predominantly by order of 10^{-7}M which is insignificant for the occurrence of efficient chemical self-purification processes in water medium [6].

The point characterized by continuous instable reducing state was the Bosernita site that is located in the proximity of the accumulation segment of the river above the Dubasari barrage. The last one was characterized repeatedly as well by instable state of the waters, since out of seven measurements of the redox state three have demonstrated an unfavorable state according to the content of hydrogen peroxide.

During the summer season, the chemical self-purification processes occur in the Dniester waters very effectively, that is why the negative impact of pollutants is partially diminished.

The degradation of the water quality of the Dniester river is influenced both by the elevated content of pollutants in tributary waters and discharges of wastewaters from municipalities located along the river above the Dubasari barrage.

4. Water management in Moldova

The results of the investigation presented above proves again that the anthropogenic impact on the water resources are manifested through radical changes of the water quality and biodiversity in aquatic ecosystems so that the management of quality of water resources and their sustainable use becomes one of the most stringent contemporary challenges. Thus, the National Program on Water Management initiated by the Academy of Sciences of Moldova has as major goal the development of the monitoring system of aquatic resources as well as all the other components related to water supply and treatment.

The realization of the program requires an active involvement of teams of specialists of high qualification and vast technical and scientific experience in the field from academia, ministries, educational institutions, industry, non-governmental organizations as well as other stakeholders. The program timeframe is set between the years 2009–2012 and has the following objectives:

1. Improvement of the legislative, normative and cadastre bases related to application of water resources, implementation of European standards of the indices of natural water quality
2. Development of the "Center of Scientific Control of Water Quality"
3. Development of a GIS database for water quality, complex monitoring of the state of the quality of water resources (based on investigation of the surface and ground water quality, identification of the sources of pollution, purification systems and evaluations of the possibilities to reuse of treated waters) in the context of provisions of the European Directive
4. Realization of fundamental investigations in the field of molecular structure and physical chemical properties of water
5. Elaboration of recommendations for conservation of river and lake ecosystems, for consolidation of concepts of integrated management and utilization of aquatic resources
6. Elaboration and implementation of new technologies of water treatment, supply and reuse, as well as rational utilization of water in the industrial, agricultural and fisheries sectors of the national economy, application of information software in the field of automation and monitoring of technological processes
7. Elaboration and construction of pilot-scale equipment and auxiliary devices for purification and reuse of wastewater in irrigation systems
8. Training of highly qualified specialists in hydrochemistry, hydrogeology, hydrology, environmental hygiene, environmental legislation, management of aquatic resources and other
9. Rising consciousness of population and involvement of the community in the decision-making processes related to implementing of the integrated management of water resources and, consequently, the improvement of the living conditions of the population

Originality of the Program consists of the development of complex investigations (hydrochemistry, hydrogeology, hydrology, ecotoxicology, etc.) that will allow the continuous estimation of the state of water resources and will contribute to the development of a geoinformation system satisfying modern requirements. On its basis, the implementation of the integrated management of water resources will be assured.

The realization of the Program will facilitate the development of fundamental and applied investigations and will contribute to improve the scientific and technological infrastructure of R&D institutions, including the development of a modern scientific Center for Water Quality Control.

The fields of application of the results of investigation include: ecology, environmental protection, drinking water supply, treatment, reuse of wastewaters, fish industry, irrigation, and other branches of economy. The Program will contribute to the development of bilateral and multilateral collaboration with other countries.

The implementation of the Program will facilitate the enforcement of the scientific recommendations that have the purpose to reorient the ecological state of the hydrographic basins of the rivers Dnister, Prut, and Danube and the Black Sea, elaboration and implementation of new standards and norms harmonized with ISO standards, modern technologies of water supply and treatment, and reuse of wastewaters. There will be proposed science-based criteria of construction and exploitation of hydro-technical systems, improvement of techniques of irrigation and optimization of water resources administration.

A system of continuous qualification of specialists from diverse fields will be developed, that will include study and utilization of surface and ground water resources. Involvement of undergraduate and graduate students, young researchers in the realization of the program as well as the implementation of the scientific results in educational process will contribute to train specialists in the field of monitoring and management of aquatic resources.

The Program will contribute to the sustainable development of the society and life quality, the amelioration of the analytical and material infrastructure of institutions and the establishment of collaborations with partners from Ukraine and Romania due to the transboundary character of the Dnister, Danube and Prut rivers and their aquifers.

The Program will assure the improvement of the technologies and sustainable supply of water to the population and the economic sectors. It will also improve the technology of irrigation, a fact that has important social, economic and environmental value as more than 60% of fresh water is used in agriculture.

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INTERMEDIATES IN PHOTOCHEMISTRY OF Fe(III) COMPLEXES IN WATER

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Abstract. The photochemistry of $Fe(OH)^{2+}$ complex and complexes formed by Fe(III) and pyruvic (Pyr), tartaric (Tart), sulfosalycilic (SSA) and oxalic (Ox) acids in aqueous solutions were studied by means of stationary and nanosecond laser flash photolysis. The application of different scavengers of transient radicals has shown that the hydroxyl radical is the primary photochemical species in photochemistry of the $FeOH^{2+}$ complex. In the photochemistry of $FePyr^{2+}$ and $FeTart^{+}$ complexes a weak absorption was found in the red spectral region which was attributed to $[Fe^{II}...R\text{-}COO^{\bullet}]^{2+}$ radical complexes. Laser flash photolysis of $FePyr^{2+}$ and $FeTart^{+}$ complexes in the presence of methyl viologen (effective scavenger of different free radicals) gave evidence of $MV^{\bullet+}$ radical cation formation with concentration as small as ~2% of Fe(III) complex disappeared. The reaction mechanism including inner-sphere electron transfer with the formation of $[Fe^{II}...R\text{-}COO^{\bullet}]^{2+}$ radical complex and its transformation to the reaction products is proposed. The main photochemical process for $Fe^{III}(C_2O_4)_3^{3-}$ complex in aqueous solutions was found to be intramolecular electron transfer from the ligand to Fe(III) ion with the formation of a primary radical complex $[(C_2O_4)_2Fe^{II}(C_2O_4^{\bullet})]^{3-}$. The yield of free radical species (i.e., $CO_2^{\bullet-}$ and $C_2O_4^{\bullet-}$) was found to be less then 6% of $Fe^{III}(C_2O_4)_3^{3-}$ disappeared after a laser pulse.

Keywords: photochemical process, Fe (III) complexes, organic acid ligands, laser flash photolysis.

1. Introduction

The most photochemically active spectral region of solar irradiation near 300 nm (290–310 nm) gives $\geq 10^{-2}$ M quanta per year [1] in layer about 10 m of ocean or river waters. This value exceeds the concentration of many impurities in natural waters (10^{-4}–10^{-6} M), and the photochemical reactions can play an important role

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in their transformation. Iron is the most abundant transition metal, typically found in concentrations of several μM in natural waters. Carboxylic acids are considered to be one of the dominant classes of organic compounds found in natural waters. Therefore, the photochemistry of iron hydroxo- and carboxylic complexes has received considerable attention over the past 50 years.

The literature [2] mechanism of Fe(III) hydroxocomplexes photolysis in water solutions is based on intramolecular electron transfer from the coordinated OH^- anion to the central ion of the excited complex with subsequent escape of a hydroxyl radical into the bulk. It is assumed that the oxidation of organic compounds is initiated by the $^\bullet OH$ radical. This mechanism was, however, usually based on the results of analysis of only final products of phototransformations. $^\bullet OH$ radical in water solutions has a weak absorption in the far UV spectrum region (a band with a maximum at 225 nm and absorption coefficient of about 500 M^{-1} cm^{-1} [3]) not easily accessible for recording because of the absorption of initial complexes. Therefore, in time-resolved photochemical experiments it can be revealed using a trap, i.e., a molecule that, in reactions with $^\bullet OH$ radical, forms an intermediate with a characteristic absorption spectrum.

The presence of carboxylic acids, in the forms of oxalate, citrate ions and so on, has a significant effect on photoactivity of Fe(III) ions, because they may form stable complexes with Fe(III) ions. The primary photochemical process for Fe(III) complexes with carboxylic acids was proposed to be an inner-sphere electron transfer with the formation of Fe(II) complex and an escape of an organic radical to the solvent bulk followed by its decarboxylation [4]. The secondary radical formed as the result of decarboxylation could react with the different components of the reaction system (e.g., Fe(III) complexes or molecular oxygen). Reaction mechanisms put forward on the basis of the nature and content of the final reaction products should be verified by the experiments on the observation of the proposed intermediates.

The aim this work was to observe intermediates in the photochemistry of $FeOH^{2+}$ complex and Fe(III) carboxylic complexes with sulfosalycilic (FeSSA), pyruvic ($FePyr^{2+}$), tartaric ($FeTart^{+}$) and oxalate ($FeOx_3^{3-}$) ions (structures of these complexes are shown in Fig. 1.1).

For recording of the intermediates, which have no absorption in the suitable spectral region, one needs to use scavengers. A scavenger should react with the studied intermediate to form another short-living species, which has a characteristic and intensive absorption in a suitable spectral region. In case of photochemistry of $FeOH^{2+}$ complex N,N-dimethylformamide (DMFA), benzene, phenol (PhOH) and nitrobenzene ($PhNO_2$) as the $^\bullet OH$ radical scavengers were used. In some other cases the dication of methyl viologene (MV^{2+}) was used as the scavenger of primary transient radicals. The molar absorption coefficient for the $MV^{\bullet +}$ radical cation in water is equal to 41,500 M^{-1} cm^{-1} at 396 nm [5].

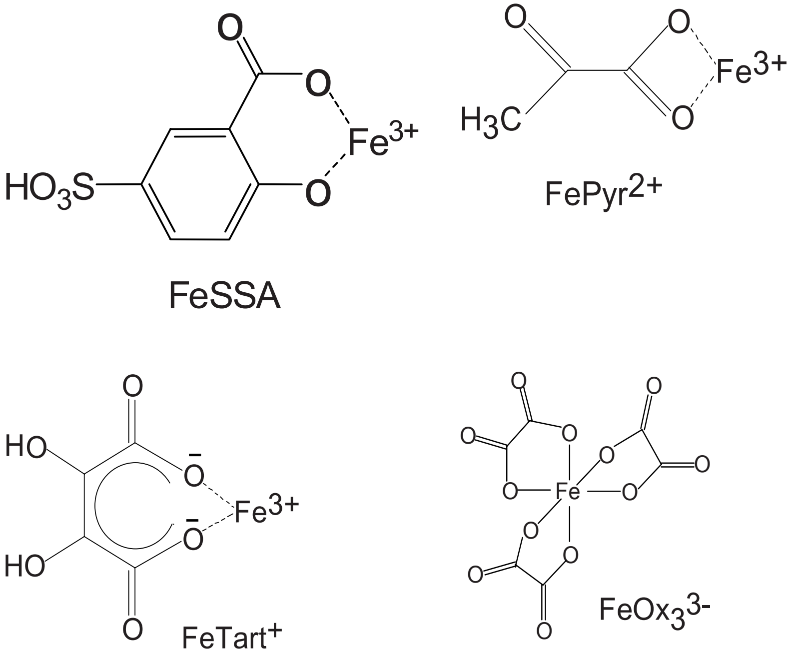

Fig. 1. Structures of Fe(III) carboxylic complexes with sulfosalycilic (FeSSA), pyruvic ($FePyr^{2+}$), tartaric ($FeTart^{+}$) and oxalate ($FeOx_3^{3-}$) ions.

2. Experimental

A set-up for laser flash photolysis with XeCl (308 nm, 15 ns, 30 mJ) or YAG:Nd (355 nm, 7 ns, 40 mJ/pulse) laser excitation [6] was used in the experiments. A steady-state photolysis was performed using irradiation of either a XeCl and YAG:Nd lasers or a high-pressure mercury lamp with a set of glass filters for the separating the necessary wavelengths. Electron absorption spectra were recorded using HP 8354 spectrophotometers. The analysis of the final products of photochemical reactions was performed by HPLC (SP8800-20 "Spectra Physics" chromatograph with an UV detector). For the numerical calculations of the kinetic curves of flash photolysis, the differential equations were solved by means of the fourth-order Runge-Kutta method.

As a source of Fe(III) ions, $Fe(ClO_4)_3 \times H_2O$ (Aldrich) was used. The absorption spectrum of $Fe(OH)^{2+}$complex contains charge transfer bands with maxima at 208 and 300 nm (absorption coefficients at these wavelengths are 4,300 and 1,985 M^{-1} cm^{-1}, respectively [2]). All the experiments with $FeOH^{2+}$ complex were carried out in solutions with pH ≈ 3. In these conditions, the ions of trivalent iron form the complexes $Fe(OH)^{2+}$ (90 %) and Fe^{3+}(aq) (10 %) [2]. Since the absorption coefficient of hydroxo-complex at the wavelength of laser radiation (308 or 355 nm) is much higher than that of Fe^{3+}(aq), the only photoactive form in the experiments was the $FeOH^{2+}$ complex.

The concentration of scavengers was much higher than that of the other substances, such as Fe(III) or ligands and was enough to capture all of transient radicals generated in the photoreaction. In spite of low absorption at 308 and 355 nm, a scavenger does not display any photochemical activity under excitation at these wavelengths, which is necessary for its application as a trap of transient radicals. All experiments were performed in oxygen-free samples with double-distilled water. When preparing samples with $Fe(OH)^{2+}$ complex, the water was also additionally treated by irradiating Fe(III) perchlorate solution for several hours with the light of a high-pressure mercury lamp to remove the organic impurities.

3. Results and discussion

3.1. The $^{\bullet}OH$ radical formation in photochemistry of $FeOH^{2+}$ complex [7–11]

Experiments on the laser flash photolysis of $Fe(OH)_{aq}{}^{2+}$ in presence of organic additives (nitrobenzene 10^{-5}–10^{-4} M, DMFA 10^{-5}–10^{-2} M and phenol 10^{-5}–10^{-4} M) have demonstrated the formation of an intermediate absorption. A characteristic time of an increase of the signals reduces with the enhancing the concentration of organic traps of $^{\bullet}OH$ radical. The intermediate absorption spectra have maxima at 410 and 380 nm in presence of nitrobenzene and DMFA and correspond to the $Ph(^{\bullet}OH)NO_2$ [12] and $HCON(CH_2^{\bullet})(CH_3)$ [13] radicals. In presence of phenol, the initial intermediate absorption spectrum has a maximum at 335 nm corresponding to that of the radical $Ph(OH)_2^{\bullet}$ [14]. After formation, the spectrum of $Ph(OH)_2^{\bullet}$ is transformed to the new absorption bands with maxima at 380 and 400 nm. These data coincide with those obtained in [14] (pulse radiolysis of aqueous phenol solutions). It is shown in [28], that the $Ph(OH)_2^{\bullet}$ radical eliminates a molecule of water with the formation of phenoxyl ($PhO^{\bullet}$) radical. $PhO^{\bullet}$ radical has two narrow close-located absorption bands at 380 and 400 nm and rather poorly absorbs in the region of $\lambda < 350$ nm [14, 15]. The observation of the kinetic curves of the formation of organic radicals for all the systems clearly supports the occurrence of these species in the reactions between $^{\bullet}OH$ radical and organic traps.

The $^{\bullet}OH$ radical can be added to a nitrobenzene molecule in three different positions to form three isomers. However, the data on the difference between the optical spectra of isomers are unavailable in the literature. Therefore, their spectra are assumed to coincide. The proposed mechanism of reactions is described by kinetic scheme (1–5) in which the primary reaction (1) is responsible for hydroxyl radical formation:

$$\mathrm{Fe(OH)^{2+}} \xrightarrow{h\nu} \mathrm{Fe^{2+}(aq)} + {}^{\bullet}\mathrm{OH} \qquad \varphi = 0.2 \tag{1}$$

$$^{\bullet}\mathrm{OH} + \mathrm{PhNO_2} \longrightarrow \mathrm{Ph(^{\bullet}OH)NO_2} \qquad k_2 = 4.7 \times 10^9\ \mathrm{M^{-1}\,s^{-1}} \tag{2}$$

$$2\,{}^{\bullet}\mathrm{OH} \longrightarrow \mathrm{H_2O_2} \qquad 2k_3 = 5.2 \times 10^9\ \mathrm{M^{-1}\,s^{-1}} \tag{3}$$

$$2\,\mathrm{Ph(^{\bullet}OH)NO_2} \longrightarrow \text{products} \qquad 2k_4 = 2.7 \times 10^9\ \mathrm{M^{-1}\,s^{-1}} \tag{4}$$

$$^{\bullet}\mathrm{OH} + \mathrm{Fe^{2+}(aq)} \longrightarrow \mathrm{Fe(OH)^{2+}} \qquad k_5 = 4.7 \times 10^9\ \mathrm{M^{-1}\,s^{-1}} \tag{5}$$

The results of modeling the experimental curves with different concentrations of nitrobenzene and $\mathrm{Ph(^{\bullet}OH)NO_2}$ radicals (varied by change in laser pulse intensity) allow to get the rate constants of all reactions in scheme (1–5). The absorption coefficient of the band at 410 nm of $\mathrm{Ph(^{\bullet}OH)NO_2}$ radical was calculated as $\varepsilon = 5660\ \mathrm{M^{-1}\ cm^{-1}}$.

3.2. Possible processes of $^{\bullet}$OH radical formation upon the excitation of FeOH^{2+} complex [8]

One can suggest the different mechanisms of $^{\bullet}$OH radical formation in reactions involving the light-excited $[\mathrm{FeOH^{2+}}]^*$ complex:

M1. The intrasphere electron transfer from hydroxide ion with subsequent escape of $^{\bullet}$OH radical into the bulk

$$[\mathrm{FeOH^{2+}}]^* \longrightarrow [\mathrm{Fe^{2+}(^{\bullet}OH)}] \tag{6}$$

$$[\mathrm{Fe^{2+}(^{\bullet}OH)}] + \mathrm{H_2O} \longrightarrow \mathrm{Fe^{2+}(aq)} + {}^{\bullet}\mathrm{OH} \tag{7}$$

M2. Electron transfer from the second coordination sphere accompanied by proton transfer into the solvent bulk

$$\mathrm{Fe(OH)^{2+}} + \mathrm{H_2O} \longrightarrow \mathrm{Fe^{2+}(OH^{-})} + {}^{\bullet}\mathrm{OH} + \mathrm{H^+} \tag{8}$$

M3. Hydrogen atom transfer from the second to the first coordination sphere

$$\mathrm{Fe(OH)^{2+}} + \mathrm{H_2O} \longrightarrow \mathrm{Fe^{2+}(aq)} + {}^{\bullet}\mathrm{OH} \tag{9}$$

It was tried to determine the mechanism of hydroxyl radical formation based on the temperature dependence of quantum yield. The idea is that when realizing mechanisms M2 and M3, based on tunneling, the activation energy of quantum yield should tend to zero. Process M1 includes the reaction of exchange of a hydroxyl radical to a water molecule in the first coordination sphere of Fe^{2+} ion.

It should possess considerable activation energy typical of the reactions of photoaquation (for $FeOH^{2+}$ ion the activation energy of water molecule exchange in the first coordination sphere is 34.7 kJ mol^{-1} [16]). Thus, in the case of great activation energy of quantum yield, one could suggest, with great probability, the realization of mechanism (M1).

The method of laser flash photolysis was used to measure the quantum yield of hydroxyl radical upon photolysis of $FeOH^{2+}$ complex in the presence of nitrobenzene. The absolute value of $^{\bullet}OH$ radical quantum yield at 298 K was found to be 0.2, which is in fair agreement with the value of 0.195 obtained upon excitation at 310 nm [2]. However, the activation energy is only 10.0 ± 1.3 kJ mol^{-1} and this low value does not allow one to choose among the different photolysis mechanisms M1, M2, and M3.

3.3. Photochemistry of Fe(III)-Pyr complex

The UV spectrum of $FePyr^{2+}$ complex was reported previously [17]. It exhibits a charge transfer band with maximum at 323 nm (ε = 1550 M^{-1} cm^{-1}) and more intense bands at shorter wavelengths. The stability constant (pK = 4.83) of $[Fe^{III}Pyr]^{2+}$ was calculated in [18]. Taking into account the dissociation constant of pyruvic acid (pKa = 2.5 [19]) and the equilibrium constants for Fe(III) hydroxocomplex [20]), the content of $[Fe^{III}Pyr]^{2+}$ complex for total concentrations of Fe(III) and pyruvate anion 5×10^{-4} M and 1.5×10^{-3} M, correspondingly, at pH 3 was about 86%. The quantum yield of $[Fe^{III}Pyr]^{2+}$ photolysis for deaerated solutions was found to be 1.0 ± 0.1.

In the experiments on laser flash photolysis a weak absorption was found in the spectral region of 580–720 nm. This absorption was attributed to $[Fe^{II}...H_3C\text{-}C(O)\text{-}COO^{\bullet}]^{2+}$ radical complex. Laser flash photolysis of $[Fe(Pyr)]^{2+}$ in the presence of methyl viologen (MV^{2+} dication) gave evidence of $MV^{\bullet+}$ radical cation formation. Its initial concentration was found to be as small as 2% of $[Fe(Pyr)]^{2+}$ disappeared. The reaction mechanism including inner-sphere electron transfer with the formation of $[Fe^{II}...H_3C\text{-}C(O)\text{-}COO^{\bullet}]^{2+}$ radical complex and its transformation to the reaction products is proposed.

$[Fe^{III}Pyr]^{2+} \xrightarrow{h\nu} Fe^{2+} + H_3C\text{-}C(O)\text{-}COO^{\bullet}$ 2% of total photoreaction (10)

$[Fe^{III}Pyr]^{2+} \xrightarrow{h\nu} [Fe^{II}...H_3C\text{-}C(O)\text{-}COO^{\bullet}]^{2+}$ 98% of total photoreaction (11)

$[Fe^{II}...H_3C\text{-}C(O)\text{-}COO^{\bullet}]^{2+} \longrightarrow Fe^{2+} + H_3C\text{-}C(O)\text{-}COO^{\bullet}$ slow (12)

$H_3C\text{-}C(O)\text{-}COO^{\bullet} \rightarrow CH_3^{\bullet}CO + CO_2$ fast (0.01-1 μs) (13)

$2\,CH_3^{\bullet}CO \rightarrow (CH_3CO)_2$ $2k = 2 \times 10^9\ M^{-1}\ s^{-1}$ (14)

$CH_3^{\bullet}CO + MV^{2+} \rightarrow CH_2CO + MV^{\bullet+} + H^+$ $k = 3 \times 10^9\ M^{-1}\ s^{-1}$ (15)

$MV^{\bullet+} + [Fe^{III}Pyr]^{2+} \rightarrow MV^{2+} + [Fe^{II}Pyr]^+$ $k = 1 \times 10^8\ M^{-1}\ s^{-1}$ (16)

So, the major channel of the $[\mathrm{Fe^{III}Pyr}]^{2+}$ photoreaction seems to be the formation of the transient $[\mathrm{Fe^{II}...H_3C\text{-}C(O)\text{-}COO^{\bullet}}]^{2+}$ radical complex. The formation of a weak absorption band in the region of 650 nm is a manifestation of the radical complex. The decay of the radical complex leads to the reaction products.

3.4. Photochemistry of Fe(III)-Tart complex [21]

The UV spectrum of Fe(III)-Tart complex contains a charge transfer band with maximum at 345 nm ($\varepsilon = 1600\ \mathrm{M^{-1}\ cm^{-1}}$) and more intense bands at shorter wavelengths. $[\mathrm{Fe^{III}Tart}]^{+}$ complex was prepared from iron(III) perchlorate (Aldrich) and tartaric acid (Aldrich). The typical concentrations of the both reagents were 5×10^{-4} M at pH 3.0. It is evident from the equilibrium constants ($\lg K_1 = 7.49$ and $\lg K_2 = 11.86$ [22]) that ca. 86% of Fe(III) was forming the $[\mathrm{Fe^{III}Tart}]^{+}$ complex. The goal of the study was the search of suitable and effective scavenger for short-living intermediates formed upon the photolysis of $[\mathrm{Fe^{III}Tart}]^{+}$ complex. To solve the problem, methyl viologen dication ($\mathrm{MV^{2+}}$) was used as a scavenger for the organic radicals.

The photolysis of $[\mathrm{Fe^{III}Tart}]^{+}$ in the absence of $\mathrm{MV^{2+}}$ leads only to the instant bleaching in the region of the absorption band of the initial complex. It means that the absorption of the intermediates in the region of 300–800 nm, if exists, is weak. If $\mathrm{MV^{2+}}$ is added, the instant decrease in absorption due to the disappearance of $[\mathrm{Fe^{III}Tart}]^{+}$ is superimposed with the formation of new sharp bands of $\mathrm{MV^{\bullet+}}$ radical cation in the region of 370–400 nm and a less intensive band with the maximum at 605 nm [5]. $\mathrm{MV^{\bullet+}}$ radical cation is formed in the reaction of $\mathrm{MV^{2+}}$ with an organic ${}^{-}\mathrm{COOH\text{-}CHOH\text{-}{}^{\bullet}CHOH}$ radical anion, which is the product of decarboxylation of the primary radical anion ${}^{-}\mathrm{COOH\text{-}CHOH\text{-}CHOH\text{-}COO^{\bullet}}$. The rate of $\mathrm{MV^{\bullet+}}$ decay was found to increase with the concentration of the initial complex. It means that the radical anion disappears in the reaction with $[\mathrm{Fe^{III}Tart}]^{+}$. This mechanism is analogous to the case of photolysis of Fe(III)-Pyr.

$$[\mathrm{Fe^{III}Tart}]^{+} \xrightarrow{h\nu} \mathrm{Fe(II)} + {}^{-}\mathrm{OOC\text{-}CHOH\text{-}CHOH\text{-}COO^{\bullet}} \tag{17}$$

$$[\mathrm{Fe^{III}Tart}]^{+} \xrightarrow{h\nu} [\mathrm{Fe(II)}\ldots{}^{-}\mathrm{OOC\text{-}CHOH\text{-}CHOH\text{-}COO^{\bullet}}]^{+} \tag{18}$$

$$[\mathrm{Fe(II)}\ldots{}^{-}\mathrm{OOC\text{-}CHOH\text{-}CHOH\text{-}COO^{\bullet}}]^{+} \longrightarrow \mathrm{Fe(II)} + {}^{-}\mathrm{OOC\text{-}CHOH\text{-}CHOH\text{-}COO^{\bullet}} \quad \text{slow} \tag{19}$$

$${}^{-}\mathrm{OOC\text{-}CHOH\text{-}CHOH\text{-}COO^{\bullet}} \longrightarrow {}^{-}\mathrm{OOC\text{-}CHOH\text{-}{}^{\bullet}CHOH} + \mathrm{CO_2} \quad \text{fast} \tag{20}$$

$$2\,{}^{-}\mathrm{OOC\text{-}CHOH\text{-}{}^{\bullet}CHOH} \longrightarrow \text{products} \qquad 2k = 6 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}} \tag{21}$$

$${}^{-}\mathrm{OOC\text{-}CHOH\text{-}{}^{\bullet}CHOH} + \mathrm{MV^{2+}} \longrightarrow {}^{-}\mathrm{OOC\text{-}CHOH\text{-}CHO} + \mathrm{MV^{\bullet+}} + \mathrm{H^{+}} \qquad k = 4.4 \times 10^{6}\ \mathrm{M^{-1}\ s^{-1}} \tag{22}$$

$$\mathrm{MV^{\bullet+}} + [\mathrm{Fe^{III}(CH(OH)COO^{-})_2}]^{+} \longrightarrow \mathrm{MV^{2+}} + [\mathrm{Fe^{II}(CH(OH)COO^{-})_2}] \qquad k = 1.8 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}} \tag{23}$$

Literature does not contain information on the decarboxylation rate constants for the radical anions like $^{-}$OOC-CHOH-CHOH-COO$^{\bullet}$, which have no absorption in the spectral range convenient for recording. It might be worth to note that the rate constants of decarboxylation were measured for different aryloxyl radicals, which have an intensive absorption in the visible spectral region. These rate constants are in the range of $10^6 – 5 \times 10^7$ s^{-1} [23].

3.5. Photochemistry of FeSSA complex [24, 25]

The spectrum of FeSSA complex contains a charge transfer band with maximum at 505 nm (ε = 1800 M^{-1} cm^{-1}) [26]. In the UV region, FeSSA complex displays a stronger band with λ_{max} = 286 nm. The absorption band with a maximum at 297 nm is typical of the free non-coordinated SSA ligand. Concentrations of Fe(III) ions and SSA were usually about 10^{-4} M and 3×10^{-4} M, accordingly. All experiments were carried out with oxygen-free samples at pH = 3 and 298 K. The experiments on pump-probe femtosecond spectroscopy were described in [25].

Just after excitation of the complex with a femtosecond pulse (λ_{ex} = 530 nm), a bleach of the 505 nm absorption band was observed. The absorption of the complex is almost completely recovered after about 5 ps, which is in fair agreement with a photochemical stability of the complex under steady state irradiation in the visible region. The analysis of this time profile by iterative reconvolution of a biexponential function with the instrument response function gives the time constants τ_1 = 260 fs and τ_2 = 1.8 ps. Such biphasic dynamics is rather typical for ultrafast ground state recovery upon CT excitation [27]. Excitation in the CT band is followed by an ultrafast internal conversion to the vibrationally hot electronic ground state, which is then thermalized by vibrational cooling. Therefore, the 260 fs component is ascribed to the internal conversion while the 1.8 ps is assigned to the vibrational cooling.

Although FeSSA complex itself does not exhibit any photochemical activity, stationary irradiation (excimer XeCl laser, λ_{ex} = 308 nm) of solutions containing both complex and free ligand initiates a rather effective disappearance of the FeSSA complex absorption. The flash excitation (λ_{ex} = 308 nm) is followed by the buildup of the absorption band with a maximum at 440 nm. A study of the spectroscopy and photochemistry of SSA aqueous solutions indicates that this band is due to the absorption of excited triplet state of free ligand ($^{T}H_2SSA^{-}$) [24], which results from the absorption of light by the free, non-coordinated $HSSA^{2-}$. When $HSSA^{2-}$ is excited into the singlet S_1 state (308 nm), the triplet state of $^{T}HSSA^{2-}$, which has a T-T absorption band with a maximum at 470 nm, is populated with a quantum yield of φ_T = 0.34 [24]. In acidic solution (pH = 3), the $^{T}HSSA^{2-}$ is rapidly protonated to form the $^{T}H_2SSA^{-}$, whose band shifts to 440 nm and has an absorption coefficient of 6.2×10^3 M^{-1} cm^{-1} [24].

The absorption of ${}^{T}H_2SSA^{-}$ decays within about 20 μs with a simultaneous buildup of a broad bleaching band (negative optical density) at 505 nm caused by the decreased FeSSA absorption. After the disappearance of ${}^{T}H_2SSA^{-}$ (50 μs), the spectrum still contains an absorption band at 400 nm, which belongs to the $HSSA^{2-\bullet}$ radical [24]. Thus, the quenching of ${}^{T}H_2SSA^{-}$ can occur by both electron transfer (24) leading to FeSSA reduction and energy transfer (25). In the latter case, the physical quenching causes no changes in the oxidation state of the Fe(III) ion.

$$FeSSA + {}^{T}H_2SSA^{-} \longrightarrow Fe_{aq}^{2+} + HSSA^{-\bullet} + HSSA^{2-} \qquad k_{24} = 9 \times 10^{8}\ M^{-1}\ s^{-1} \qquad (24)$$

$$FeSSA + {}^{T}H_2SSA^{-} \longrightarrow FeSSA + H_2SSA^{-} \qquad k_{24} = 1.3 \times 10^{9}\ M^{-1}\ s^{-1} \qquad (25)$$

Thus, when the solution contains both FeSSA and non-coordinated $HSSA^{2-}$ ligand, UV irradiation causes a photo-reduction of the complex. This process is due to the electron transfer from the non-coordinated ligand in the triplet state to the FeSSA complex. The energy transfer between these species, which fails to cause any photochemical reaction, competes with the electron transfer. As applied to photo-processes in natural water, the data obtained allow us to define one of the important mechanisms of photo-degradation of organic compounds in anaerobic conditions, i.e., the photo-reduction of transition metal complexes due to the electron transfer from the long-lived triplet states of organic aromatic acids.

3.6. Photochemistry of Fe(III)-oxalate complex [28]

Among Fe(III)-(poly)carboxylate complexes the photochemistry of trioxalate Fe(III) complex ($Fe^{III}(C_2O_4)_3^{3-}$) is of intense interest because this species exhibits high photochemical activity in natural waters under sunlight [29] and is widely used as stable and sensitive chemical actinometer [30]. The total process of $Fe^{III}(C_2O_4)_3^{3-}$ photolysis could be presented by reaction (26) [31]

$$2\,Fe^{III}(C_2O_4)_3^{3-} \xrightarrow{hv} 2\,Fe^{II}(C_2O_4^{2-})_2^{2-} + 2CO_2 + C_2O_4^{2-} \qquad (26)$$

The quantum yield of Fe(II) formation in reaction (26) is independent on the excitation wavelength in the range 270–365 nm and equals to 1.24 [30]. There are two different points of view on the primary photo-process following by excitation of $Fe^{III}(C_2O_4)_3^{3-}$. One of them is intramolecular electron transfer from the ligand to Fe(III) ion. The long-lived excited state, the radical complex $[(C_2O_4)_2Fe^{II}(C_2O_4^{\bullet})]^{3-}$ or the $C_2O_4^{\bullet-}$ radical are proposed as primary intermediate(s) [32, 33]. Another mechanism is the sequential cleavage of Fe(III)-O bond (between one oxalate ligand and Fe(III) ion) and the C-C bond of the ligand. Biradical complex $[(C_2O_4)_2Fe^{III}(CO_2^{\bullet})_2]^{3-}$ [34] or $CO_2^{\bullet-}$ radical are assumed as primary intermediate(s) [35, 36].

Laser flash photolysis experiments carried out in the wide range of initial parameters provide new evidences that intramolecular electron transfer from ligand to Fe(III) ion is a main photochemical process in $Fe^{III}(C_2O_4)_3^{3-}$ photochemistry. As primary intermediate the radical complex $(C_2O_4)_2Fe^{II}(C_2O_4^{\bullet})^{3-}$ is formed, yield of organic radicals in the primary photo-process is negligible.

Kinetic scheme of $Fe^{III}(C_2O_4)_3^{3-}$ photolysis was proposed including formation of $(C_2O_4)_2Fe^{II}(C_2O_4^{\bullet})^{3-}$ (in ground electronic state), its reversible dissociation on the oxalate ion and secondary radical complex $(C_2O_4)Fe^{II}(C_2O_4^{\bullet})^{-}$ and decay of both radical complexes. In the framework of this scheme absorption spectra and rate constant of formation and decay of all intermediates were determined.

$$Fe^{III}(C_2O_4)_3^{3-} \xrightarrow{h\nu} (C_2O_4)_2Fe^{II} + CO_2 + CO_2^{\bullet-} \qquad \text{6\% of total photoreaction} \tag{27}$$

$$Fe^{III}(C_2O_4)_3^{3-} \xrightarrow{h\nu} (C_2O_4)_2Fe^{II}(C_2O_4^{\bullet})^{3-} \qquad \text{Radical Complex1 (RC1)} \tag{28}$$

$$(C_2O_4)_2Fe^{II}(C_2O_4^{\bullet})^{3-} \longleftrightarrow C_2O_4^{2-} + (C_2O_4)Fe^{II}(C_2O_4^{\bullet})^{3-} \qquad \text{Radical Complex2 (RC2)}$$

$$K_{29} = 3.8 \times 10^{4}\ s^{-1}$$

$$k_{29} = 3.6 \times 10^{6}\ M^{-1}\ s^{-1} \tag{29}$$

$$RC1 \longrightarrow Fe^{II}(C_2O_4)_2^{2-} + C_2O_4^{\bullet-} \qquad k_{30} = 1.5 \times 10^{2}\ s^{-1} \tag{30}$$

$$RC2 \longrightarrow Fe^{II}(C_2O_4) + C_2O_4^{\bullet-} \qquad k_{31} = 2.0 \times 10^{2}\ s^{-1} \tag{31}$$

$$RC2 + Fe^{III}(C_2O_4)_3^{3-} \longrightarrow 2\,Fe^{II}(C_2O_4)_2^{2-} + 2\,CO_2 \qquad k_{32} = 1 \times 10^{6}\ M^{-1}\ s^{-1} \tag{32}$$

The addition of MV^{2+} to the solutions containing $Fe^{III}(C_2O_4)_3^{3-}$ leads to formation and decay of additional transient absorption signal at 396 nm of the $MV^{\bullet+}$ radical cation. The observed rate constant of the signal formation depends linearly on MV^{2+} concentration. The bimolecular rate constant of $MV^{\bullet+}$ formation $k \approx 1.2 \times 10^{10}\ M^{-1}\ s^{-1}$ is close to value of the rate constant of reaction of $CO_2^{\bullet-}$ radical with MV^{2+} [24]. However, the yield of $MV^{\bullet+}$ radical cation (and $CO_2^{\bullet-}$ radical, respectively) is lower than 6% of total $Fe^{III}(C_2O_4)_3^{3-}$ photo-decay. So, the main way of photoreaction is the $(C_2O_4)_2Fe^{II}(C_2O_4^{\bullet})^{3-}$ radical complex (RC1) formation.

4. Conclusions

Mechanisms of primary photochemical processes are revised for several Fe(III) complexes with organic acids ligands. Intramolecular electron transfer from ligand to Fe(III) ion with the formation of transient radical complex is the main photochemical process for Fe(III) complexes with carboxylic acids. Spectral and kinetic parameters of transient species, such as free radicals and radical complexes, are determined.

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THE HYDRO-CHEMICAL CHANGES OF LAKE SEVAN WATER AFTER THE ARTIFICIAL LOWERING OF THE WATER LEVEL

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Abstract. The paper is aimed to show the influence that the dynamics of artificial lowering of a lake water level has on the hydro-chemical regime and the lake itself, on the example of Lake Sevan. Lake Sevan is one of the world's largest high-altitude fresh-water lakes. Studies of chemical composition of its water were launched at the end of the 19th century, and the first salt balance was determined in the 1930s. According to routine observations, one liter of the lake's water contains about 0.7 g salts. Almost all the ion concentrations have been changed by about 5–10% as a result of the lake level drop. There have also been changes in the general mineralization of the lake that are related to the drop of the lake level and the magnitude of its flow. In 1928–1930, well before the artificial change in lake level, total mineralization was 718,4 mg/l, while today it is 673 mg/l (1999–2002). The decrease of total general mineralization of the lake water is strongly related to the massive outflow of salty water, removing the salts, which had been accumulating in the lake for ages. In conclusion, it must be noted that the drop of the lake level, and the economic development in the basin brought about the change in the hydro-chemical regime of the lake.

Keywords: Lake Sevan, anthropogenic changes, hydro-chemical composition and regime, mineralization, eutrophication.

1. Introduction

Numerous rivers, lakes and, in general, water bodies have undergone considerable changes under the impact of the economic activity of man. As a result, hydrological, biological conditions as well as the morphometrical elements of these bodies have been destroyed. Lake Sevan and its basin may serve as a classical example in this respect (Fig. 1.1).

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Lake Sevan is one of the high-altitude freshwater lakes in the world and is the largest lake in Caucasus. Lake Sevan is regarded to be a large reservoir of fresh water not only for Armenia, but also for the countries of the region.

Originally, before 1930, the surface of Lake Sevan was on the height of 1916 m above sea level. The surface of the drainage area of the lake before its artificial drop (1930s) was 3475 km^2, that is larger than the surface of the lake by 2.5 times (1416 km^2), and the volume of lake water was 58 billion m^3 (Table 1.1).

Fig. 1.1. The river network of Lake Sevan.

Table 1.1. Some hydrometric indices of Lake Sevan.

Indices	Unit of measurement	Before the drop of the level	Present-day condition
Drop of lake level	m	0.0	19.43
Height above sea level	m	1915.89	1896.46
Watershed surface	km^2	3475	3649
Lake surface	km^2	1416	1242
Mean depth	m	41.3	25.9
Maximum depth	m	98.7	79.4
Water amount	km^3	58.5	32.8

The anthropogenic changes in the level of Lake Sevan took place during the last 70 years after the decision to deepen the riverbed of the Hrazdan river - the only river flowing out of the lake, with the aim of using the lake water for irrigation and energy generation.

The aim of the research was to explore the influence of the dynamics of the artificial lowering of the lake's level on the hydro-chemical composition and regime of the lake (in the last 70 years), with the case of Lake Sevan.

2. Results and discussion

In the world limnology, there was no other case when a lake level was artificially lowered for 18 m within 3–4 decades (1930–1970), and by another 2 m in the last decade (1990–2000) (Figs. 2.1 and 2.2).

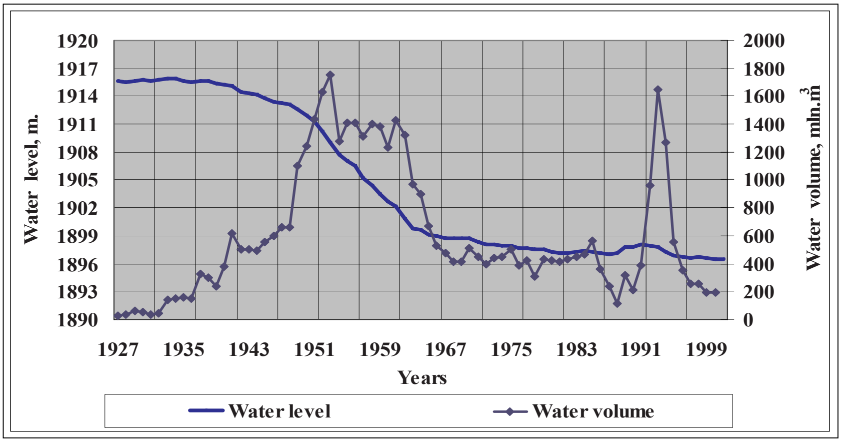

Fig. 2.1. The graph of perennial fluctuation of Lake Sevan level: annual total water outflow volume and average lake level.

In this respect, Lake Sevan is the only lake, which is considered to be a large natural laboratory, where one can observe all those processes connected with the decrease of erosion basis of flowing into the lake rivers, and which cannot be studied under laboratory conditions. Among these processes, the hydrological, thermal, hydro-chemical and carbon regime of the lake, as well as biological conditions, which have served as a rich material for scientific researches, are rather important.

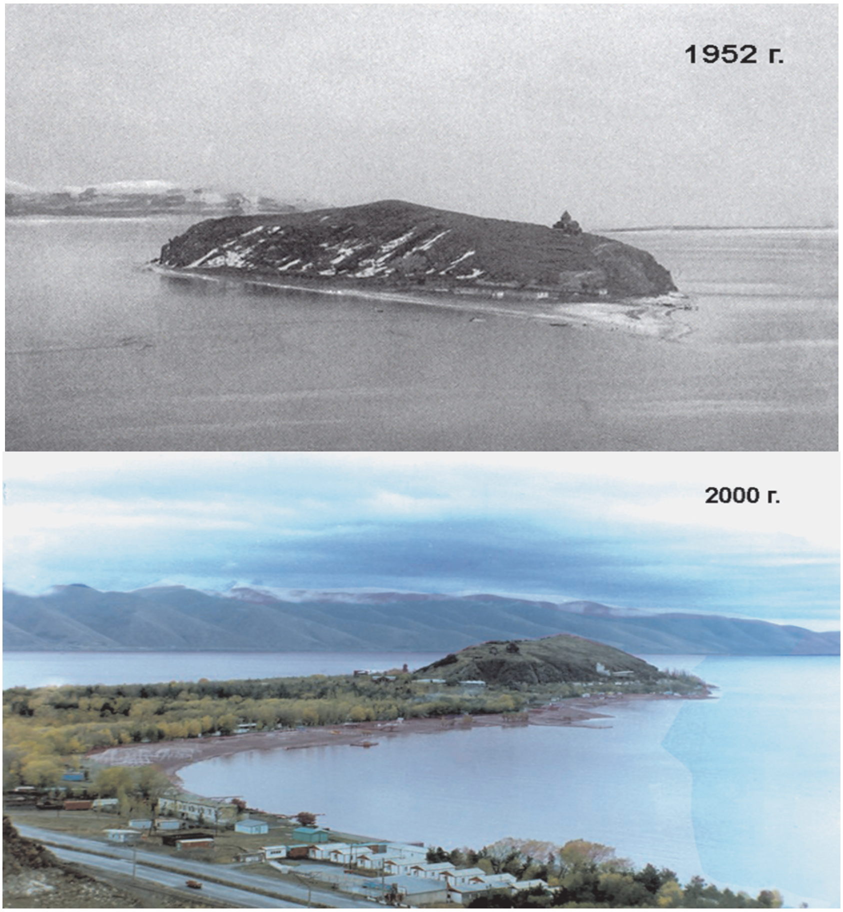

Fig. 2.2. As a result of the decrease of the lake's water level, the island became a peninsula.

The decrease of erosion basis caused the activation of channel processes of the rivers flowing into the lake (Fig. 2.3). It brought about the violation of the balanced profiles of river valleys, formed within thousands of years. The active down-cutting erosion destroyed the foundations of bridges and caused their collapse.

Table 2.1 and Fig. 2.4 allow to figure out the chemical composition of Lake Sevan water in natural state, i.e., before its artificial lowering (1930), and the changes that have taken place since then.

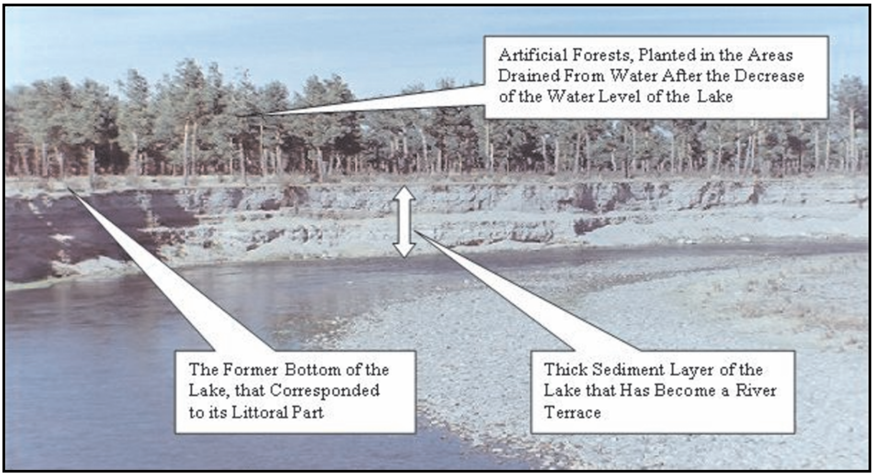

Fig. 2.3. The riverbed of the Argichi River, which has been deepened as a result of the drop of Lake Sevan level.

Table 2.1. The mineralization of Lake Sevan water and its ionic composition in different years.[a]
∑U = Total Mineralization (mg/l).

Ionic composition	Before the drop of the level (1928–1930)	Present-day condition
Ph	9.2	8.6
Ca	33.9	20.6
Mg	55.9	55.4
Na+K	98.7	92.8
HCO_3	414.7	373.0
CO_3	36.0	21.2
Cl	62.3	68.0
SO_4	16.9	29.2
∑U[a]	718.4	660.2

Lake Sevan is one of the world’s largest high-altitude fresh-water lakes. Studies of the chemical composition of its water were launched at the end of 19th century, and the first salt balance was determined in 1930s [1]. According to routine observations, one liter of the lake’s water contains about 0.7 g salt in ionic form. The hydro-carbonate ion (HCO_3) and chlorine (Cl), at 414.7 mg/l and 62.3 mg/l, respectively, dominate in the ionic composition among non-metals. Among cations, magnesium (Mg) with 55.9 mg/l, and sodium plus potassium (Na + K), with 98.7 mg/l, dominate.

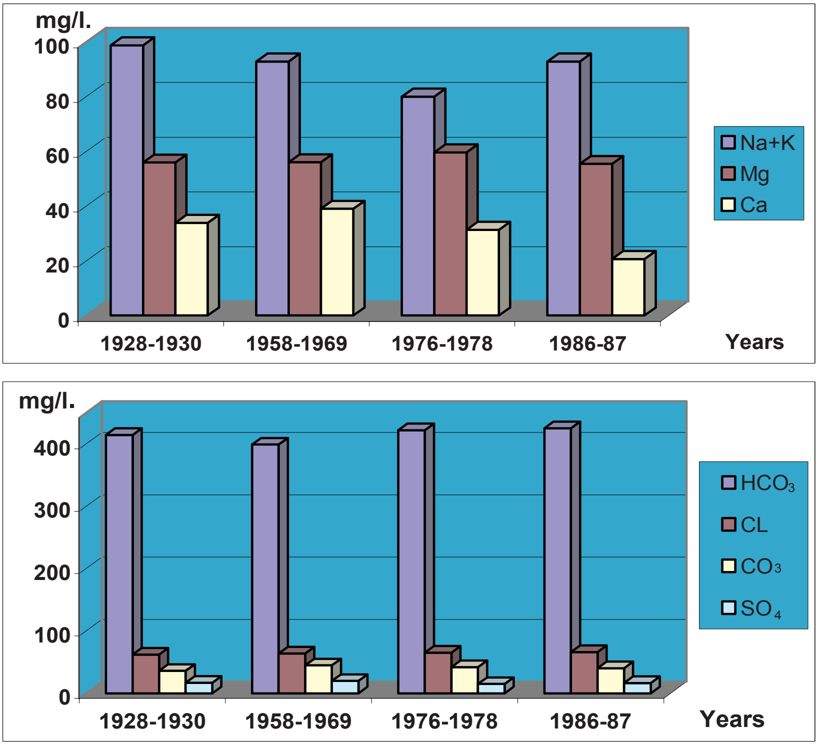

Fig. 2.4. The change of the main ions in the chemical composition of the lake.

Almost all the ion concentrations have been changed by about 5–10% as a result of the drop of the lake level. The calcium concentration has been changed the most. At the end of 19th century, calcium concentration was 38 mg/l, while a century later it was only 21 mg/l [2]. This phenomenon has not yet been closely studied, but some opinions link the lack of calcium in Sevan water to the intensification of plankton photosynthesis. The concentration decrease started in 1978. At the same time, the lake productivity dropped and the growth of blue-green algae abruptly decreased. These changes were observed after an increase of turbidity. The current low level of calcium may lead to another change. The lake water is a rich solution containing Ca^{2+} and CO_3^{2-} which form a poorly soluble $CaCO_3$ carbonate, which settles on the lake bottom.

At present, the ion concentrations in the water are as follows:

$$HCO_3 > Na{+}K > Cl > Mg > SO_4 > CO_3 > Ca$$

To start with $HCO_3 > Mg + Ca$ indicates that according to Aliokhin's classification, Lake Sevan belongs to the magnesium group of the hydro-carbonate lake category.

There have also been changes in the general mineralization of the lake that are related to the drop of the level and the magnitude of its flow (Fig. 2.5).

In 1928–1930, well before the artificial change in lake level, the total mineralization ∑U was 718.4 mg/l. Even during the rapid changes of 1958–1969 it changed little, being 716 mg/l. After 1980 the mineralization sharply decreased, becoming 706.9 mg/l as low as 660 mg/l in 1986–1987 and 673 mg/l at present (1999–2002).

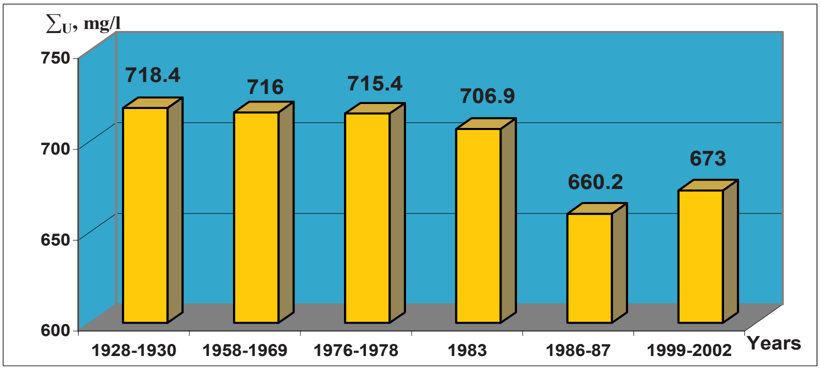

Fig. 2.5. The change of the total mineralization (∑U, mg/l).

The decrease of the total general mineralization of the lake water is strongly related to the massive outflow of salty water, removing the salts, which had been accumulating in the lake for ages.

For comparison, the total mean mineralization of the river waters flowing into the lake is 160–180 mg/l [3].

3. Conclusions

In conclusion, it must be noted that the drop of the lake level and the economic development in the basin brought about the change in the hydro-chemical regime of the lake. The latter caused the disruption of the thermal and hydro-chemical regimes of the lake. The quality of the water deteriorated, water turbidity increased. The inner circulation of the water constituents as well as the circulation of the biological substances altered, as well.

In the next 20–30 years it is envisaged to increase the level of the lake by only 4-6 m, because if the level rises more than that, the recent coastal constructions (roads, railway, resort houses, and others) as well as tree-shrub vegetation (they were artificially planted and grown after the drop of water level) will go under water. However, the latter one is reality today. In the recent 5 years, the water level of the lake has increased by more than two meters, which is the effect of the growth of surface flow and decrease of outflow from the lake.

As a result, a new issue emerged; namely the coastal green zone is under water. Considerable water lever increase took place so fast and unexpectedly, that there was no time to clear the coastal line from its green cover, thus, endangering the lake with eutrophication.

It is hard to predict the future developments of these processes. However, the issue of Lake Sevan is not entirely settled, the ecosystem of the lake is damaged, undergoing the process of eutrophication. The flora and fauna of the water and coast underwent serious and irreversible changes.

These are the old and new issues of Lake Sevan and its basin.

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STATE-OF-THE ART OF WASTEWATER AND SLUDGE TREATMENT IN TURKEY

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Abstract. As a candidate country for the EU membership, proper wastewater treatment and disposal is one of the crucial challenges in Turkey, which should be fulfilled during the next 15 years. More than 3,000 treatment plants are necessary in order to comply with the EU legislation. Huge investments are required for the rehabilitation and new construction of sewage networks as well as for the wastewater treatment plants. Protection of the environment and the need of treated water during the long and dry summer months make the wastewater and sludge treatment process more important than ever.

Keywords: wastewater, sludge treatment, nutrients removal, treatment facility.

1. Introduction

Wastewater treatment has always been one of the main environmental and infrastructural problems which as an EU candidate Turkey is facing. Parallel with the population increase (1.5–1.9% per year) wastewater related problems shows increasing tendency. Due to lack of financial sources, rate of sewage network and treatment plant construction lies far behind the urbanization rate. The dimension of wastewater and sludge management is considerably high, as wastewater produced by over 70 million residents has to be managed.

In the framework of EU accession process of Turkey, harmonization of the EU legislation is ongoing. The relevant EU legislation has already been transferred into Turkish legislation. In the report of National Environmental Strategy (2003–2023) [1], certain time limits are set for the implementation of the wastewater related EU directives such as Water Framework Directive, Urban Wastewater Directive, etc. It is planned to fulfill the requirements of the directives until year 2023. For this purpose significant amount of investments are necessary: It is foreseen that the initial investment and rehabilitation costs of the wastewater treatment plants and networks between years 2007–2023 will be 18 billion Euro. One of the

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main reasons that lead to this huge amount of investments is the uneven distribution of the population within the 3,225 municipalities and 140,00 villages. According to the statistical data (2006), 78% of the population is living in the municipalities (urban population) and the remaining in villages (rural population) [1]. However, official statistics covers only the "urban" population. As seen from Fig. 1.1, 96% of the municipalities have population less than 50,000, which are classified as small-medium sized municipalities. On the other hand, 58% of the urban population lives in only 135 centers. Unfortunately, only 11.2% of the municipalities, in which 42% of the urban population lives, are served by wastewater treatment plants; whereas in the remaining municipalities, the produced wastewater is discharged untreated, mainly to water bodies as the receiving environment.

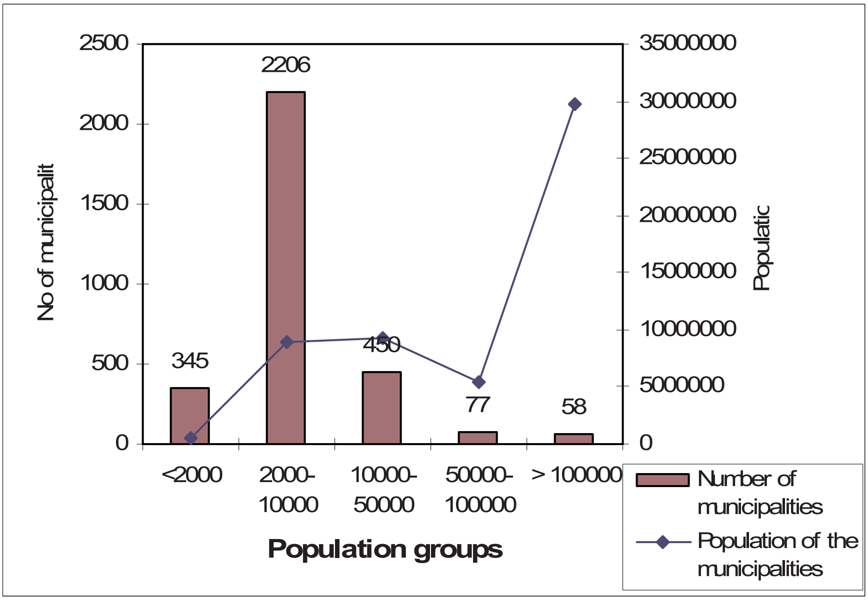


Fig. 1.1. Distribution of the number of municipalities and population according to population groups.

In addition to the necessity of the protection of the receiving environments, water plays a very crucial role in Turkey, especially during the long lasting summer months: The overall climatic condition in Turkey is classified as arid-semiarid. In order to satisfy the irrigation water demand of agriculture, as well as to supply the residents and touristic facilities with potable and drink water, considerable amount of good quality water is needed. Due to climatic conditions summer months usually do not have contribution on the water budget of the country. Therefore, treated wastewater is a very important source of water.

In this study, the current stand of the wastewater and sludge treatment in Turkey is analyzed and proposals for sustainable wastewater management are introduced.

2. Wastewater treatment

In 2,321 of the 3,225 municipalities 3.4 million m^3 wastewater is collected through sewage systems (Table 2.1). This corresponds to 87% of the total population [2].

On the other hand, the stand of wastewater treatment is not well developed to this extend and in addition to this it is not evenly widespread throughout the country. Only 184 wastewater treatment plants are currently under operation, in which secondary and advanced treatment are applied [2]. 2.1 million m^3 municipal wastewater produced in 362 municipalities is treated in one of these WWTPs. It means that only 42% of the total population is served with a wastewater treatment plant. The secondary treatment plants are initially constructed to remove the organic matter content of the wastewater. Parallel with the increasing sensitivity and awareness regarding the receiving water environments, other parameters than only BOD_5 and COD are also taken into consideration. As a result Nitrogen and Phosphorus are removed in wastewater treatment plants especially located along the touristic coastal areas. From Table 2.1, it is evident that 62% of the produced wastewater receives biological and advanced treatment. As it will be discussed more in detail below, advanced treatment comprises from advanced biological treatment facilities, in which nutrients such as nitrogen and phosphorus are removed besides organic matter.

Table 2.1. Main wastewater indicators of municipalities 2006 [2].

Number of municipalities served by sewerage system	2,321
Rate of population served by sewerage system in total population (%)	72
Rate of population served by sewerage system in municipal population (%)	87
Amount of wastewater discharged (million m^3/year)	3,367
Number of wastewater treatment plants	184
Physical	22
Biological	135
Advanced	23
Total capacity of wastewater treatment plants (million m^3/year)	3,648
Physical	1,329
Biological	1,511
Advanced	808
Amount of wastewater treated by treatment plants (million m^3/year)	2,140
Physical	714
Biological	927
Advanced	500
Number of municipalities served by wastewater treatment plants	362
Rate of population served by wastewater treatment plants in total population (%)	42

An evaluation of the distribution of the treatment systems in comparison to the number of treatment plants and with respect to the volume treated in these plants indicates some discrepancy. Number of conventional activated sludge plants is not much but they are mostly large treatment facilities (Fig. 2.1a). As a matter of fact, approximately 70% of the treated wastewater is processed by conventional and nutrient removing activated sludge systems (Table 2.2).

Especially during the last 10 years, in order to avoid sludge treatment, extended aeration systems (EAS) are constructed (Fig. 2.1b). These plants are the modifications of CAS, with longer sludge retention time (15–30 d), longer hydraulic retention time (12–36 h) and lower F/M ratio (0.05–0.15 mg BOD_5/mg ML SS·d). The main advantage of these systems is the fact that the primary sedimentation and external sludge treatment units can be avoided that helps to reduce the construction costs.

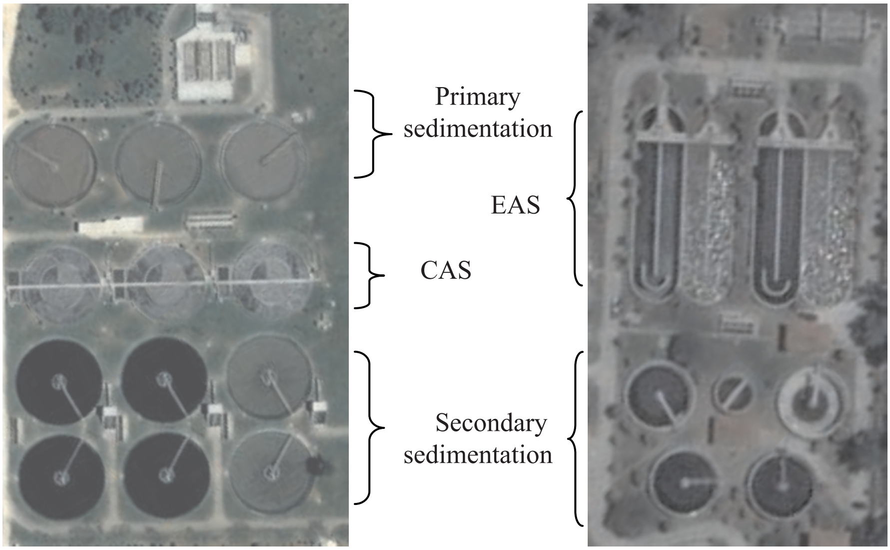
Table 2.2. Distribution of the applied treatment systems based on the number of plants and volume of treated wastewater [3].

System	Based on the number of treatment plants (%)	Based on the amount of treated waste water (%)
Conventional Activated Sludge (CAS)	20	47
CAS + Nutrient Removal (BNR)	5	23
Extended Aeration Systems (EAS)	61	25
EAS + Nitrogen Removal	3	3
Biological filters + N-removal	11	2

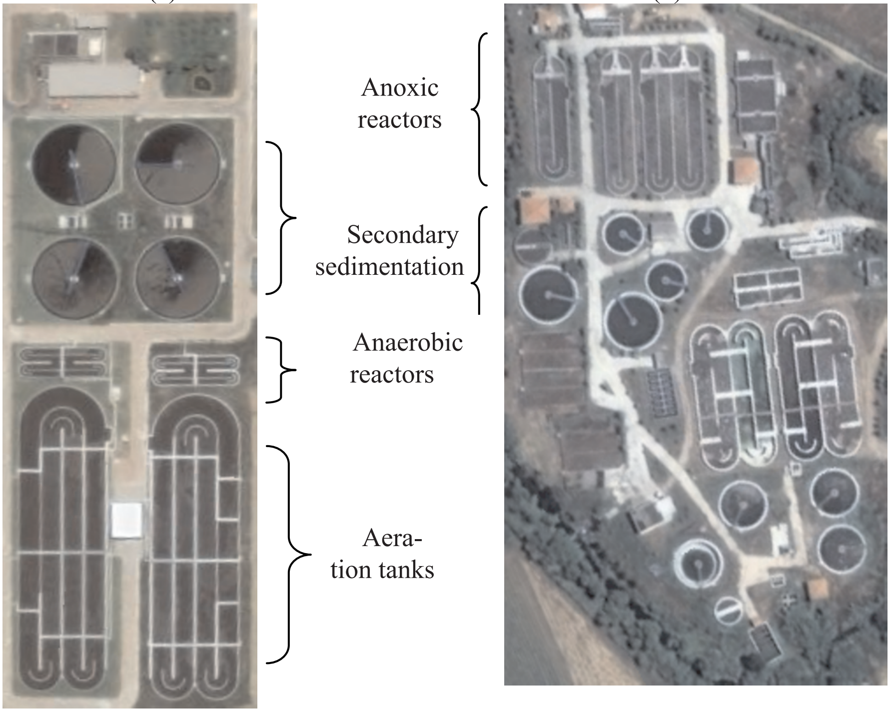
By taking into consideration the increasing sensitivity of the receiving water body several new constructed plants are designed as biological nutrient removal (BNR) plants. Typical example to this is the main wastewater treatment plant of Antalya City (500,000 PE) shown in Fig.2.1c. In this plant, wastewater, which passes through screens, grit and scum removal units, are directly derived into the anaerobic tank in which phosphorus removal is encouraged. The following aeration tank is operated in extended aeration mode. Secondary settling tank is followed by deep marine discharge units. The phosphorus concentration of the discharged water is low (<1mg/l) and the other parameters fulfill the requirements of discharge criteria.

Along the costal zone of Antalya, three existing treatment plants, which are considered as oxidation ditches were upgraded with anoxic tanks for removal of nitrogen (Fig. 2.1d).

In addition to the problems of insufficient treatment capacity, there are several problems that the existing plant operators have to face with. Dilution of the incoming wastewater due to infiltration of ground water along the coastal regions is very common. Treatment plants, which are designed for municipal wastewater, have to deal with industrial influents also. In addition to overloading of the central plants located in touristic regions during summer months, which lead to sludge bulking and low dissolved oxygen levels in the aeration tanks, is very common.



(a) CAS (b) EAS



(c) BNR (d) EAS + Nitrogen removal

Fig. 2.1. Views of the existing wastewater treatment plants.

In order to fulfill the requirements of Urban Wastewater Treatment Directive, approximately 2,942 new treatment plants with various capacities are required to be established for residential units with a population more than 2,000 inhabitants. In the small municipalities and villages with population less than 2,000, appropriate treatment and disposal methods will be used. As investment costs are the main concern two scenarios are developed:

- Highest Cost Scenario

All waters of the country are classified as sensitive areas and advanced treatment was recommended for all wastewater collection areas of more than 10,000 PE

- Lowest Cost Scenario

Marmara, Aegean and Mediterranean coastal zones are classified as sensitive. Other areas, Bosporus and Black Sea are considered as less sensitive for discharges.

As the highest cost scenario can be a significant financial burden, lowest cost scenario was chosen for the implementation of the Urban WWT Directive. The goal set in the Environmental Approximation Strategy [1] is to install sewage systems and treatment plants until the year 2020, so that the population that will benefit from the treatment plants in the provinces, which have more than 50,000 inhabitants. By deciding on the technology of the treatment plant the criteria of sensitive and less sensitive areas will be considered.

2.1. Economics of waste water treatment

The evaluation of the initial and operational costs of the existing treatment plants show dependency on the degree of treatment and the source of financing [3]. The high variability in the per capita investments is partly related to the financing sources. In cases where investments were made through international loans, costs are usually high. On the other hand, the lower is the investment costs when national financial sources are used.

From Table 2.1.1 it is obvious that,

- The highest costs are those for nutrient removing EAS systems, and the lowest are for conventional activated sludge.
- Activated sludge units are operated at the lowest cost.
- The EAS and nitrogen removing EAS plants appear to have the highest operational costs.

The BNR plants operate at a lower cost than nitrogen removing EAS systems. This is possibly due to the difference in the sizes of treatment plants. The selected nutrient removing activated sludge plants are larger facilities while nitrogen removing EAS are smaller units.

Table 2.1.1. Costs of the applied treatment technology [3].

Treatment technology	Initial cost (€/capita)	Unit operational cost (€/m^3)
Conventional Activated Sludge (CAS)	13.76–46.67	0.0146–0.0903
Nutrient Removing Activated Sludge (BNR)	32.30–266.2	0.0473–0.0553
Extended Aeration Activated Sludge (EAS)	29.00–49.85	0.0320–0.1260
Nitrogen Removing EAS (EAS-NR)	12.72–83.47	0.0528–0.1534

3. Sludge treatment

Proper sludge disposal is the weak point of sludge management in Turkey. Due to lack of financial sources sludge treatment units are designed thrifty. In treatment plants with large capacity, anaerobic sludge treatment is applied. With the application of extended aeration systems it is planned to omit the primary sedimentation tanks, at the same time as sludge stabilization in the aeration tanks is achieved, external sludge treatment units were also omitted. In the majority of the plants constructed during the last years, thickening is the first stage of sludge treatment followed by dewatering units (belt press or centrifuges) to 25% DM. This conversion of the sludge to a solid ‘cake’ form is followed by disposal in landfills. As the landfill operators are increasingly against landfilling of sludge and as WWTP sludge traditionally has a very limited usage as fertilizer in the agriculture, it is common practice that produced and dewatered sludge are deposited in unsanitary landfills which in turn causes serious environmental problems.

Anaerobic digestion is applied in a limited number of plants. In order to manage the increasing amount of sludge, usage of treatment plant sludge as fuel in cement factories is allowed and several cement factories have license to incinerate sludge. In 2008, the first sludge drying system has become operational in Antalya.

It is expected that the quantities of sludge requiring disposal would continuously increase with the implementation of the EU Directive. The production of municipal sludge is estimated to increase up to more than 1 million tons DM/a in 2020. The new Environmental Approximation Strategy [1] foresees the treatment and controlled usage in the soil and final disposal of the sludge from treatment plants through appropriate technologies.

4. Conclusions

In order to comply with the relevant EU Directives high investments are required. These investments are needed for the renovation of the networks, construction of new networks, renovation of the existing wastewater treatment plants, for the construction of more than 2,900 new WWTP’s and for proper sludge handling, which should be realized till 2020. Due to high costs it is envisaged to maintain treatment services only in residential centers >50,000 population. Strengthening institutional capacity plays also a considerable role. It is estimated that approximately 10,000 additional technical personnel are required. As the applied wastewater treatment technology affects the quality of the sludge, in the newly constructed plants water and sludge treatment units should be planned as a whole. Life cycle assessment methodology can help to decide on the most appropriate method in taking environmental and economic conditions into consideration.

Acknowledgments. This study was granted by the Scientific Projects Support Unit of Akdeniz University, which is gratefully acknowledged.

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SUSTAINABLE ADOPTED WASTEWATER TREATMENT AND REUSE IN AGRICULTURE

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Abstract. Insufficient water supply is an important problem in arid and semi-arid regions. This problem is magnified further by uneven water distribution and also by water pollution due to the fast growing industry and cities. An innovative and interdisciplinary approach is necessary to reduce this problem. Wastewater treatment should be done cost effectively and reuse of reclaimed wastewater would contribute partially to the solution of the water shortage problem. Efficiency could be achieved by employing adapted technologies in treatment of wastewater. The reclaimed wastewater could be used for irrigating forestry and agriculture. Thus, advanced treatment steps of the reclaimed wastewater would take place in the soil. In this work, Konya (Turkey) is selected as an example of semi-arid land. The city is surrounded by a sparsely populated forest area and agricultural zones, which are cultivated employing irrigation where water is available. Domestic and industrial wastewater of Konya are collected by combining sewerage system and discharged to main drainage channel, which is about 150 km long and discharges wastewater to the salt lake. Characteristic of wastewater was determined. Treatment processes were evaluated in terms of suitability and efficiency for the reuse of effluent as irrigation water for forestry and agriculture. Quality criteria of the reclaimed water were evaluated for reuse as irrigation water.

Keywords: wastewater, agriculture.

1. Introduction

Water amount in Turkey is declining since 1927 considering the population growth. It is estimated 1,000 m^3 water potential per person in 2030. This amount puts Turkey in water poor countries class border. Moreover, this water potential is not distributed evenly. Larger part of Turkey is in a semi-arid climate area. To overcome this water shortage [1], various strategies could be suggested such as development of fossil water stores, draining or redirection of surface waters, more

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efficient use of the available water resources, water saving measures, desalination of seawater, and reusing wastewater after treatment for irrigation in agriculture.

Some positive effects of reusing wastewaters for irrigation could be suggested as following. Reuse of wastewater for irrigation increase yield in agriculture and serves for the reforestation and, therefore, prevents erosion, which is an important problem in the Mediterranean Region. Reuse of reclaimed wastewater could encourage a sustained environmental awareness. Types of reuse applications are urban reuse irrigation, of restricted-access-area, agricultural reuse, recreational impoundments, landscape impoundments, construction uses, industrial reuse, groundwater recharge, and indirect potable reuse. Disinfected, tertiary treated effluent can be used in all of these applications [2–4]. Water needed for irrigation in some places accounts for >80% of total demand, regulations and guidelines vary widely about reuse in the world. Benefits of agricultural reuse could be suggested as high concentrations of nutrients may reduce the demand for fertilizers, long-term soil enrichment, decreases demand on potable water supply, additional treatment in soil, and water being not discharged to receiving waters. Thus, water pollution would be prevented. There are also some disadvantages of agricultural reuse such as health risk from associated pathogens, health risk from other contaminants (e.g., heavy metals, chemicals, and pharmaceuticals), decrease in soil quality from accumulation of salts and soil acidification, and infiltration of pollutants into groundwater [5, 6]. For the reuse of secondary effluent (SE), sometimes advanced treatment consisting of chemical treatment with coagulation, flocculation, clarification, and filtration is suggested [7]. Chemical treatment depends on quality of SE and is also expensive. If the turbidity of SE is less than 10 NTU clarification step could be skipped. So the advanced treatment is usually called direct filtration and consists of coagulation, flocculation, and filtration steps. Sometimes taking out the flocculation step would not influence the treatment procedure and, hence, so called contact filtration consisting of coagulation and filtration could be applied. In Table 1.1 the effects of advanced treatment processes on some water quality parameters are given.

Table 1.1. Effectiveness of advanced treatment steps on quality parameters.

Constituent	After secondary treatment with BNR plus disinfection	After secondary treatment with BNR plus depth filtration and disinfection	After secondary treatment with BNR plus microfiltration, RO and disinfection
TSS	5–20	1–4	≤1
BOD	5–20	1–5	0–2
TN	2–12	2–12	≤1
NO_3	1–10	1–10	≤1
Phosphorus	0.1–0.5	0.1–0.5	≤0.5
Turbidity	2–6	≤2	0.1–1
Bacteria	2.2–240	≤2.2	≈0
Protozoan	5–10	≤1	≈0
Viruses	100–10,000	≤0.0001	≈0

BNR, biological nutrient removal; RO, reverse osmosis.

2. Study area

Usable part of surface water and ground water sources of Turkey is 112 × 10^9 m^3/year. 36% of total freshwater was used as 29.6 × 10^9 m^3/year for irrigation, 6.2 × 10^9 m^3/year for domestic use, 4.3 × 10^9 m^3/year for industry. There are 3,215 municipalities in Turkey. A total of 1327 municipalities have working sewerage systems, 87% of population connected to sewerage systems, 45% of total population are connected to wastewater treatment plants. 2.08 × 10^9 m^3 wastewater is treated per year and there are 138 wastewater treatment plants serving population above 3,000 persons. Treated wastewater discharge ratios to different receiving media are as follows: 55.2% is discharged to sea, 35.2% is discharged to rivers, 6.3% is discharged to land, 3.3% is discharged to lakes or dams. Raw wastewater discharge ratios to different receiving media are as follows: 52.5% is discharged to rivers, 17.2% is discharged to sea, 7.2% is discharged to land, 5.2% is discharged to dams, 1.1% is discharged to lakes, 10.3% is discharged to other receiving media. Total area of Turkey is 78 × 10^6 hectare (ha). 27.7 × 10^6 ha of this area is farmland (35%), 8.5 × 10^6 ha farmland could be irrigated economically (31% of farmland), 5.3 × 10^6 ha of this land is provided with irrigation (55%) [8].

Konya is a city with a population of a million, annual mean temperature is 11.5°C and average precipitation is about 325 mm. City has semi-arid climate and limited water sources. This is especially a problem for wide agricultural land irrigation water demand. Water shortage is faced because of increasing population. Water demand is increased. Uncontrolled drilled boreholes and water abstraction intensified water shortages. Disposal of wastewater will be achieved by its reuse. This will prevent environmental pollution and partial irrigation water demand will be met by reuse of wastewater. Wastewater of Konya is collected in a combined sewer system from residential and industrial areas and discharged to Konya Main Drainage Channel without any treatment at present. The drainage channel is about 150 km long, an open channel built for floods and for excess water returning from irrigation. Waters of the channel are discharged to the Salt Lake, which is a unique natural source for salt production. Industrial activity classes discharge to Konya sewerage system are food, mining, glass, textile, leather, chemical, metal, vehicle maintenance workshops, paper, sunflower oil production, fruit and vegetable processing, wood processing, repair and maintenance workshops, petrol station, and motor vehicle part washing [9–11].

At the general outlet of the sewer system Konya's wastewater treatment plant has been constructed and will be put in operation these days. Wastewater treatment plant was selected as classical activated sludge processes consisting of pumping station, coarse and fine screen, aerated grit and oil chamber, pre-sedimentation tanks, aeration tanks, final settling tank, sludge treatment facilities, UV disinfection units. Plant was designed according to target year of 2030, constructed according to year 2015. Total area of the plant is 750,000 m^2. Design criteria of the wastewater treatment plant 2015 year equivalent population is 1,000,000 persons. Design discharge is 200,000 m^3/day. 2030 year equivalent population is 1,600,000 persons. Design discharge is 300,000 m^3/day. Raw wastewater quality before treatment plant are BOD_5 320 mg/L, SS 295 mg/L, Total Kjeldahl Nitrogen 50 mg/L, Total Phosphorus 15 mg/L, Oil and grease 150 mg/L. Discharge criteria for 2015 and 2030 are SS<20 mg/L, BOD_5<20 mg/L, COD<90 mg/L, pH 6–9 [9, 10].

3. Materials and methods

Wastewater samples were taken from general outlet of sewerage system at connection channel to main Drainage Channel. SS, TDS, Sulphate (SO_4), Chloride (Cl^-), BOD contents of samples were measured according to Standard methods (1989). pH, EC, and temperature were measured with WTW 2001 P4 pH meter. COD, TKN, NH_3-N, NH_4-N, F were measured with Dr. Lange CADAS 30S 2001 spectrophotometer and its ready kits. Fecal coliform bacteria analyses were carried out employing membrane filtration technique [12]. Calcium (Ca), Magnesium (Mg), Sodium (Na), Potassium (K), Iron (Fe), Manganese (Mn), Aluminum (Al), Boron (B), Zinc (Zn), Barium (Ba), Silver (Ag), Copper (Cu), Cadmium (Cd), Lead (Pb), Chromium (Cr), Arsenic (As), Antimony (Sb), Cobalt (Co), Lithium (Li), Nickel (Ni), Selenium (Se) Analyses were carried out with Perkin Elmer 2100 ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy).

4. Results and discussions

Irrigation water quality criteria in Turkish water pollution control regulations [13, 14] and Konya wastewater parameters are given in Table 4.1. Electrical conductivity (EC) is an important parameter for determining the irrigation water quality since it is an indication of salinity. High saline irrigation waters cause increased and accumulation salinity levels in soil. High salinity in irrigation water and soil has toxic effects on plants. EC value of Konya wastewater is 1788 μS/cm level. According to irrigation water quality criteria given in Table 4.1 Konya's wastewater is in the 3rd class useable water. Sodium adsorption ratio (SAR) is an indication of the Na amount adsorbed by soil. Na may pose soil permeability problems. As SAR value increases so changeable Na percentage (Na%) also increases. SAR value of Konya wastewater is 20.5 while Na percentage value is 51.6%. These values also place Konya wastewater in 3rd class useable water category according to irrigation water quality criteria. Chloride content of Konya wastewater is 172 mg/L and according to irrigation water quality criteria it is in good quality irrigation water class. The pH of wastewater affects disinfection, coagulation, metal solubility as well as alkalinity of soils. Normal range in municipal wastewater is pH 6.5–8.5, but industrial waste can influence the pH significantly.

pH value of Konya wastewater is 7.1 hence it is within an acceptable range. No detrimental effects are usually noticed as Total Dissolved Solids (TDS) values are below 500 mg/L. TDS values being between 500 mg/L and 1000 mg/L, they can affect sensitive plants irrigated. At 1000 mg/L to 2000 mg/L, TDS levels can affect many crops and careful management practices should be followed. Above 2000 mg/L, water can be used regularly only for tolerant plants on permeable soils. TDS value of Konya wastewater is 1300 mg/L, which puts the wastewater at the 3rd class and may be used as irrigation water.

Table 4.1. Irrigation water quality criteria and Konya wastewater parameters.

Parameter	Irrigation water class					
	1st class (very good)	2nd class (good)	3rd class (may be used)	4th class (use with care)	5th class (hazardous)	Konya wastewater
EC25 × 10^6 (µS/cm)	0–250	250–750	750–2,000	2,000–3,000	>3,000	1,788
Na%	<20	20–40	40–60	60–80	>80	51.59
SAR	<10	10–18	18–26	>26		20.51
Cl^- meq/L	0–4	4–7	7–12	12–20	>20	172
mg/L	0–142	142–249	249–426	426–710	>710	
SO_4^{2-} meq/L	0–4	4–7	7–12	12–20	>20	166
mg/L	0–192	192–336	336–575	575–960	>960	
TDS	0–175	175–525	525–1,400	1,400–2,100	>2,100	1,300
Boron (mg/L)	0–0.5	0.5–1.12	1.12–2.0	>2.0	–	0.881
Irrigation water class	C1S1	C1S2, C2S2, C2S1	C1S3, C2S3, C3S3, C3S2, C3S1	C1S4, C2S4, C3S4, C4S4, C4S3, C4S2, C4S1	–	C3S4
NO_3^- or NH_4^+ mg/L	0–5	5–10	10–30	30–50	>50	
Fecal Coliform (CFU/100 mL)	0–2	2–20	20–100	100–1,000	>1,000	200,000
BOD_5 (mg/L)	0–25	25–50	50–100	100–200	>200	340
SS (mg/L)	20	30	45	60	>100	83
pH	6.5–8.5	6.5–8.5	6.5–8.5	6.5–9.0	<6.0 or >9.0	7.07

This water contains very high contents of sodium and salts, therefore, it is in 4th irrigation water class that should be used with precautions (see Fig. 4.1) [14]. Careful plant type selection and salt control of soil should be applied if this wastewater is used for irrigation. This water will cause some problems in soil as high sodium ratio will decrease the permeability of soil and chemical and physical structure of soil will be changed.

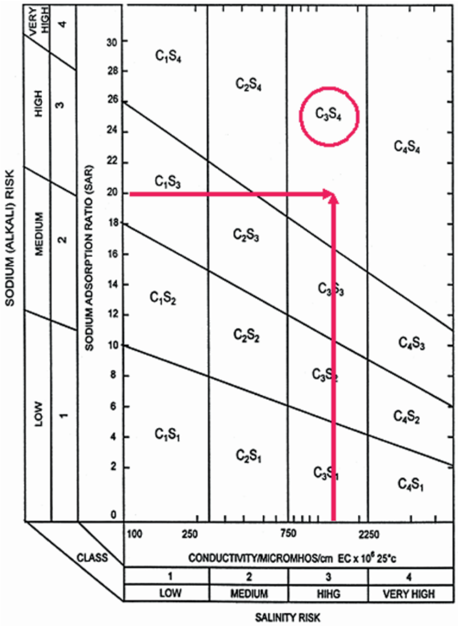

Fig. 4.1. Irrigation water class.

Nitrogen, phosphorus and potassium are essential nutrients for plants growth and their presence normally enhances the value of water for irrigation. When discharged to the aquatic environment, nitrogen and phosphorus can lead to eutrophication. When applied at excessive levels on land, nitrogen can also lead to nitrate build-up in groundwater. NH_3, NH_4 and Total-N contents of Konya wastewater are 2.65 mg/L, 5.75 mg/L and 91.5 mg/L as N, respectively. Organic contaminants are adsorbed on particles. Suspended matter can shield microorganisms from disinfectants. Before treatment, SS and turbidity contents of Konya wastewater are about 83 mg/L and 80 NTU, respectively,. Biodegradable organics such as BOD, COD, TC can cause aesthetic and odor problems. Organics provide food for microorganisms, adversely affects disinfection process, make water unsuitable for some industrial or other uses, consume oxygen, and may result in acute or chronic effects if reclaimed water is used for potable purposes [2, 3]. Before treatment, COD and BOD contents of Konya wastewater are about 875 mg/L and 340 mg/L, respectively. However, these parameters will be much more improved after wastewater treatment.

Additional irrigation water classification is given for boron concentrations in water pollution control regulation in Turkey (Table 4.2) [14]. Boron is an essential trace element for plant growth with an optimum concentration between 0.1 and 0.2 mg/L. However, boron is toxic above 1 mg/L for a variety of sensitive plants and reduces production yields and the growth rates. Usually, it is contained in sufficient quantities in reclaimed water in order to correct soil deficiencies. Some lawn types and most grasses are tolerant to boron concentrations between 2-10 mg/L. Boron concentrations of Konya wastewater is 0.88 mg/L. This boron concentration puts wastewater in 3rd class of irrigation water usable for sensitive plants such as chestnuts, lemons, figs, apples, grapes, and beans. 2nd class is suitable for medium level tolerant plants such as wheat, barley, corn, oat, olive, and cotton; and finally 1st class is used for highly tolerant plants such as sugar beet, clover, bean, onion, lettuce, carrot.

Table 4.2. Irrigation water classification according to plants tolerance against boron.

Irrigation water class	Boron concentrations in irrigation water (mg/L)		
	Sensitive plants	Medium level tolerant plants	Highly tolerant plants
I	<0.33	<0.67	<1.0
II	0.33–0.67	0.67–1.33	1.00–2.00
III	0.67–1.00	1.33–2.00	2.00–3.00
IV	1.00–1.25	2.00–2.50	3.00–3.75
V	>1.25	>2.50	>3.75

Some heavy metals accumulate in environment and are toxic to plants and animals. Their presence may limit the suitability of the reclaimed water for irrigation or other uses. Aluminum can cause non-productivity in acid soils but soils at 5.5–8.0 will precipitate the ion and reduce the toxicity. Toxicity to plants varies widely for Beryllium, ranging from 5 mg/L for kale to 0.5 mg/L for bush beans. Cadmium is toxic to beans, beets and turnips at concentrations as low as 0.1 mg/L in irrigation water. Cobalt is toxic to tomato plants at 0.1 mg/L in irrigation water. Fluoride is inactivated by neutral and alkaline soils. Copper is toxic to a number of plants at 0.1–1.0 mg/L in irrigation water. Iron is not toxic to plants in aerated soils, but can contribute to soil acidification and loss of essential phosphorus and molybdenum. Lead can inhibit plant cell growth at very high concentrations. Lithium is tolerated by most crops at up 5 mg/L mobile in soil and toxic to citrus at low doses; the recommended limit is 0.075 mg/L. Manganese is toxic to a number of crops at a few mg/L in acid soils. Nickel is toxic to a number of plants at 0.5 to 1.0 mg/L and shows the reduced toxicity at neutral or alkaline pH. Selenium is toxic to plants at low concentrations and to livestock if forage is grown in soils with low levels of added selenium. Zinc is toxic to many plants at widely varying concentrations; it shows a reduced toxicity at increased pH (6 or above) and in fine-textured or organic soils [2, 3].

Maximum allowable heavy metals and toxic elements for irrigation waters and measured values for Konya wastewater are presented in Table 4.3 [14]. Only Cd, Co, F are above the limit values for continuous irrigation for any type of soil. However, these toxic elements will be reduced after treatment plant until probably acceptable levels. These toxic elements even before treatment are not exceeding limit values for clayey soils for irrigation less than 24 years (pH between 6.0 and 8.5).

Table 4.3. Maximum allowable levels of heavy metals and toxic elements for irrigation waters.

Elements	Maximum allowable concentrations		Konya wastewater, mg/L
	Limit values for continuous irrigation for any type of soil, mg/L	Limit values for clayey soils for irrigation less than 24 years (pH between 6.0 and 8.5), mg/L	
Al	5.0	20.0	0.808
As	0.1	2.0	0.013
Be	0.1	0.5	–
B	–	2.0	0.881 μg/L
Cd	0.01	0.05	0.036 μg/L
Cr	0.1	1.0	0.047
Co	0.05	5.0	0.957 μg/L
Cu	0.2	5.0	0.046
F	1.0	15.0	1.250
Fe	5.0	20.0	0.795
Pb	5.0	10.0	0.038
Li	2.5	2.5	0.026
Mn	0.2	10.0	0.076
Mo	0.01	0.05	–
Ni	0.2	2.0	0.021
Se	0.02	0.02	0.002
V	0.1	1.0	–
Zn	2.0	10.0	0.198
Ba	–	–	0.111
Ag	–	–	0.001
Sb	–	–	0.654 μg/L

Fecal coliform content of Konya's wastewater is about 200,000/100 mL. Reuse of this water is not possible for growing fruits, viniculture, grapes, fiber and seed plants. Once the wastewater treatment plant is put in operation, secondary effluent will also be disinfected by UV radiation, then the effluent would be used for fiber and seed plants.

5. Conclusions

About 1.5 × 10^6 ha of land in Turkey is classified as salty and containing Na. Problematic land in terms of salt and sodium are widely seen especially in first irrigation areas such as Konya, Adana, and Niğde. In a lot of irrigated areas salinity and drainage problems were seen in parallel to the irrigation. Konya is a semi arid region and has very wide farmland. High temperature, low precipitation due to global climate change increased water demand. Konya wastewater falls in 4th class irrigation water that could be used for irrigating of forest areas according to water pollution control regulation (WPCR). Maximum allowable heavy metals and toxic elements limits for irrigation waters are given by WPCR. Heavy metal and toxic elements contents in Konya wastewater are below the maximum levels for less than 24 years irrigation for any type of land. Konya has 2,750,000 ha of farmland. 1,357,557 ha is cultivated. In about 85% of this land grain (wheat, barley, rye, oat) is grown. 6% pulse (chickpea, bean, lentil) is grown. 10% of national grain production is conducted in Konya. Water demand of grain crop is about 2,155 m^3/ha consisting of 535 m^3/ha in April, 1,470 m^3/ha in May, 150 m^3/ha in June. Another important issue about water reuse for irrigation is the storage requirement. Storage volume according to crop type, irrigation needs and meteorological data is determined. If the effluent is stored during only the irrigation period of 3 months, 8,353 ha of land could be irrigated. If the effluent is stored for a year, 33,874 ha could be irrigated. Hotamış Lake could be used for the effluent storage. This is a natural lake but it was dried recently due to the decrease in precipitation and over-abstraction of ground waters. By storing of effluents in Hotamış Lake, water will be provided for 5% of grain growing land; this will also help the recreation of the lake.

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INVESTIGATION OF THE OIL-PRODUCTS SOLUBILITY IN WATER: QUALITATIVE COMPOSITION AND QUANTITATIVE LIMITS OF THE OIL–WATER MIXTURES

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Abstract. Gasoline–water mixtures have been investigated using UV-spectrophotometry. It was found that such mixtures can be characterized with two absorption bands. The first one is located within wavelengths from 180 to 230 nm and the second is located within 240–280 nm. The first absorption band is very intense and cannot be used for any analytical determination while the second one exhibits distinct dependence on the gasoline concentration. Calibration diagrams have been built in the coordinates: optical density *vs* gasoline concentration for the UV-light absorption peak at 260 nm. Assumption on the qualitative composition of the gasoline–water mixtures has been made basing on the pattern and the peaks distribution along the light absorption spectra. It has also been found that the maximum concentration of the relatively soluble gasoline components reaches approximately 0.35 g/l. However, higher concentrations can be achieved at longer contacting between gasoline and water.

Keywords: oil–water mixtures, UV-spectrophotometry, qualitative composition, quantitative limits.

1. Introduction

Oil-products are very dangerous and toxic pollutants of water. Annual world discharge of oil-products reaches 1.5–2.5 million tons [1]. They contaminate river, sea and ocean water and come from various industrial wastewater discharges, tanker ballast waters exchange and other anthropogenic sources [2]. Severe local contamination always occurs at tanker incidents, oil pipelines ruptures and other technical accidents.

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Accurate assessment of negative effect of the oil-products contamination is impossible without reliable and accurate methods of analytical determination of the oil-products concentration.

There are many well-known analytical methods, which have been embodied in various types of analytical equipment produced commercially. Infrared spectroscopy, fluorescent spectroscopy, gas and gas-liquid chromatography can be mentioned as such accurate and reliable methods of the oil product content determination. However, these methods require long and complicated samples preparation including extraction of oil-products from water (like infrared photometry or fluorescence methods) and/or some expensive and rather large lab equipment, which can be used only in a stationary laboratory (like gas or gas-liquid chromatography) [3–5].

Field or express analysis require faster and simpler method of the oil-products content determination. This method can ensure lower accuracy but requires shorter time and less equipment.

We propose an express method for analytical determination of the oil-products content in water. It requires quite simple lab equipment and does not involve extensive samples preparation operations. This method can be realized in a simple lab (potentially even in a mobile one) providing possibility of on-a-spot determination of water contamination with oil-products.

2. Oil–water mixtures: solubility, composition and spectrophotometry investigation

Most oil products and water are considered as non-soluble in each other. It is well known that gasoline, oils, grease or diesel fuel can form thin film spreading wide on the water surface. This contamination results in many negative ecological effects: oil film on the water surface blocks up normal gas exchange with atmosphere lowering oxygen content in water. This leads to anoxaemia and suffocation of fish and other water organisms. Water birds suffer of the feathering dirtying, try to clean themselves, swallow oil from their feathering and die of poisoning. Same situation also happens to other organisms including mammals, which can eat birds, fish or other organisms perished after oil-products poisoning.

This kind of pollutants may also stay captured in the shore and offshore area soils for years and be released periodically because of weather and/or sea condition changes.

Oil and water were considered as almost completely dissoluble components. However, it was recently found that long-term contacting of water and oil may result in dissolution of some oil-components in water. Solubility of crude oil in water can reach 0.2–1.9 mg/l at the contacting time of 120 h. Solubility of diesel fuel at the same conditions can reach 0.8 mg/l.

Gasoline is even more dissoluble since it contains relatively higher amount of the aromatic compounds. It was found that aliphatic gasoline compounds concentration can reach 11.9 mg/l and concentration of aromatic compounds can reach 134 mg/l.

It is known that some classes of relatively better dissoluble compounds (methyl and polymethylbenzenes, etc.) are present in the oil products, especially in the high-octane gasoline [3, 6]. Some small amount of these compounds can be dissolved in water and contaminate deep-water ecosystems as well as surface ones. Such contaminated water can travel a long distances (especially with the river flow) and distribute pollutions over long range. Naturally, express control and determination of such a contamination would require fast and mobile analytical methods and laboratories, which would be able to follow the contaminated water spot.

So, necessity of elaboration of some relatively simple but still reliable analytical techniques to determine oil-product content in water is obvious.

It is known that many aromatic compounds can actively absorb light in the closer UV range [7]. This can be used for direct UV-spectrophotometry determination of their concentration in water. This analytical method would not require intense samples preparation and needs simple analytical equipment.

This assumption was verified through recording of UV-spectra of diluted water-gasoline mixtures. An ordinary A-95 gasoline was used as a test oil compound and its concentration in water was ranged from 0.03 to 0.35 g/l. All the spectra were recorded immediately after preparation of the solutions using standard LOMO SF-26 spectrophotometer. Typical UV spectrum of the gasoline–water system can be seen in Fig. 2.1

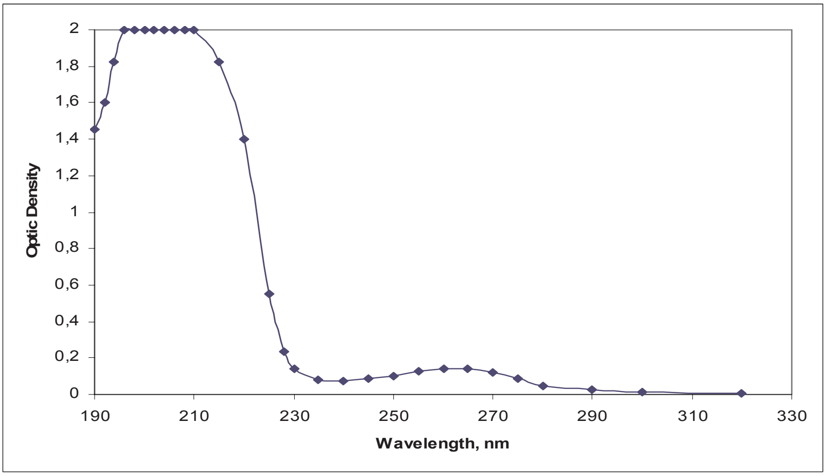

Fig. 2.1. Typical UV spectrum of the gasoline–water system.

One can see a band of a very intense light absorption located around wavelength 230 nm and further to the short-wave part. Another absorption band is located between 240 and 280 nm. The first band is very intense and almost independent from the gasoline concentration (non-analytic light absorption peak). Intensity of light absorption within the second band was found dependent on the gasoline concentration (analytic absorption peak). This absorption band is enlarged in Fig. 2.2.

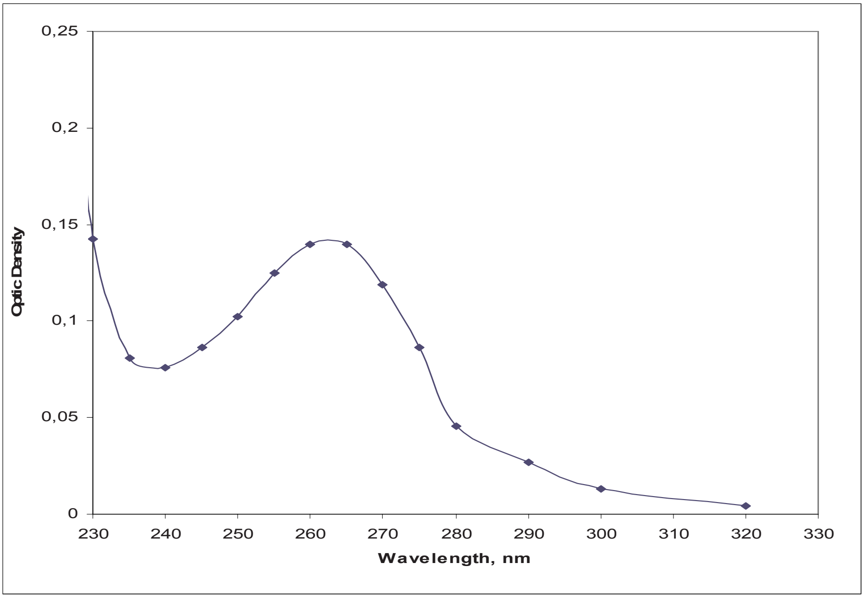

Fig. 2.2. Part of the gasoline–water UV-spectrum with the analytical adsorption peak found.

It is seen that the maximum light absorption is registered at the wavelength 260 nm. This peak can be used to build a calibrating diagram connecting optical density of a solution (D) and concentration of gasoline (c). This dependence was found linear and corresponding to the calibrating equation D = 0.315 c + 0.0112 (see Fig. 2.3). It fits experimental values with the pair correlation coefficient 0.97 or higher along all above mentioned range of the gasoline concentrations and can be used for express UV-spectrophotometry determination of the gasoline content in water.

Then the water-gasoline spectrum pattern was compared to typical spectra of various aromatic compounds [7, 8]. This class of organic substances can be found in gasoline and they actively absorb UV radiation. As a result, we have found that a spectrum and its pattern was very similar to our experimental results (see Fig. 2.4). This is a spectrum of 1,3,5-trimethylbenzene and it practically agrees with an experimental light absorption pattern recorded near 260 nm.

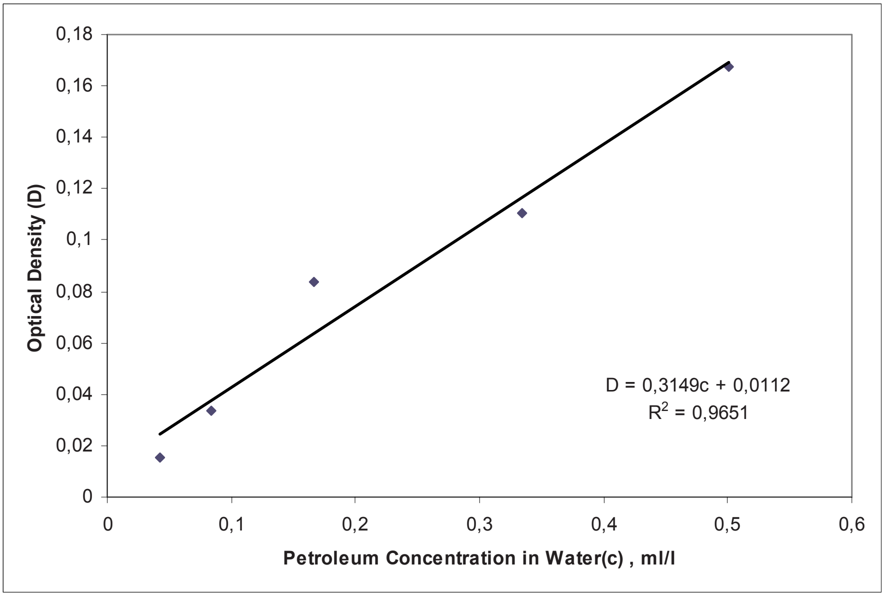

Fig. 2.3. Calibrating diagram for determination of gasoline concentration through UV-light absorption at 260 nm.

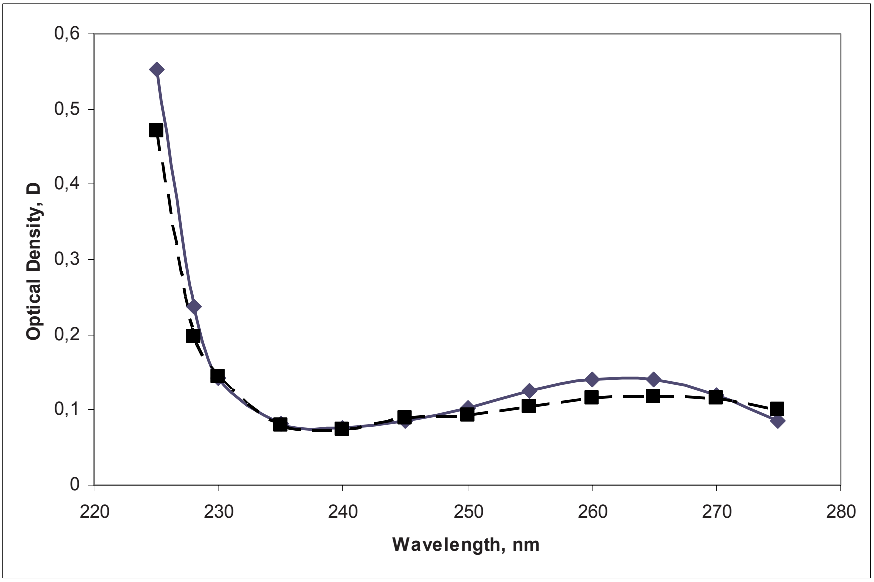

Fig. 2.4. UV spectra of the gasoline–water solution (solid line) and 1,3,5-trimethylbenzene (broken line) [7].

Therefore, we suppose that 1,3,5-trimethylbenzene or its close homologues can be those relatively well-dissoluble gasoline compounds, which form pattern of the analytical absorption peak for the water-gasoline mixtures. It is also known that aromatic compounds determine higher octane number of the high performance motor fuel and in fact they are present in the high-octane gasoline. This result can be used for express analytical determination of the oil-compounds content in water objects.

Using this method we have also determined quantitative limits of the gasoline–water solution. It was found that optical density of the light absorption band 260 nm reaches maximal value at the gasoline concentration of 0.35 mg/l. Further adding of gasoline did not lead to the changes in optical density. This result proves that a solution of A-95 gasoline in water can reach maximal concentration of 0.35 mg/l. Higher concentration can potentially be reached at longer gasoline/water contacting time.

3. Conclusions

An original UV-spectrophotometry method can be recommended for the test determination in order to investigate its reliability in analytical determination of the oil contamination of water. It is simpler and less expensive comparing to other analytical methods. However, its usage is limited by high-octane motor fuels containing 1,3,5-trimethylbenzene or its homologues. These compounds are in fact registered through 260 nm UV light absorption band. Maximal concentration of 1,3,5-trimethylbenzene or its homologues in water is 0.35 mg/l are reached after the short contacting time.

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APPLICATION OF LOW-COST SORBENT FOR OIL SPILL SORPTION USING RESPONSE SURFACE METHODOLOGICAL APPROACH

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Abstract. The paper deals with oil spill clean-up using peat as low-cost sorbent material. Light fuel oil of regional production has been used in all experiments as the representative petroleum product. The design of experiments and response surface methodological approach has been used for the investigation of sorption process. A regression equation (response surface model) has been proposed for the prediction of removal efficiency as a function of design variables (factors), i.e., sorbent dosage, drainage time and initial thickness of oil slick on water. A very good agreement between the experimental data and response surface model has been found. The linkage between the removal efficiency and factors has been illustrated via response surface plots and contour lines maps. Based on the regression equation the maximal removal efficiency has been found by optimization.

Keywords: oil spill, low-cost sorbent, response surface methodology.

Abbreviations:

CCD – central composite design
DoE – design of experiment
LFO – light fuel oil
RSM – response surface methodology
RS-model – response surface model

1. Introduction

Spills of oil on land and waters (marine, rivers, lakes and groundwater) as a result of oil transportation and storage cause serious environmental pollution and

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consequently call for prompt action to be taken. The spilled oil conducts to an undesirable taste and odor of drinking water and causes serious environmental damage. Contaminated oily waters cannot be used for municipal water supply, for industry, nor for irrigation. Increasing environmental concerns, especially after several hazardous accidental oil spills in the past decades renewed the interest for investigation of cleanup methods. Physical, chemical and biological processes can be used to remove oil spill from water surface or to decompose it in situ.

In case of marine oil spills pollution, dispersants [5], booms [10] and skimmers [6] can be used as clean-up methods to remove oil slicks from water surface. Likewise, the application of sorbent materials is an attractive method for combating of oil spill pollution mainly due to the lower costs and high effectiveness. In this respect, the use of low-cost materials is very important. The low-cost sorbents are defined as materials, which are abundant in nature or as by-products or waste materials from another industry that require usually little processing [2]. Different types of sorbents such as organic, inorganic and synthetic materials have been successfully used for oil spill sorption [4, 9]. However, only natural organic sorbents such as: kapok, peat moss, straw, hay, sawdust, ground corncobs, feathers, and other readily available carbon-based products are considered as efficient low-cost materials for oil spill clean-up. The major factors promoting the use of organic products are: biodegradability, use of renewable resources, waste recycling of life cycle extension, lower cost per unit, lower impact on ecosystem if released or lost during clean-up operations, and public perception that the products are environmental friendly.

To address different local environmental issues, the regional available peat was prepared correspondingly as a low-cost sorbent for oil spill and heavy metals sorption.

In our previous works [3, 7] the application of peat-based sorbents for the removal of heavy metals ions from wastewater were investigated. Thus, the ability of local available peat for sorption of lead and copper ions from aqueous solution has been determined using batch experimental techniques. The sorption equilibriums have been studied at different pH values. Different types of mathematical model isotherms have described the equilibrium adsorption capacity of peat sorbent, namely: Freundlich, Langmuir, Redlich-Peterson, Sips, Temkin, Toth and Dubin-Radushkevich isotherms. The thermodynamic parameters like free energy changes for adsorption of heavy metal ions by peat have been ascertained and discussed.

In the present work the ability of peat-based sorbent was tested for oil sorption using response surface methodological approach. The optimization of sorption conditions has been figured out and discussed in this paper.

2. Experimental

2.1. Materials

The peat employed in the sorption tests is the abundant material of natural origin that was collected from Romanian peat-land Poiana Stampei. The wet raw material was previously dried at the room temperature for 14 days in open area. After that, the raw material was cut up using the cutting mil GRINGOMIX GM 200 (Retsch, Germany). The obtained disperse material was sieved and the fraction with particle sizes of 1–7 mm had been dried in a hot-air oven at 105°C for 6 h and stored for further use.

The petroleum-based liquid employed in the sorption tests was Light Fuel Oil (LFO) of regional production provided by PETROM Company (Romania). The viscosity of LFO was measured using an Ubbelohde viscometer and its density was determined using a common pycnometer. Three runs of the measurements were made at room temperature of 22 ± 2°C. Taking into consideration the average values of measurements, the following results obtained for LFO in terms of viscosity and density: 6.13 ± 0.03 cSt and 0.920 ± 0.005 g/cm^2, respectively.

2.2. Methods and analysis

Two tests regarding oil spill sorption were carried out in this paper. The test no. 1 deals with determination of initial sorption capacity of sorbent as the pick-up ratio. It is expressed as the ratio between amount of oil (g) retained per unit mass of sorbent (g). The procedure for determining oil sorption capacity generally followed the known standard methods for testing of oil spill sorbents, i.e., ASTM F 726-99 and CAN/CGSB-183.2-94. Thus, a fresh sorbent sample has been placed on a 7.5 mm layer of LFO. The sample is left for a period of 15 min for complete saturation with oil product. The sorbent is then removed from liquid phase using a mesh basket and the weight of sorbent is measured as oil drips after 30 s. The initial sorption capacity *S* (g oil/g sorbent) has been determined by gravimetric method of analysis using a digital balance with resolution of 0.001 g and may be written as follows:

$$S = \frac{W_{SO} - W_S}{W_S} = \frac{W_O}{W_S} \tag{2.1}$$

where W_S means the weight of fresh sorbent sample (g), W_{SO} denotes the weight of sorbent saturated with oil product (g) and W_O is the weight of oil product retained into sorbent matrix (g). Note that, under normal conditions, a sorbent will not be exposed to sufficient oil layer thickness to become completely saturated. Therefore, this test gives the maximum sorption capacity data without the competing presence of water.

The second test deals with removal of oil slick by sorption in the presence of water.

The application of peat as floating sorbent to remove LFO slick from water surface involves the performing of following experiment. A test cell with 74 mm (diameter) × 100 mm (depth) was filed with 300 cm^3 of distilled water, obtaining a column of water with approximately 80 mm height. Then V_0 volume of LFO product was added into the test cell. The added volume of LFO was selected in that way to form a 3/8 mm floating layer on water surface. A fresh sample of the sorbent (previously weighed) was lowered into the test cell using a mesh basket with 1 mm openings. The test cell was covered and left for 15 min for complete saturation of sorbent with LFO. After saturation the sorbent was removed allowing the liquid to drain for 12/48 s (drainage time). The performance of oil slick removal from water surface was measured in terms of removal efficiency Y (%) that can be written as:

$$Y = \frac{V_0 - V_R}{V_0} \times 100 \tag{2.2}$$

where V_0 is the initial (added) volume of LFO in water (cm^3) and V_R is the remained volume of LFO in water after sorption test (cm^3).

Taking into consideration the different experimental methods for determination of remained volume fractions of LFO after sorption the following relationship is valid:

$$V_R = V_R^{(1)} + V_R^{(2)} \tag{2.3}$$

where the volume fraction $V_R^{(1)}$ refers to remained visible layer of LFO on water surface while $V_R^{(2)}$ fraction includes LFO shines on water and eventually dissolved components of oil product in the aqueous phase. The volume $V_R^{(1)}$ was determined by collecting the remained oil layer from water surface using an oleophilic skimmer and graduated cylinder. After removing of visible oil layer by skimmer, the volume fraction $V_R^{(2)}$ of LFO in water was determined by means of UV-VIS spectroscopic method. Of course, in the most experiments the condition of $V_R^{(1)} >> V_R^{(2)}$ was obviously. Note, that all experiments were conducted at room temperature of 22 ± 2°C.

3. Results and discussion

3.1. Sorption capacity

The sorption capacity of peat for LFO was determined in triplicate according to *test no. 1* and the results are given in Table 3.1.1 together with average value and standard deviation data.

Table 3.1.1. Initial sorption capacity of peat for LFO, T = 22 ± 2°C.

	Run no. 1	Run no. 2	Run no. 3	Average	Standard deviation
S (g/g)	7.387	7.472	7.878	7.579	0.214

The initial sorption capacity of 7.579 ± 0.214 g/g is given by the properties of sorbent such as porosity and capillaries as well as by the properties of oil product as viscosity, density and surface tension. The sorption capacity of 7.579 g/g is relatively high suggesting that the retention of liquid phase into sorbent matrix occurs due to adsorption and capillary phenomena.

3.2. Experimental design and response surface modeling for oil slick removal by sorption

The removal of oil slick from water surface by sorption (*test no. 2*) was investigated using the design of experiments (DoE) and response surface methodological (RSM) approach.

The experimental design used for the modeling of sorption process was carried out choosing three main factors (design variables), namely: the dosage of sorbent, drainage time and the initial thickness of oil slick on water surface. Since the clean-up process occurs on the top surface of water column it is appropriate to express the sorbent dosage as amount of sorbent per unit of surface area. Thus, in this application the sorbent dosage was expressed as sorbent amount in (g) per unit of polluted area given in (dm^2), M (g/dm^2). The drainage time is given in seconds, t(s). As regards the third factor, i.e. initial thickness of oil slick h (mm), it is in linear relationship with the initial volume of oil product V_0 (cm^3).

Since in real environmental issues concerning oil spill pollution the thickness of oil slick is one of the most important factors in selection of the clean-up method, it is more appropriate to work with thickness of oil later rather than with the volume of spilt oil.

A central composite design (CCD) of orthogonal type was employed in this study for planing the experiments as it is shown in Table 3.2.1. Thus, the operating ranges and the levels of the considered variables are given in actual and coded values (Table 3.2.1). The results of response, i.e., removal efficiency Y %, were determined experimentally according to experimental runs of CCD in order to ascertain the performance of sorption process.

Table 3.2.1. Central composite orthogonal design and experimental response.

Run number (N) and type[a]		Factors (controllable input variables)						Response
		Sorbent dosage		Drainage time		Initial thickness of oil slick		Removal Efficiency
		M g/dm^2	level[b] x_1	t (s)	level[b] x_2	h (mm)	level[b] x_3	Y (%)
1	O1	4.64	1	45	1	7.4	1	60.04
2	O2	2.32	–1	45	1	7.4	1	21.37
3	O3	4.64	1	15	–1	7.4	1	65.51
4	O4	2.32	–1	15	–1	7.4	1	34.12
5	O5	4.64	1	45	1	4.2	–1	90.23
6	O6	2.32	–1	45	1	4.2	–1	57.56
7	O7	4.64	1	15	–1	4.2	–1	95.31
8	O8	2.32	–1	15	–1	4.2	–1	67.16
9	S1	4.89	α	30	0	5.8	0	76.88
10	S2	2.07	$-\alpha$	30	0	5.8	0	34.72
11	S3	3.48	0	48	α	5.8	0	53.72
12	S4	3.48	0	12	$-\alpha$	5.8	0	62.82
13	S5	3.48	0	30	0	7.8	α	45.25
14	S6	3.48	0	30	0	3.9	$-\alpha$	89.14
15	C1	3.48	0	30	0	5.8	0	56.11
16	C2	3.48	0	30	0	5.8	0	55.90

[a] O = orthogonal design points. C = center points. S = star or axial points.
[b] –1 = low value. 0 = center value. +1 = high value. +/– α = star point value.

As can be observed from Table 3.2.1, the maximum value of removal efficiency in the experiments was of 95.31 % while the minimal value of this response was 21.37%. In order to enhance the removal efficiency ($Y > 95\%$) the optimization approach was applied using the response surface methodology.

Thus, based on experimental design the response surface model has been developed. The least square estimations of the regression coefficients from this model have been calculated by means of Multiple Linear Regression (MLR) method and can be written as follows [1, 8]:

$$\beta = (X^T X)^{-1} X^T Y \tag{3.1}$$

where β is a $(L \times 1)$ vector of regression coefficients, X is a $(N \times L)$ extended design matrix of the coded levels of input variables, Y is a $(N \times 1)$ column vector of response determined experimentally according to the arrangement points into

CCD, N is the number of experimental runs and L is the number of regression coefficients within the extended RS-model.

According to experimental results given by experimental design (Table 3.2.1.) the RS-model has been developed by MLR-method to figure out the functional relationship for approximation and prediction of removal efficiency. Thus, the second-order model with coded terms is as follows:

$$\hat{Y} = 57.831 + 16.627x_1 - 4.013x_2 - 16.667x_3 - 1.924x_1^2 + 5.802x_3^2 + 1.475x_1x_2 + 1.155x_1x_3 \tag{3.2}$$

subjected to: $-\alpha \le x_i \le +\alpha \; \forall\, i = \overline{1,\ 3}$

Note that, all terms in Eq. (3.2) are the meaningful terms retained according to statistical analysis given by Student's *t*-test. The empirical model in terms of real variables is as follows:

$$\hat{Y} = 156.731 + 18.135\ M - 0.563\ t - 38.875\ h - 1.43\ M^2 + 2.266\ h^2 + 0.085\ M\ t + 0.622\ M\ h \tag{3.3}$$

subjected to $2.07 \le M \le 4.89$ (g/dm^2); $12 \le t \le 48$ (s); $3.9 \le h \le 7.8$ (mm)

The significance of regression model was tested by means of analysis of variance (ANOVA). In Table 3.2.2 the ANOVA results are presented summarizing the sum of squares of residuals and regressions together with the corresponding degrees of freedom, *F*-value, *P*-value and ANOVA coefficients (i.e. coefficients of multiple determination R^2 and adjusted statistic R_{adj}^2). The mathematical expressions used for calculation of the ANOVA estimators (i.e., *SS, MS, F*-value, R^2, R_{adj}^2) are given in the literature concerning RSM [1, 8].

Table 3.2.2. Analysis of variance (ANOVA) of RS-model (response: removal efficiency).

Source	DF[a]	SS[b]	MS[c]	*F*-value	*P*-value	R^2	R_{adj}^2
Model	7	6455.05	922.15	318.716	<0.0001	0.996	0.993
Residual	8	23.147	2.893				
Total	15	6478.197					

[a]Degree of freedom; [b]sum of squares; [c]mean square.

All ANOVA statistical estimators exhibit that the RS-model developed for the prediction of removal efficiency is statistically validated for the approximation of the response over the range of experimentation.

Also, the model fitness can be easily estimated by the examination of the residuals that may be defined for any observation *j* as [8]:

$$e_j = Y_j - \hat{Y}_j \quad \forall j = \overline{1,\ N} \tag{3.4}$$

where $\hat{Y}_j$ is a model prediction of the corresponding observation Y_j. The plot of predicted and experimental responses, as well as the plot of the residuals versus the observation order (N) is shown in Fig. 3.2.1. A goodness-of-fit between RS-model and the corresponding experimental data can be evidently observed.

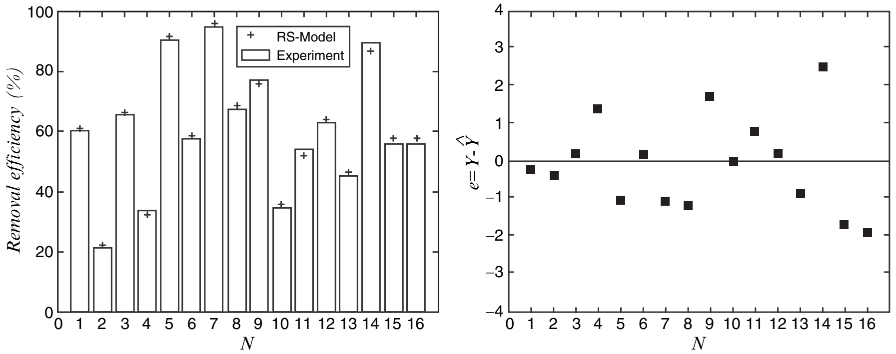

Fig. 3.2.1. Experimental data plotted against the predicted ones for removal efficiency (a) and residual analysis (b).

The response surfaces plots and contour-lines maps have been drawn and analyzed. The most representative response surface plot is shown in Fig. 3.2.2. revealing the influence of factors (design variables) upon the removal efficiency. Thus, the response surface indicates that the increasing of sorbent dosage *M* conducts to enhancing of removal efficiency. While the increment of both drainage time *t* and initial thickness of oil slick *h* leads to decreasing of removal efficiency. As the magnitude of influence upon response, the factors *M* and *h* have similar importance. By contrast, the drainage time has the most reduced main effect being 4-fold lower than the main effects of other factors. Small interaction effects appear between sorbent dosage and other two factors.

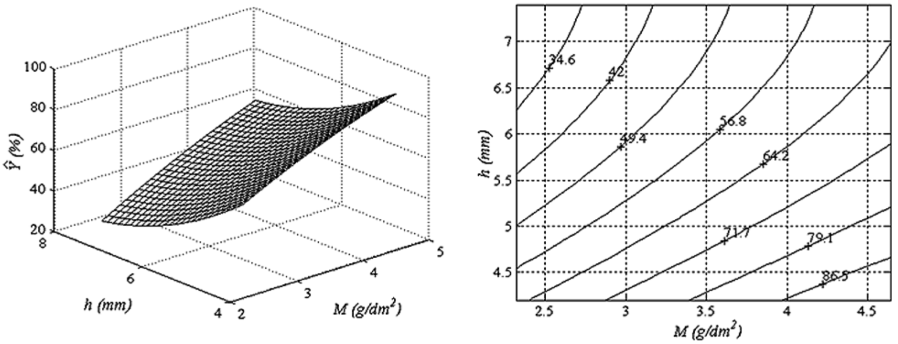

Fig. 3.2.2. Response surface plot and contour-lines map depending on *M* and *h* factors, holding the other factor at its center level $t = 30$ s.

In addition, based on RS-model (regression equation) the optimization problem has been solved. The optimization problem consists in searching by simulation, the input combination of design variables (factors) that maximize the investigated response (removal efficiency). In this respect, the response function in terms of coded variables, i.e., Eq. (3.2), was used for simulation and optimization over the valid region of experimentation. Thus, the formulation of objective function for optimization may be written in this case as:

$$\max_{\bar{x}}\left\{\hat{Y}\left(x_1,\ x_2,\ x_3\right)\right\} \tag{3.5}$$

subjected to: $-\alpha \le x_i \le +\alpha\ \forall\, i = \overline{1,\ 3}$

The optimization problem was solved by means of Monte Carlo method based on stochastic simulations. The computed optimal point in terms of actual factors is as follows: $M^* = 4.89$ $t^* = 12$ s and $h^* = 3.9$ mm. For these optimum conditions the predicted response is 105% while the experimental value is about 98.74%.

The experimental value of $Y^* = 98.74\%$ given by optimal conditions is the highest removal efficiency obtained in all experiments conducted in this work. The optimal solution found suggests that the oil sorbents in high dosage are more efficient to remove thinner oil slicks while for thicker layers the other methods should be applied like skimming assisted by booms. All computations were performed by means of Mathcad and Matlab software.

4. Conclusions

The application of peat as floating sorbent for oil slick (LFO) removal from water surface was investigated using the design of experiments and response surface methodology. In this respect, the central compositional design has been used to develop the response surface model that predicts the dependence between the removal efficiency and design variables (factors).

The response surface plots indicate that the removal efficiency is influenced considerably by the sorbent dosage and the initial thickness of oil slick on water. The optimal solution determined for sorption process over the region of experimentation is as follows: sorbent dosage of 4.89 g/dm^2, drainage time of 12 s and the initial thickness of oil slick of 3.9 mm. In such conditions a maximum removal efficiency of 98.74% was obtained experimentally.

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COMBINED PHOTO-BIOCHEMICAL REACTOR FOR THE DESTRUCTION OF ORGANIC POLLUTANTS IN WATER

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Abstract. A new type of a hybrid photocatalytic reactor, working under the combined natural solar and artificial UV-irradiation, and a biochemical aerobic reactor with floating package with fixed microflora are described. The destruction process can be performed either under homogeneous conditions when Fenton's reagent based on iron trioxalate and hydrogen peroxide was used as catalyst, or under heterogeneous conditions, when dispersed TiO_2 with an anatase structure was applied. It was synthesized by electrochemical dissolving of Ti anodes in alkaline medium under application of periodic current with regulated impulse. Titanium hydroxide thus formed was annealed under the special regimes so as to reduce the probability of ruthil and brukite formation. The two-stage photocatalytic and biochemical treatments of benzothiazoles-containing solutions were studied, dependent on the oxidant and dispersed TiO_2 concentration. Theoretical aspects of this problem are discussed.

Keywords: photocatalytic reactor, benzothiazoles, dispersed TiO_2, heterogeneous catalysis.

1. Introduction

Benzothiazoles (BTs) are broadly used in the industry, mainly due to their high chemical stability. They make parts of synthetic colorants, pesticides, herbicides, vulcanization accelerators and are applied in many technological processes. Their estimated worldwide production reaches thousands of tons, although they were confirmed to possess toxic and carcinogenic properties. That is why their distribution in the environment is a matter of serious concern. These substances cannot be easily destroyed using the conventional chemical and microbiological methods, so new approaches for their de-toxication are needed. Earlier research [1] have evidenced the efficiency of photocatalytical methods for their destruction. In a

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number of investigations, a combination of photocatalytical and biochemical processes in special reactors have been applied [2–3]. The processes of water treatment systems in integrated photocatalytical reactors have been studied, with the removal of colorants, polyphenols, pesticides, and other persistent compounds [4]. As catalysts, Fenton systems are used based on hydrogen peroxide, or other oxidizing agents in homogeneous medium. To conduct the heterogeneous catalytic processes, metal oxides (of Ti, Fe, Zn, Al, Ru, etc.) are used, being introduced into the reactor as suspensions. Among them TiO_2 has the highest stability in photochemical processes, is non-toxic and is most photo-active.

2. Integrated bench-scale reactors

The study of the primary photocatalytical destructive treatment of biochemically hardly degrading organics was performed in an integrated flow-through reactor, with the alternative application of solar energy and UV-lamps. Such reactor (Fig. 2.1) is combined with the aerobic biochemical reactor, in which the microbial treatment of water is provided.

Photo-biocatalytical reactor [5–7] involves quartz glass tube canals with reflectors, fixed on the inclined framework in order to ensure the solar and artificial irradiation of the treated liquid. The hydro-mechanical unit is designed for the cleaning of their interior surfaces. This unit is equipped with a rotable brush and a motor, which at the same time acts as a transportation pump for the permanent recirculation of the liquid from the reception reservoir through the photocatalytic system. Due to this design, the liquid is moved upstream the pipes, with the overflow through the upper collector into the reception reservoir recirculating thereby. The DRP-400 UV-lamps used had the power capacity of 15–20 W/m^2.

The treated solution and photocatalytic activators (TiO_2) are pumped with the dosing pump. Switching from solar to artificial irradiation is provided with the programmer with a photoelectric sensor, which also ensures the rotation of inclined framework following the sun movements within the daytime.

After the photocatalytic destruction cycle is ended, the treated liquid will flow through the vertical tube into the biochemical compartment of the reactor, filling up its volume. The particles of floating solid substrate with fixed microflora reach the level of limiting grid, which prevents their removal from the reaction zone, thus stabilizing the microbiological destruction processes.

Then the air blowing device is switched on, and air partly flows through the pipe, enters the aerolift system, ensuring the permanent upward movement of the treated solution. This intensifies the mass-exchange and mass-transfer processes, and provides the enrichment of the treated circulating liquid with air, thus promoting the biochemical processes. At the same time, a part of air from the air blower is transported into the aeration system.

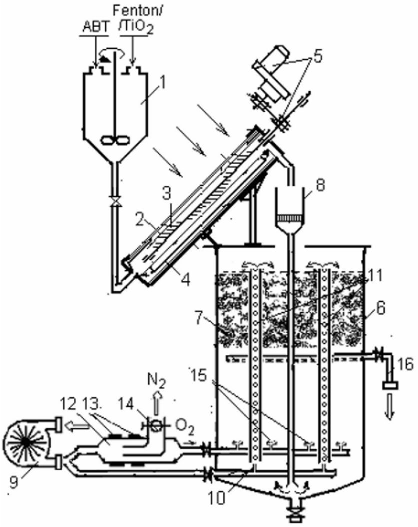

Fig. 2.1. The scheme of the combined photocatalytic and biochemical reactors for the destruction treatment of water, containing persistent organic compounds: 1 – inclined framework; 2 – quartz tubes; 3 – brush; 4 – UV-lamps; 5 – motor; 6 – bioreactor’s case; 7 – substrate for microflora fixation; 8 – filter; 9 – air blower; 10 – air inlet; 11 – aerolift; 12 – oxygen enrichment; 13 – magnets; 14 – regulating choker; 15 – bubbling; 16 – outlet for treated water.

The air is enriched with oxygen in the magnetic field. The enrichment principle is based on that the oxygen is the only magnetic-susceptible air constituent; therefore, it is attracted from the air flow to the inferior walls of the cylinder and is moving along the walls. Then the oxygen-enriched air enters the aeration system. The low-oxygen part of air, from the middle part of air flow, enters the curved air pipe and flows away through the outlet, with the help of regulating choker.

Thus, the oxygen content in the air, used for the biochemical process, is increased by 3–5%, compared to the conventional value, which is beneficial for the development of aerobic microorganisms. Under these conditions, the organic molecules are further subjected to the microbial destruction, forming non-toxic metabolites up to their complete mineralization.

3. Experimental

The subject of the research was a 0.5 mM water solution of benzothiazole (BT). BT concentration was determined by HPLC. (Agilent Technologies, RP 18 column 15 × 3 mm, acetonitrile:water (20:80), flow rate 1 ml/min, UV detector 265 nm.)

The tests of integrated photo-biochemical reactor were based on the estimation of the BT photocatalytic destruction under heterogeneous conditions. Using photocatalytically active Fenton's reagent based on hydrogen peroxide and iron (III) salts, present as the hydrocomplex $Fe(OH)^{2+}$ as the source of active oxidizing $^{\bullet}OH$ radicals, is impossible in acid medium, as it provokes the inactivation of microorganisms under the low pH regime. At the same time, at neutral pH favourable for the biochemical processes, the formation of $Fe(OH)_3$ precipitates proceeds, which reduces its catalytic activity.

As the neutral pH is needed for microorganisms, our photo- and biochemical experiments were carried out pH 7.5, and titanium dioxide was used as photoinducer for BT degradation. This reagent is known to be photocatalytically active and does not inhibite the biochemical processes. However, its particles were used in the photo-chemical reactor only and they did not reach the biochemical reactor due to filtration effects.

There are three crystalline modifications of TiO_2 known: anatase, ruthyl and brukite, from which mainly anatase exert the photocatalytic activity [8]. This activity is explained with the processes running under UV-irradiation with the formation of electron holes (h^+) and free electron (e^-) following the reaction: $TiO_2 + h\nu \rightarrow e^- + h^+$, which in their turn promote the formation of $^{\bullet}O^{2-}$ radical: $e^- + O_2 \rightarrow {}^{\bullet}O^{2-}$, and $TiO_2(h^+) + H_2O_{ads} \rightarrow TiO_2 + {}^{\bullet}OH_{ads.} + H^+$. Apart from this, the formation of other reactive radicals is possible, which contribute to the destruction of persistent organic pollutants.

Meanwhile, commercial TiO_2 as a rule consists of the mixture of three crystallic modificatios, which makes it necessary to develop a method of preparation of the anatase structure. In order to obtain the titanium dioxide of atanase structure, the cryochemical method was used. For this purpose, the ammonium complex of titanium chloride with the general formula $TiCl_4{\cdot}nNH_3$ was squeezed through the system of micro-inlets, with the jet break into the super-cooled liquid (liquid nitrogen) for the formation of spherical particles of cryo-hydrate. Then the cryohydrated salt particles were exposed to sublimation, hydrolytic decomposition and low-temperature oxidation under heating up to 500–550°C [9]. As a result, TiO_2 fine particles are nanostructurized, possess' high specific surface and improved photocatalytic properties. Also, another method for obtaining TiO_2 was tested, when metallic Ti was electrochemically dissolved using alternating current [10], and Ti hydroxide was subsequently annealed under the same temperature as before. The TiO_2 particles formed have mainly atanase crystalline structure with the following crystalline lattice parameters, Å: a = 3,782, c = 9,509. The mean particle size, estimated on the base of the scanning electron microscopy data, was within the limits 10-25 nm, while the specific surface determined by the BET method, made 24.7 m^3/g.

Titanuim dioxide thus synthesized was introduced into the solutions to be treated in concentrations of 0.5–2.0 g/l.

As microflora, the aerobic culture *Rodococcus rhodochrous* was used, which was found to be the most efficient for the microbiological destruction of this class of compounds especially. As a floating hard carrier for microflora fixation the suspended micro- and micro-porous perlit can be used, which possess a low bulk density and floating properties.

4. Results and discussion

BT is stable in water and its degradation in water solution is not observed in the absence of light at 25–35°C. Moreover, it does not absorb wavelengths above 300 nm, and no degradation is observed in the reactor in this case. BT is characterized with three absorbtion maxima at 215, 251 and 284 nm with the molecular absorbtion coefficients of 21,379, 7,018 and 2,441 M^{-1} sm^{-1}, accordingly.

HPLC chromatograms of BT solutions in water are characterized with an R_T of 10.0 min. However, after the treatment the intensity of this peak decreases from 125 to 20 mV, which testifies the destruction processes occurred. Measuring of these peaks area makes it possible to assess the decrease of BT concentration and its destruction degree. Small peaks appeared on chromatograms have not been unambiguously identified.

The tests in photocatalytic reactor have shown (Fig. 4.1) that in the absence of light no BT destruction was observed. Under the photocatalytical treatment the destruction increases with the increase of the amount of introduced TiO_2, reaching 44%, 60% and 84%, which might be associated with the photocatalytic properties of TiO_2, which can be explained on the base of zonal structure of its electronic levels.

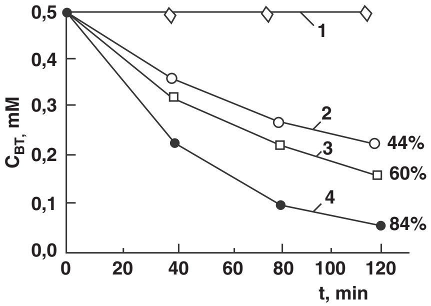

Fig. 4.1. Efficiency of BT photocatalytic destruction (0.5 mM) at pH 7,5 and combined solar and artificial irradiation, dependent on TiO_2 concentration, g/l :1 – 0; 2 – 0.5; 3 – 1; 4 – 2.0.

It is known that out of the three known crystalline structure types of TiO_2 – atanase, rutyl and brukite, only atanase possess the high photocatalytic activity. The UV light with the wavelength $l < 385$ nm excites the electron from the valence zone to conductivity zone, forming the pair electron-hole. Two reagents may be absorbed at the same time during the photocatalysis, which can be reduced and oxdized under an efficient light absorbance ($hv \geq Eg$). The electron transfer capacity from the conductivity zone to the absorbed particle (acceptor) depends on the position of energy zone (energy band) of semiconductor and the redox-potential of the absorbant. If the absorbed pairs consist of water and dissolved oxygen (H_2O/O_2), then water will be oxidized with the positive holes and will be disintegrated forming $^{\bullet}OH$ and H^+. As oxygen is an easily reducible substance, its reduction with photoelectron within the conductivity zone provokes the generation of superoxide-radical anions ($^{\bullet}O_2^-$), which in their turn react with H^+, generating the hydrogen dioxide radical ($^{\bullet}HO_2$). As a result of the further collisions with electron, hydrogen dioxide radical HO_2^- is formed, and then the formation of hydrogen ion and H_2O_2 molecule is possible. Therefore, the above-described reaction chain result in the formation of a series of reactive oxygen-containing particles such as H_2O_2, $^{\bullet}O_2^-$, $^{\bullet}OH$, etc. [8].

Thus, the main heterogeneous reactions causing the formation of active radicals on TiO_2 particles under UV-irradiation, within the conductivity zones (e^-) might be represented as follows:

$TiO_2(e^-) + O_2 \rightarrow TiO_2 + {}^{\bullet}O_2^-$

$TiO_2\,(e^-) + {}^{\bullet}O_2^- + 2H^+ \rightarrow TiO_2 + H_2O_2$

$TiO_2\,(e^-) + H_2O_2 \rightarrow TiO_2 + {}^{\bullet}OH + OH^-$

${}^{\bullet}O2^- + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + O_2; {}^{\bullet}O2^- + H^+ \rightarrow {}^{\bullet}HO_2$

$TiO_2\,(e^-) + {}^{\bullet}HO_2 \rightarrow TiO_2 + HO_2^-$.

The main photocatalytic reactions within the valence zones (h^+) on the activated surface of microparticles, are:

$TiO_2(h^+) + H_2O_{ads} \rightarrow TiO_2 + {}^{\bullet}OH_{ads} + H^+$

$TiO_2\,(h^+) + 2H2O_{ads} \rightarrow TiO_2 + 2H^+ + H_2O_2$

$TiO_2\,(h^+) + OH^-_{ads} \rightarrow TiO_2 + {}^{\bullet}OH_{ads}$.

Hydroxyl-radical $^{\bullet}OH$ is a highly reactive but a short-living species. Superoxide radical-anion $^{\bullet}O_2^-$ is a longer-living radical having a negative charge, which is like hydrogen peroxide a precursor of hydroxyl-radical, providing the photocatalytic destruction of complex organic molecules.

Therefore, during the photo-irradiation in the presence of TiO_2 under the studied conditions, the BT destruction is provided, which might be connected with the opening of the aromatic ring, resulting in the formation of photoproducts which could not identified with an HPLC with UV-detector. The accumulation of intermediates was not observes.

At the biochemical stage of the treatment in the combined photo-bioreactor, the destruction cycle of BT molecules is finalized with their complete mineralization. According to the research findings presented in [11], the main products identified in the biochemical process formed by the *Rodococcus rhodochrous* bacteria, are the intermediate metabolites – 2-hydroxybenzothiazol (OBT) and 2,6-dihydroxybenzothiazol (di-OBT) (Fig. 4.2). Their subsequent complete mineralization proceeds according to the following proposed scheme.

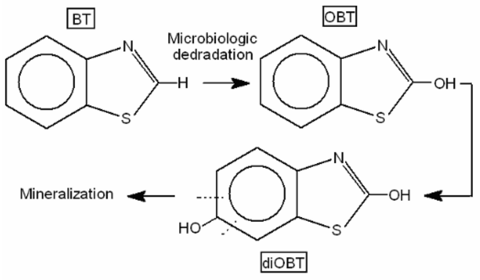

Fig. 4.2. Microbial BT degradation with *Rodococcus rhodochrous* bacteria [11].

UV-visible light spectra of OBT are characterized with the absorbtion maxima at 211; 243; 279 and 286 nm, while those for di-OBT – at 212; 252 and 297 nm.

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PART III. SOIL POLLUTION AND PREVENTION

SOURCES AND FORMS OF SOIL CHEMICAL DEGRADATION

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Abstract. The main sources of soil pollution, the types and the forms of chernozem degradation are presented in the present article. It was established that in a period of 100 years, as a result of the mineralization processes, 40–47% of the initial humus reserves were lost, which constitutes 0.5–0.6 t/ha or 0.013–0.018% annually. In the course of 105 years, 3.4 t/ha of N, 0.9 tons of P_2O_5 and 6.8 t/ha of K_2O were extracted and exported with the harvest from the soils of the Republic of Moldova. The chemical degradation of the soils led to the intensification of the physical and biological degradation processes, and as consequence the production capacity of the agricultural fields decreased. In order to stabilize or to increase the humus contents in the chernozems, it is necessary to minimize the soil erosion to the admissible limits, to observe the scientifically proven crop rotation system with the quota of perennial grasses of 10–15% and to incorporate an average of 10 t/ha manure and 150–180 kg/ha of NPK per crop rotation annually.

Keywords: chernozem, humus degradation, soil degradation, soil nutritive elements.

1. Introduction

The soils constitute the main and, in fact, the only natural wealth of the Republic of Moldova. The efficient usage of this natural gift conditions, to a great extent, the economic development of the country and the population's well-being. The fertile soils and the favorable thermal regime make possible the cultivation of a large spectrum of important agricultural crops such as: vines, oil plants, vege tables, fruits (including nuts and plums), sun-flower, etc.

The Republic of Moldova is characterized by a very complex soil cover. The variability and the zone areas of the soils are determined by the peculiarities of the climate, relief, the geomorphic construction, and the vegetation. The chernozem predominate in the structure of soil covers; their quota constitutes about 70%. The brown and grey soils, formed under forest vegetation, occupy 10% of the land

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fund surface. An important group of soils, as being used in agriculture and forming an ecological niche for biodiversity conservation, is that of alluvial soils including the hydromorphic ones (8.4% or about 300,000 hectares).

The uneven geomorphologic structure, the sedimentary geological rocks, the hilly relief as well as other natural and anthropoid factors very often favour the soil degradation processes [1].

The average solvability mark of the soils from the Republic of Moldova constitutes 64 points as of 12.01.2008. The natural soil fertility secures the yield of 2.5 t/ha of autumn wheat.

According to the Land Cadastre of the Republic of Moldova [2], on January 2008, the total surface of terrains constituted 3.38 million hectares, including 2.51 million ha (75%) of agricultural lands out of which 1.82 million hectares are arable lands (73%), about 12% are orchards and vine yards, and about 14% are pastures. The forest fund is quite small and constitutes about 12%.

Based on the submitted data, the quota of agricultural fields is inadmissibly large (75%), while that of the forest fund is by two to three times smaller than the optimal one. The ecologic lack of balance between the natural and anthropoid ecosystems determine the promotion and intensification of various types and forms of soil degradation [3–6], including the chernozems used in agricultural purposes [7]. In the present article, we include the experimental data obtained in the course of the last 130 years in the process of studying the chernozems from the point of view of their chemical degradation.

The main sources of soil pollution are: residual household and industrial waters, chemicals used for plant protection, irrigation water that contains an increased degree of mineralization, oil products, exhaust gases, industrial wastes, and organic wastes from animal farms.

Chernozem degradation is grouped into five types and 40 forms [7]. The chemical degradation is of 10 forms, including dehumification, soil wearing out of nutritive elements (N, P, K, Ca), insufficiency and/or surplus of microelements, surplus of salts in the soil, and radio nuclide pollution.

This paper will refer to the most widely spread forms of chemical degradation of chernozems and namely: mineralization of the humus and soil wearing out of nutritive elements (nitrogen, phosphorus and potassium).

1.1. Humus degradation

The humus is one of the main indicators of soil fertility. This fundamental component determines, to a great extent, the physical, chemical, and biological properties of the soil. At the same time, it constitutes a source of nutritive elements for the plants. Being a multi-componential substance, the humus also represents an accumulator of conserved energy.

The humification represents a complex process of transforming the organic matter incorporated in soil [8]. The accumulation of humus in soil took place in a long period of time, from the first stages of solidification until the inclusion of the stiffened soils in the arable agricultural circuit. This period lasted for about 10–15 thousand years. Simultaneously with the increase of the contents of organic matter in soil, the accumulation of nitrogen and of other biophile elements occurred.

The chernozems, including the ones from the Republic of Moldova, were studied in details by the founder of genetic pedology, V. Dokuceaev [9]. After a century, research on the topics investigated by the great scholar has been done anew. Analyses of the contents and the state of humus in different subtypes of chernozems have been undertaken again. Generalizations are presented in multiple scientific works [7, 10, 11]. It was stated that in the course of 100 years (from 1881 up to 1981) the contents of humus in different subtypes of chernozems from various regions in Russia decreased by 27–53% (Table 1.1.1). The annual humus losses constituted 0.5–0.9 t/ha for this period. According to the data [7, 11] in the conditions of the Republic of Moldova, the humus losses from common chernozems constituted 30–40% or 50–70 t/ha for the same period. The speed of mineralization of the organic matter constituted 0.5–0.7 t/ha annually.

The experimental data obtained by A. Ursu [12] about the modification of the humus contents in the chernozems of the village Napadova, Floreshti district, which were studied by V. Dokuceaev in 1877 (Table 1.1.2), are of special interest. In the period of 83 years (1877–1960), the contents of humus decreased by 2.04% or by 35.7% of the initial ones. The speed of organic matter mineralization constituted annually 0.025%, while the humus losses constituted 0.89 t/ha. In the following 43 years (1960–2003), the contents of humus decreased only by 0.32%. In this period the speed of mineralization of the organic matter decreased considerably and constituted 0.007% annually. The losses of organic matter in soil constituted 0.27 t/ha. The agrochemical researches of the agricultural fields in the village Napadova carried out by the laboratory *Soil Agro-chemistry and Plant Nutrition* of “Nicolae Dimo” Institute in the year 2004 and 2007 demonstrated that the average contents of humus constitutes 3.30% and is identical with the data obtained later [12]. Since 2007 this field is included in the polygon network of “Nicolae Dimo” Institute in order to carry out the ecopedologic monitoring.

As consequence, in the course of 126 years (1877–2003), 2.36% of humus were mineralized or 41.3% of the initial reserves. The speed of dehumification of the organic matter constituted 0.018% annually. The annual humus losses constituted 0.67 t/ha.

The most significant humus losses in soil occur because of two processes: biological (dehumification) and soil erosion. In the Republic of Moldova, the surface of eroded soils constitutes about 40% of the arable lands. The annual losses of organic matter caused by erosion constitute 0.4 t/ha (Table 1.1.3).

Table 1.1.1. Modification of humus contents in different chernozem subtypes in the period of 100 years [10] (the layer of 0–30 cm).

Subtype of chernozem	Region	Humus contents and reserves				Humus losses		
		1881		1981		in 100 years (t/ha)	Annually (t/ha)	% from the initial contents
		%	t/ha	%	t/ha			
Typical	Tambov and Voronedz	10–13	300–390	7–10	210–300	90	0.9	23–30
	Kursk and Kharkov	7–10	221–315	4–7	142–248	69–79	0.7–0.9	21–36
Levigated	Stavropol Region	7–10	231–330	4–7	150–263	67–81	0.7–0.8	20–34
Common	Voronedz	7–10	221–315	4–7	150–263	52–71	0.5–0.7	17–32
	Republic of Moldova	4–7	126–221	2–4	75–150	51–71	0.5–0.7	32–40
Typical	Kuibishev	13–16	390–480	8–10	240–300	150–180	1.5–1.8	38–39
Common	Orenburg	9–11	270–330	6–8	180–240	90	0.9	27–33
Levigated	Ulianovsk	13–16	390–480	4–7	120–210	270	2.7	56–69

Table 1.1.2. Comparative data of the morphometric indicators and the humus contents [12].

Indicators		1877 (steppe)	1960, ploughed land		2003	
			Profiles		Ploughed land	Forest strip
			No. 42	No. 43		
1. Morphologic construction of the profile	A	0–61	0–43	0–44	0–50	0–50
	B	62–91	44–101	45–92	51–98	
	C	92	102	93	99	
	Effervescence	–	92	65	70	–
2. Humus contents	0–20	5.718	3.75	3.60	3.36	4.2
	30–40	–	3.65	3.30	3.15	3.0
	50–70	–	2.34	2.73	1.94	
	70–90	–	1.59	1.57	1.68	

Table 1.1.3. Evolution of humus balance in arable soils in the period 1971–2006, t/ha [5].

Year	Applied organic fertilizers (t/ha)	Humus balance	
		Without erosion losses	With erosion losses
1971–1975	2.9	–0.5	–0.9
1976–1980	3.9	–0.4	–0.8
1981–1985	6.0	–0.1	–0.5
1986–1990	5.6	–0.1	–0.5
1991–1995	2.6	–0.4	–0.8
1996–2000	0.1	–0.7	–1.1
2001–2006	0.1	–0.7	–1.1

At the present stage of agricultural development, the humus balance in soil is negative and constitutes annually minus 1.1 t/ha [5]. The reduction of humus contents in soil, as a result of biological and erosion processes, leads to the worsening of its agro-physical, physico-chemical, chemical and biological properties. As a result, the production capacity of soils decreases, the obtained yields are low and of a bad quality.

It was found out that by the end of the 19th century the content of humus in Moldovan soils constituted 5–6%, and the reserves in the arable stratum were of 200 t/ha (Table 1.1.4).

With this amount of organic matter, the mineralization ability of the soil was high and contained 135 kg/ha of mineral nitrogen. In 50 years the content of organic matter constituted 4–5%. The amount of humus losses was about 25–30%, and the reserves of organic matter were reduced by 50 t/ha. The mineralization speed of the organic substance constituted about 1 t/ha annually. At the end of the

90s of the XX century the humus content decreased to 3.0–3.5%. According to the latest estimates [6, 13], the humus contents in Moldovan soils constituted an average of 3.1% in 1990.

Table 1.1.4. Modification of humus content in the soils of the Republic of Moldova.

Year	Humus (%)	Reserves in the layer of 0–30 cm (t/ha)		Mineral N, kg/ha
		Humus	Nitrogen	
1877	5.0–6.0	200	10	135
1950	4.0–5.0	150	8	115
1965	3.5–4.0	130	6	105
1990	3.0–3.5	110	5	80
2025	2.5–3.0	90	4	70

The estimates indicate that in the period till 2025, the humus content will reduce by 0.50% (35 years × 0.015%) or by18 t/ha and will constitute 2.5–3.0%, an average of 2.7%.

In these conditions, the primary actions to be undertaken for the improvement of the humic state of soils [6, 13] will include:

- Minimizing soil erosion through the implementation of a complex anti-erosion action system.
- Applying, to a great extent, the system for soil conservation which provides soil protection from erosion and reduces organic mater decomposition in soil.
- Utilization, production and application of organic fertilizers, optimal dozes of compost of about 9–10 t/ha in average in the crop rotation systems.
- Rational application of mineral fertilizers, 150–180 kg of NPK in average in crop rotation systems (Table 1.1.5).

Table 1.1.5. Modification of humus content depending on the active time and the system of soil fertilization (%) [6].

Type and sub-type of soil	Before the experience foundation	In 25–30 years		
		Unfertilized	$N_{60}P_{60}K_{60}$	$N_{120}P_{60}K_{60}$
Brown	2.5	2.4	3.0	2.5
Chernozems:				
Leache	4.0	3.2	3.6	3.8
Ordinary	3.0	2.7	2.8	3.0
Carbonated	3.8	3.1	3.5	3.2
Average	3.3	2.8	3.2	3.1

The implementation of the complex of measures in the Experimental Stations of "Nicolae Dimo" Institute led to the conservation and increase of soil fertility, including the organic matter [6].

1.2. Soil wearing off with nutritive elements

Any nutritive regime has its specific peculiarities. In the conditions of the Republic of Moldova that nutritive regime is considered optimal that ensures the obtaining of production determined by humidity. According to the estimates [5, 6], the multi-annual average precipitation quantity permits to obtain a yield of 4.2–4.5 tons of autumn wheat, 5.5 tons of corn for seeds, 2.5 tons of sunflower. In order to obtain these yields, a needed quantity of nutritive substances is necessary.

The chernozems of the Republic Moldova are characterized by a moderate content of humus (about 3.0%), a decreased content of mobile phosphorus, and an optimal quantity of changeable potassium. It was established [14] that in the course of the last 105 years the balance of biophile elements in Moldova's soils was negative. The years 1980–1990, which was the period of intensive use of chemicals in agriculture, were an exception. In this period the balance of nutritive elements was positive. According to the data in the period of 105 years, 11.1 t/ha of NPK, including 3.4 N; 0.9 t P_2O_5; 6.8 t/ha K_2O were extracted and exported with the obtained harvest.

The chemical degradation led to the intensification of worsening the physical and biological properties of the soil and, as a result, the productivity of the agricultural lands decreased.

At present, phosphorus and nitrogen are the nutritive elements of prior minimum. The nitrogen issue in agriculture can be solved positively without harming the environment only by the creation of a neutral or positive balance of the humus in soil and of the closed nitrogen circuit in the chain – soil – agricultural farm – soil. The creation of the closed nitrogen circuit in the rural region would result in diminishing soil pollution, and especially of the surface waters, with nutrients, and first of all, with nitrates and the improvement of the ecological state.

In order to improve the mineral nutrition of the agricultural cultures with nitrogen, the following actions should be undertaken: the use of biological nitrogen in the quantity of 30–35 kg/ha by increasing the quota of vegetable cultures in crop rotation up to 20–25%; the production of organic fertilizers and their application in phyto-techniques in optimal dozes; the rational use of nitrogen fertilizers according to the needs of the agricultural cultures [5].

The efficiency of nitrogen fertilizers depends, to a great extent, on the quantity of the mobile phosphorus in soil. The natural fund of this element in Moldova's soils is low and ensures the formation of 24–27 g/ha of autumn wheat. In the period of intensive use of chemicals (1966–1990), about 960 kg of phosphorus were incorporated in soil per hectare [14]. The systemic application of fertilizers in crop rotation fields radically improved the nutritive regime and plant nutrition with phosphorus. By the year 1990, the contents of mobile phosphorus in the agricultural fields was the following: 24.4% low, 33.6 moderate, and 42.4 high. The average doze of P_{55} achieved in the year 1990 was sufficient to form a multiannual cycle of the optimal level of mobile phosphorus by 3–4 mg/100 g of soil. Since 1990 the quantity of phosphorus applied in agriculture radically decreased and in the last 5–6 years constituted 1 kg/ha.

In order to conserve the already formed level of mobile phosphorus in soil and to decrease the speed of degradation the following actions are to be undertaken: incorporation of P_2O in soil simultaneously with the sowing of cultures; the systematic application of fertilizers in recommended dozes in order to form optimal levels of mobile phosphorus in soil and maintaining them by compensating the export of P_2O_5 with the harvests. In the fields possessing an optimal or high level of mobile phosphorus in soil, it is necessary to apply recommended dozes of nitrogen fertilizers aiming at decreasing the speed of immobilization and observing the advanced technologies.

In order to obtain high yields, the agricultural crops extract considerable quantities of potassium from soil. Moldova's soils are rich in total and changeable potassium. It has been established experimentally that the quantity of potassium of 20 mg/100 g of soil is sufficient for obtaining high yields [13]. In the period of intensive use of chemicals a balanced equilibrium of potassium in soil was formed. At present the balance of this element is extremely negative. In spite of the fact that the soils are rich in potassium accessible to plants, in a period of over 150–200 years the reserves may be exhausted. Hence, it is necessary to compensate the potassium losses by applying fertilizers and first of all organic ones.

2. Conclusions

1. A lengthy utilization of soil in agriculture (after unfallowing) leads to the decrease of humus content in the soil. Losses of organic matter occur because of biological (dehumification) processes and soil erosion. In a period of 100–135 years the reserves of humus in Moldovan soils decreased by 40–47% because of mineralization.
2. In various periods of chernozems utilization in agriculture, the soil losses were different and constituted:

   0.035–0.025% of organic matter is mineralized annually in the first 5–30 years;

   in the following 30–100 years, the mineralization speed of organic matter is lower and constitutes 0.025–0.018% or 0.5–0.9 t/ha annually; soil losses are great and constitute 20–40% from the initial amount (before unfallowing);

   in a period longer than 100 years (from 100 to 300) humus losses constitute 40–47% out of the initial amount. Annually, 0.013–0.018% or 0.5–0.6 organic matter is mineralized.

3. It was stated that in a period of 105 years 3.4 t/ha N, 0.9 t P_2O_5 and 6.8 t/ha K_2O were extracted and exported with the harvests from the soils of Moldova.
4. The soil chemical degradation led to the intensification of physical and biological degradation and as result the production capacity of agricultural lands decreased by 35–40%.
5. In order to increase the soil fertility, the Complex Plan for the improvement of degraded soils and the increase of soil fertility was elaborated which determines the set of agrochemical, phytotechnical, and pedo-improvement measures. Its implementation guarantees the increase of yields by 40–45% and the environmental protection from degradation and pollution.

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VETERINARY MEDICINAL PRODUCTS IN MANURES AND SOILS – PROBLEMS AND SOLUTIONS

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Abstract. In order to improve the prospective evaluation of veterinary medicinal products (VMP), a technical guidance for laboratory tests on degradation in liquid manures and degradation and sorption in manured soils has been developed. Since the representative and reproducible sampling of manure from high-volume tanks is regarded impossible, an innovative research concept has been developed. First, excrement samples of cattle and pigs individually kept at an experimental stable were taken. These samples were thoroughly matrix characterized. Then, tap water was added to prepare reference manures of defined dry substance contents. Subsequently, the long-term degradation of VMP applied as ^{14}C-labeled radiotracers was investigated in those manure samples. On the basis of the degradation tests, test manures with 7-day aged VMP residues were prepared and applied in laboratory tests on degradation and sorption in manured soils. By means of this experimental approach, the impacts of aging processes during manure storage and of the manure matrix on the fate of VMP in soils can be assessed already under laboratory conditions.

Keywords: liquid manure, degradation, manure soils, degradation test.

1. Introduction

Due to the technical progress of analytical chemistry within the last decades, ecological chemistry has targeted the research activities at new classes of environmental chemicals. After the century of using DDT, polychlorinated biphenyls, polycyclic aromatic hydrocarbons and polyhalogenated dibenzo-p-dioxins and furans have been identified as priority contaminants and conventionally defined as persistent organic pollutants (POPs). Today, the most modern xenobiotics belong to different product groups of, e.g., brominated flame retardants, phthalates, polysiloxanes, pharmaceutical and personal care products, perfluorinated tensides, etc. The environmental risk assessment of already existing chemicals has to be

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understood as an end-of-pipe strategy. In case of the worldwide POPs problems, nothing else remains to be done as a thorough inventory in each country followed by a save transport to recycling or incineration plants in order to destruct highly contaminated materials. In contrast, new chemicals undergo compulsory authorization procedures today before those may be placed on the market. This contribution to a prospective evaluation of chemicals, however, requires the availability of appropriate reference-sample matrices and sophisticated test systems at laboratory or field scales.

Concerning this matter, the authorization procedures of plant protection products have worked cutting-edge by defining criteria for decision-making on, e.g., the physical-chemical properties of plant protection products, their environmental fate and behavior and their ecotoxicological effects [1]. For this purpose, analytical methods and laboratory-test systems have been developed and finally established in the OECD guidelines for testing chemicals. This authorization procedure has thus acted as the crucial pulse transmitter for the authorization of chemicals via REACH [2], biocidal products via the European Directive 98/8/EC [3] as well as human and veterinary medicinal products via the Law on the Trade in Drugs [4].

Besides pesticides, veterinary medicinal products (VMP) enter soil environments after administration to production animals, excretion, storage in manure tanks, and application of manures as organic fertilizers. Since the mid of the 1990s, this fact has been taken into account by the VMP authorization procedure [5–7]. Within Phase I of the tiered environmental impact assessment, the compliance of the predicted environmental concentration of soil (PEC_{soil}) is assessed by exposure analysis [8]. Thus, the degradation of VMP during manure storage is disregarded. Within Phase II, tests on acute ecotoxicological effects and on degradation and sorption in soil follow, if PEC_{soil} exceeds the trigger of 100 μg VMP kg^{-1} soil. Those tests are mandatory for antiparasitics applicable to pasture animals. Like testing of pesiticides, the test substances are applied as appropriate standard solutions (standard application). Hence, possible matrix effects by the manures, e.g., on fate and behavior of sulfonamide antibiotics and benzimidazole antiparasitics in soil [9–11], are disregarded, too. Therefore, a technical guidance has been developed for laboratory tests on the degradation of VMP in bovine and pig manures as well as on degradation and sorption in manured soils.

2. Reference excrements and manures

Manures are heterogeneous matrices of high complexity and variability. This heterogeneity is dependent on the animal species, the animals' age, feeding conditions, and VMP administration. Additionally, residues of feeding stuff and straw as well as disinfection and cleaning agents may be released into the storage tanks by farming practices. Finally, organic constituents and pollutants of manures undergo decomposition processes during the storage of manures up to several months [12]. Due to those aspects, the representative and reproducible sampling of manure from tanks up to a volume of 10,000 m^3 is regarded impossible.

In order to close this lack, an innovative research concept was developed. First, excrement samples of cattle and pigs individually kept at an experimental stable were sampled and matrix characterized. The determined parameters were: dry substance (ds), pH, redox potential (Eh), dissolved oxygen (O_2), ammonium and total nitrogen (NH_4-N, N_{total}), total organic carbon (TOC) and biological oxygen demand (BOD). The excrements were then conditioned at ambient temperature for 21 days to decompose readily degradable substances and to reach strictly anaerobic conditions. Thereafter, the reference excrements could be directly used for further analytical processing or long-term stored at –20°C without any quality losses as proven by further matrix characterization (Table 2.1).

Table 2.1. Matrix characterization of reference pig excrements.

Parameter	ds [%]	pH	Eh [mV]	O_2 [mg L^{-1}]	NH_4-N [g kg^{-1}]	N_{total} [g kg^{-1}]	TOC [g kg^{-1}]	BOD [g kg^{-1}]
Minimum[a]	13	5.7	–180	–	3.4	6.8	56	21
Median[a]	17.5	6.6	–95	< 0.1	5.8	9.2	72	24
Maximum[a]	23	7.4	40	–	9.2	13.8	103	28
Excrements conditioned for 21 days[b]	14.3	6.0	–30	<0.1	4.4	8.8	67	18
Excrements stored at –20°C[c]	14.5	6.1	49	<0.1	4.8	8.6	57	21

[a] Excrements sampled from different aged animals and kept at different feeding conditions (2004–2006), conditioned for 21 days and matrix characterized.

[b] Excrements sampled in November 2007, conditioned for 21 days and matrix characterized.

[c] Excrements sampled in November 2007, after conditioning stored at –20°C until July 2008, re-conditioned and matrix characterized.

On the basis of the characterized excrement samples, reference-manure samples were prepared for laboratory tests on degradation of VMP. For this purpose, the dry substance contents of bovine and pig manures of 10% and 5%, respectively, were adjusted by adding tap water to the related excrement samples. Additionally, both manure matrices were tested at 2%, 5%, 10% to identify the impacts of different dry substance contents. Consequently, the prepared manure samples were matrix characterized. Experimental details are described by Kreuzig et al. [13, 14]. Following this concept, reference manures of definitely higher homogeneity than tank manures became available for reproducible laboratory testing.

3. Degradation of VMP in reference manures

For testing the degradability of VMP in reference manures, the respective test substance, i.e., sulfamethoxazol, acetyl-sulfamethoxazol, sulfadiazine, erythromycin, ketoprofen and paracetamol, was applied as a ^{14}C-labeled radiotracer providing the advantage of balancing their fate and behavior. For this purpose, closed laboratory-batch systems allowing for a discontinuous gas exchange were used [15, 16]. The reference-manure samples were then fortified by the respective test substance and incubated under anaerobic conditions in the dark at 20 ± 1°C up to 177 days. The internal ^{14}C-carbon dioxide absorbing potassium hydroxide solutions were exchanged every 7 days and liquid scintillation counted to determine the mineralization (MIN) rates. At defined incubation intervals, the manure samples were extracted by means of organic solvents to determine the extractable residues (ER). Those fractions were additionally screened by means of radio-thin-layer chromatography (RTLC) to differentiate between parent compounds initially applied and metabolites formed during incubation. Finally, the already extracted manure samples were combusted to transfer non-extracted radioactivity into ^{14}C-carbon dioxide and amounts of non-extractable residues were thus quantified by means of scintillation counting. Further experimental details are described by Kreuzig et al. [13].

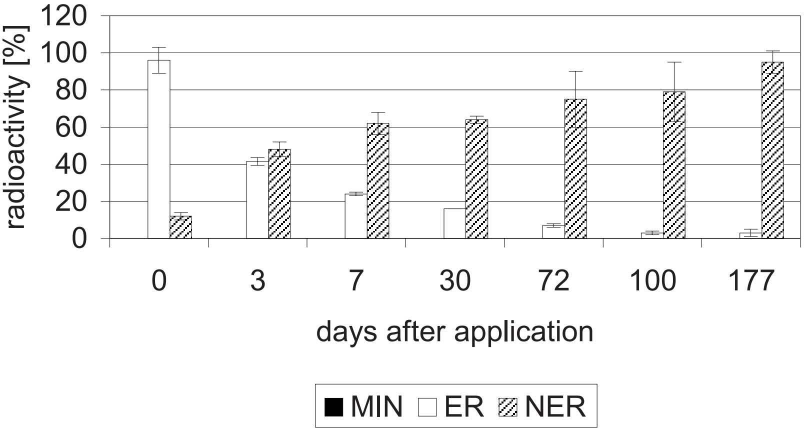

Fig. 3.1. Degradation of ^{14}C-sulfamethoxazole in bovine manure (balances: 89 ± 10 %). MIN: mineralization, ER: extractable residues, NER: non-extractable residues.

3.1. Long-term degradation tests

In the first test series in 2005, ^{14}C-sulfamethoxazole was applied at an initial concentration of 560 µg kg^{-1} bovine manure. The balances of those tests are illustrated in Fig. 3.1. Within the 177-day incubation period, the extractable ^{14}C-sulfamethoxazole residues continuously dropped from 96% to 3% of the initially applied radioactivity while the non-extractable ones simultaneously increased up to 95%. Mineralization was < 0.1%.

These results were confirmed by those of the second test series in 2006, although bovine excrement samples were used after a 180-day storage at –20°C. The respective reference-manure samples, furthermore, were then spiked with 1250 µg sulfamethoxazole kg^{-1} manure to improve the boundary conditions for the RTLC metabolite screening. Despite the enhanced concentration of sulfamethoxazole, the ethyl acetate extracts could only be RTLC screened up to the samples of day 0, 3, and 7 because of the rapid formation of non-extractable residues. Within this period, sulfamethoxazole disappeared rapidly. In the extractable fraction of the 0-day sample, 67% of the initially applied radioactivity accounted for sulfamethoxazole as the unchanged parent compound. This amount dropped within 7 days to 6%. In the same period, the amounts of unidentified metabolites increased from 19% to 25%.

3.2. Impacts of dry substance content and incubation temperature in bovine manure

In short-term degradation tests with incubation intervals of 3, 7 and 30 days, the impact of dry substance contents on the transformation of extractable into non-extractable ^{14}C-sulfamethoxazole residues was studied. This process slowed down within the first 7 days when dry substance contents were adjusted at 2.5% and 5%. In the 30-days samples, however, the differences to the batch tests with manure of 10% dry substance content were nearly compensated.

Similar tendencies were found when the manure samples were incubated at different temperatures, considering relevant that temperatures in manure tanks were only dependent on ambient outdoor conditions. At 5°C and 10°C, the transformation also slowed down due to the temperature depending activity of manure inherent microorganisms. After 30 days, however, those differences were leveled, too.

3.3. Impacts of different bovine manure matrices

Within the different degradation tests, three different manure matrices were included taking different ages of cattle and different feeding conditions into account. Due to the herbivore nutrition type of cattle, only minor differences in pH values, ammonium and total nitrogen contents as well as in biological and chemical oxygen demands were found.

The results of the matrix characterization were also reflected by the corresponding degradation tests. Taking the analytical deviations between replicates of one manure matrix into account, relevant differences between different bovine manure matrices were not found. The extractable ^{14}C-sulfamethoxazole residues of approximately 40% after 3 days dropped continuously to 13% on average while the non-extractable residues increased up to approximately 80% after 30 days.

3.4. Long-term degradation tests in pig manure

The comparison between the degradation tests in bovine and pig manures (Fig. 3.4.1.) clearly showed the higher affinity of ^{14}C-sulfamethoxazole residues to the bovine manure matrix. Thus, a slower decrease of extractable ^{14}C-sulfamethoxazole residues was found in pig manure. During the 177-day incubation period in 2005, the extractable fraction never fell below 20% of the initially applied radioactivity. Simultaneously, non-extractable residues increased until 72 days.

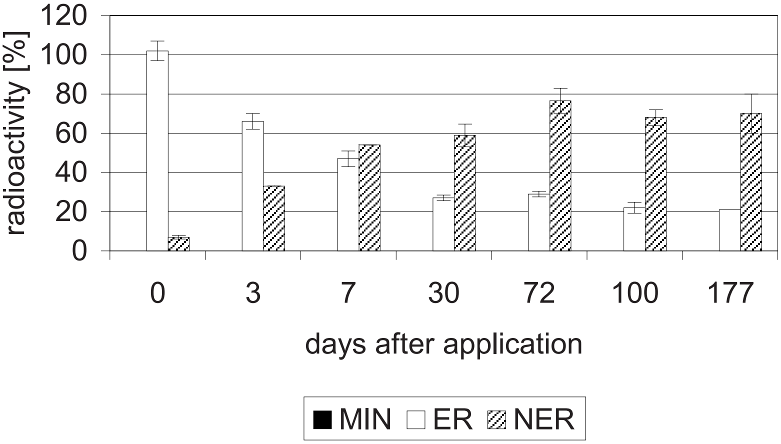

Fig. 3.4.1. Degradation of ^{14}C-sulfamethoxazole in pig manure (balances: 97 ± 9%). MIN: mineralization, ER: extractable residues, NER: non-extractable residues.

The RTLC metabolite screening performed for the extracts of the degradation test at 1250 μg sulfamethoxazole kg^{-1} pig manure revealed a rapid disappearance of the parent compound. In the 0-day sample, 71% of the radioactivity initially applied were identified as the unchanged test substance. Within 7 days, this amount dropped to 18%. In the extracts of the 30-day samples, only unidentified metabolites were detected.

Due to those differences of the metabolic dynamics of sulfamethoxazole, observed also for other test substances, the metabolic dynamics of one VMP found in bovine manure cannot be transferred to pig manure and vice versa. Therefore, degradation tests in both manure matrices are required, if a VMP is applicable to cattle and to pigs.

4. Preparation of test manures

In order to simulate the manure application already under laboratory conditions, test manures with short-term aged VMP residues were prepared. For this purpose, reference-manure samples were fortified with the respective ^{14}C-labeled test substance and incubated under anaerobic conditions in the dark at 20 ± 1°C for 7 days. Those test manures were then used to fortify soil samples in order to study degradation under aerobic conditions typical for terrestrial topsoils and sorption in manured soils [16–19]. Further experimental details are described by Kreuzig et al. [13].

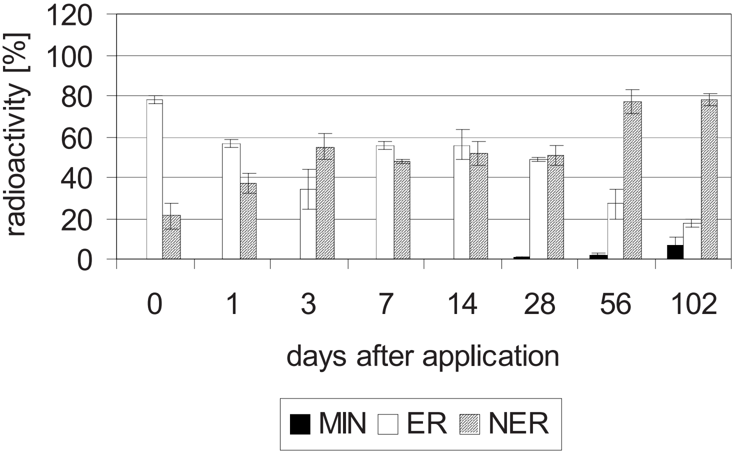

Fig. 4.1. Degradation of ^{14}C-erythomycin in silty-clay soil after standard application (balances: 101 ± 6%). MIN: mineralization, ER: extractable residues, NER: non-extractable residues.

5. Degradation tests in manured soils

Fate monitoring studies on selected VMP clearly showed that degradation as well as sorption might be affected by manure-matrix effects. In comparison to the standard application, the formation of non-extractable residues of the sulfonamides sulfadiazine and sulfamethoxazole was accelerated revealing a high affinity to the matrix of manured soil [9, 10]. Similar tendencies were found for ^{14}C-erythromycin. After standard application, the extractable residues decreased successively from 78% to 18% of the initially applied radioactivity within the 102-day incubation period (Fig. 4.1). Along with this decrease, a release of ^{14}C-carbon dioxide by mineralization was found after 14 days. Starting at 0.2%, finally 7% was reached. Simultaneously, the non-extractable residues increased up to 78% after 102 days.

These processes were accelerated by the test-manure application (Fig. 5.1). Within the 56-day incubation period, the metabolic dynamics was determined by an immediate formation of non-extractable residues already exceeding 80% of the initially applied radioactivity in the 0-day samples. This fraction remained nearly constant until 56 days of incubation. In this period, the extractable fraction amounted to 10% and mineralization increased from 0.1% after 7 days up to 8%. Thereafter, mineralization escalated up to 40% accompanied by the decrease of non-extractable residues up to 58%. This process indicated that ^{14}C-carbon dioxide was released out of the non-extractable fraction [20]. The extractable fraction simultaneously underwent only a less considerable decrease to 5% containing 2% of the unchanged parent compound. From that, however, the enhanced mineralization rates could not be derived.

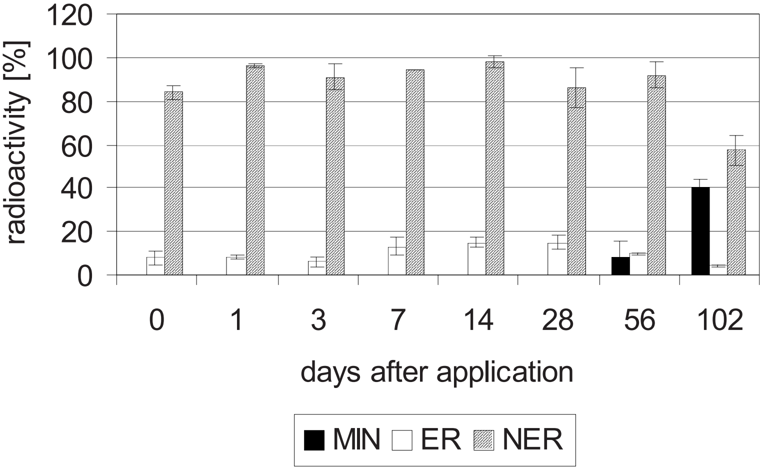

Fig. 5.1. Degradation of ^{14}C-erythomycin in silty-clay soil after test-manure application (pig manure) (balances: 103 ± 7%). MIN: mineralization, ER: extractable residues, NER: non-extractable residues.

6. Sorption tests in manured soils

The sorption behavior of VMP may be also affected by the test-manure application. After standard application, the sulfonamides sulfadiazine and sulfamethoxazole were revealed as potential leachers because soil/water distribution coefficients (K_d values) were below 5 L kg^{-1} [21]. After test-manure application, however, the K_d values increased. For ^{14}C-sulfadiazine, K_d values were 14 L kg^{-1} in a silty-clay soil and 84 L kg^{-1} in a silty-sand soil. This strong sorption to manured soils was also found in laboratory-lysimeter and test-plot studies [9]. There, sulfadiazine was retained in the superficial soil layer mainly as non-extractable residue.

Complementary effects were found for ^{14}C-erythromycin. After standard application, K_d values were 24 L kg^{-1} for the clay soil and 14 L kg^{-1} for the sand soil, resulting in a slight mobility. After test-manure application, however, K_d values dropped to 3 and 1 L kg^{-1}, respectively. Thus, the leaching potential of erythromycin would be underestimated by the conventional K_d value determination.

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LICHENS (*Punctilia rudecta*) AS BIOINDICATORS FOR AIR POLLUTION IN OHIO, USA

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Abstract. Lichens were used as bioindicators for the assessment of atmospheric pollution with trace metals in Ohio, USA. The concentration of Iron, Copper, Cadmium, Manganese, Nickel, Lead, Zinc, and Cobalt were determined in lichen samples collected from the vicinity of Shelby town, Ohio. The hierarchical cluster analysis showed that the investigated sites are classified into three main groups. The first group included eight sites that might be affected by similar anthropogenic activities due to similar heavy metals distribution profiles, while the other groups that consisted of only two sites are separated from the first group. That means that other types of anthropogenic activities might have affected them. These findings were confirmed using two-principle components analysis.

Keywords: lichens, heavy metals, atmospheric pollution, cluster analysis, Ohio.

1. Introduction

Lichens are considered the results of a symbiotic association of fungus and algae. Lichens do not have roots or well developed cuticle, therefore, they depend strongly on the mineral nutrients on wet and dry deposition making them a good bioindicators for monitoring purposes [4, 12].

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Many investigations were done worldwide using lichens as environmental bioindicators [2, 7]. Lichens are effective biomonitors of metal deposition, as they possess many similar characteristics as air particulates. The metal concentrations in lichen (*Rhizocarpon geographicum* (L.) DC) have been shown to correlate with atmospheric dry deposition in Amman city, Jordan [11].

Lichens were first used as bioaccumulative indicators in relation to point emission sources, where decreasing metal concentrations in species correlated with the increasing distance from the source [4]. Various physical-chemical processes can take place either in the atmosphere or/and in the plant that can lead to metals accumulation in the lichens: trapping insoluble particles, extra cellular, ion exchange processes, adsorption and active uptake [1, 8]. Additionally, lichens have proved to be good accumulators of many elements, particularly heavy metals and radionuclides [10]. Some heavy metals such as Pb, Zn, and Cu can be considered toxic for many other living organisms, that may be accumulated simultaneously in one lichen specimen, and appear to be unharmed [9]. Sampling period plays an important role in the levels of Cu, Zn, and Pb in lichens as higher levels are found usually in summer than in winter [3]. Since anthropogenic emission of trace metals such as Cd, Cu, Zn, and Pb to the atmosphere may give an environmental impact to flora and fauna, their survey is of key importance for the entire living environment. The main objective of this study is to use Lichens as bioindicators for the assessment of atmospheric pollution with trace metals in Ohio, USA. The data were used to classify the investigated area into different clusters or zones, based on distribution of heavy metals and dominating anthropogenic activities.

2. Materials and methods

2.1. Study area

Shelby is a small city in Ohio/USA with a population of around 10,000 people. The investigated site is located in a humid region as it gets around 970 mm of rain per year falling over 137 days. The temperature ranges from 29°C during July to –8°C during January. Geologically, the main outcrops of the area are limestone and shale exposed at 330–405 m ASL altitudes with no hills or deep valleys.

Lichens sampling was performed during summer 2008 from different parts of Shelby city, Ohio/USA. The sampling sites were chosen randomly from different parts of the city as the main source of pollution is mainly originated from traffic activity and a small coal burning power plant, as there is no major industry in the city (Fig. 2.1.1).

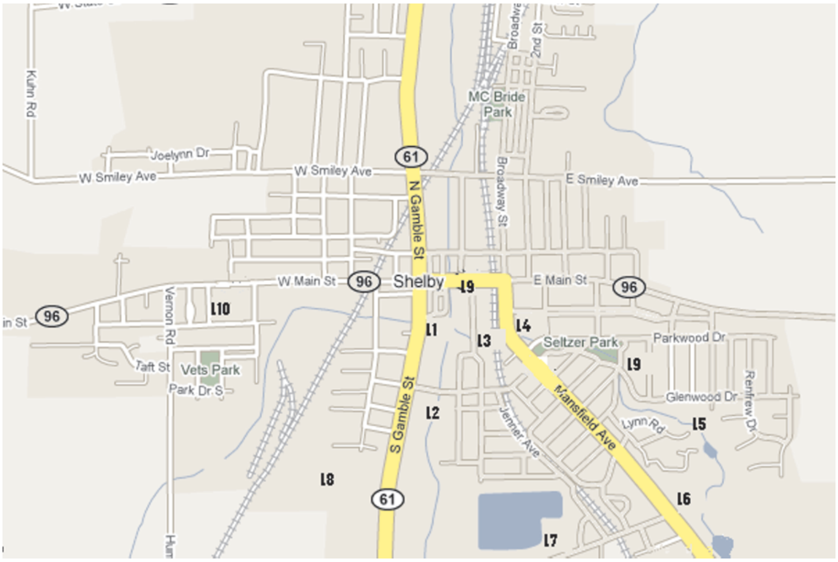

Fig. 2.1.1. Location map of investigated sites L1–L10.

2.2. Sample collection

Healthy lichens from rock surfaces were collected from 10 locations in Shelby town, Ohio, USA during summer 2008, representing different sites within the town (Fig. 2.1.1). Three replicates were collected from each site to get a representative sample and accurate results. The heavy metals are selected in the investigation area based on their toxicity and possible sources of metal pollution. The following elements were investigated: Cd, Cu, Pb, Zn, and Co in the lichen thallus species *Punctilia rudecta* from a well-defined family of lichens that usually grows on rocks in Ohio [5].

Demonstrated that the younger, more external part of the thallus (corresponding to biomass produced the previous year) contained lower concentrations than the older, more internal part. In a study all part of lichens were used to eliminate lichens age on the results.

2.3. Sample analysis

Directly after collecting hydrated lichens from previous rain, the samples were transferred to the laboratory and washed with distilled water for about 25 s to remove any collected dust on the lichens surface that might interfere with the analysis; elemental composition of unwashed samples is affected by soil dust contamination, thereby leading to incorrect interpretations of baseline concentrations and relationships between elements [7]. Washing the samples should not have any effect on the trace metal content as the metals are more tightly bound or sequestered within lichens and, therefore, more slowly released [6, 9]. Washed samples were dried at room temperature and then oven-dried to a constant weight at 80°C. The dried lichens samples were then prepared for metal analysis after being ground, using an agate mortar to avoid metal contamination. A 0.5 g amount of dried lichens samples was digested in a mixture of concentrated HNO_3 and $HClO_4$ (2:1) at 80°C using heating blocks overnight. The samples were filtered through Whatman filter paper no. 42 and diluted to 25 ml with deionized water (18.3 mOhm cm^{-1}). The total concentrations of Cd, Cu, Pb, Zn, and Co in the samples were determined using Shimadzu atomic absorption spectrophotometer (Japan). The concentrations of trace metals were measured using external calibration of a multi-element standard solution ($r^2 > 0.9995$). The analyses were carried out in triplicate, and the average values were reported. Instrument precisions were determined by introducing the same quantity of one sample 20 times, and then the relative standard deviation was calculated (RSD < 5%).

3. Results and discussion

The concentrations of heavy metals in the samples taken from different parts of Shelby city Ohio are summarized in Table 3.1. Heavy metal ranges were measured on dry weight basis as follows: Cu 13.9–63.3 $\mu g \cdot g^{-1}$; Fe 1644.2–9823.6 $\mu g \cdot g^{-1}$; Ni: 4.2–60.2 $\mu g \cdot g^{-1}$; Pb: 9.6–538.6 $\mu g \cdot g^{-1}$; Cd: ND-3.5 $\mu g \cdot g^{-1}$; Zn: 52.0–669.0 $\mu g \cdot g^{-1}$; Co: 1.8–7.4 $\mu g \cdot g^{-1}$; Mn: 150–458.4 $\mu g \cdot g^{-1}$, Table 3.1.

Table 3.1. Concentrations of trace metals (mg/kg) in Lichens.

Site nos.	Location	Cu	Fe	Cd	Mn	Ni	Pb	Zn	Co
L1	State Route 61	28.0	7785	0.0	416	6.0	82.4	83.3	2.8
L2	Tucker Avenue	45.6	6485	0.0	238	5.0	99.8	59.8	2.1
L3	Railroad	63.3	8685	0.0	183	4.4	34.7	86.6	1.9
L4	Light Plant Stack	51.7	1644	0.0	150	60.2	21.3	110.2	4.0
L5	Glenwood Curvert	15.7	6606	0.0	458	4.5	9.6	52.0	2.8
L6	Kehoe CTR	32.5	7915	0.0	250	4.2	20.1	156	1.8
L7	Mikckey Road	21.1	4509	1.4	255	4.4	217	154	1.9
L8	Cemetery	13.9	5336	0.0	241	4.3	110	669	2.3
L9	Main Street (Demers Office)	58.5	9823	0.0	406	4.9	200	247	3.1
L10	Rogers House-State Route 9b	38.4	7485	3.5	275	5.7	538	131	7.4

The maximum concentrations were found at the sampling sites surrounding the city center. High values of Cu, Fe, Cd, Mn, Ni, Pb, Zn and Co were measured in different parts of Shelby city, however, city center showed higher concentration levels. The main source of pollution was mainly from traffic and not from coal burned power station which was negligible as the results did not show any trend indicating that there is no point source pollution in the investigated area although a small coal burning plant exists in the area. Thus, Pb levels were found to be relatively high in *Punctilia rudecta*. The highest concentrations among analyzed metals were found for Mn, which ranged from 150 to 458 mg kg^{-1} with an average value of 290 mg kg^{-1}. These high concentrations are due to the use of unleaded fuel, which is known to contain high levels of Mn. The distribution of analyzed trace metals are shown in Fig. 3.1.

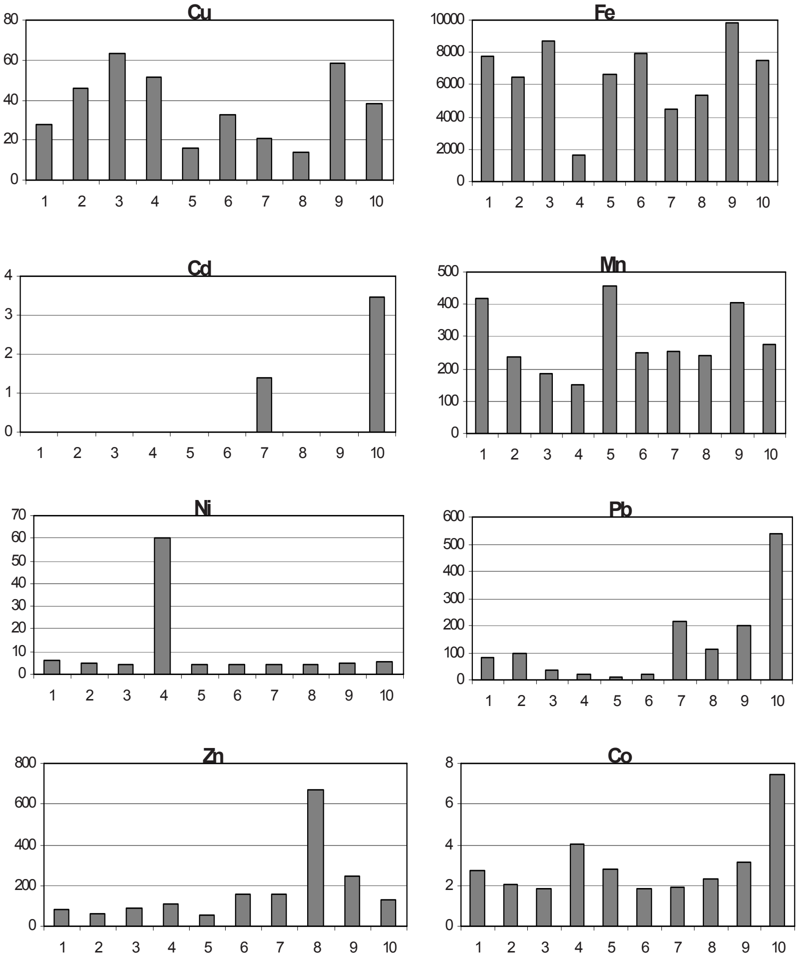

Fig. 3.1. Concentrations (mg/kg) of trace metals at investigated sites (L1–L10).

The correlation coefficients (r) between common metals in lichens were calculated in order to evaluate the possibility of a potential common source. Significant correlation coefficients ($r < 0.05$) of 0.93, 0.80, and 0.79 for Pb-Cd, Co-Cd and Pb-Co, respectively, indicating that the vehicular emission is the main source of heavy metals in lichens[2].

Hierarchical cluster and principle component statistical analyses were done, using NTSYSY-pc software version 4.0, for more data manipulation and interpretation. The hierarchical cluster analysis was carried out in order to classify the sampling locations into different groups. Therefore, Euclidean distance coefficient was calculated for all investigated locations (L1–L10) based on heavy metals concentration. The result is presented by hierarchical analysis (dendrogram), Fig. 3.2.

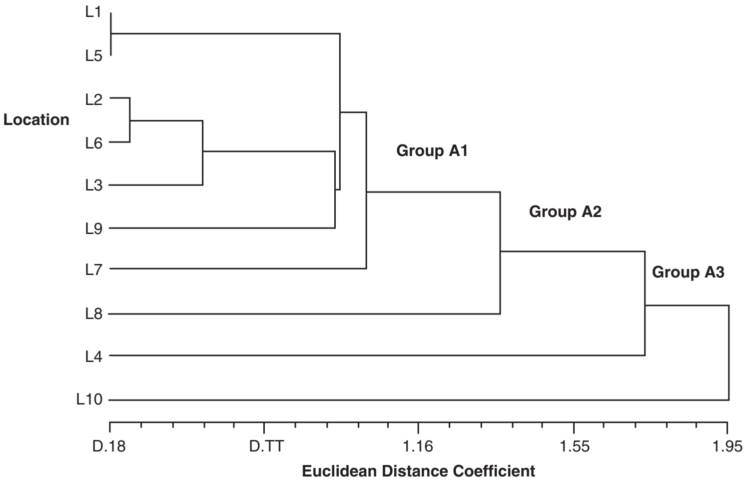

Fig. 3.2. Dendrogram representing the hierarchical analysis of sample locations (L1–L10) according to analyzed metal concentrations.

The results allowed to classify the investigated sites into three main groups: A1, A2, and A3. The first group included those sites (L1, L2, L3, L5, L6, L7, L8 and L9) that might be affected by similar anthropogenic activities. While the dendrogram showed that groups A2 and A3 are separated from group A1, that means that the locations (L4 and L10) might be affected by other anthropogenic activities which leads to the occurrence of different heavy metal levels. Furthermore, group A1 can be divided into two subgroups, A1-a includes locations (L2, L3 and L6) and A1-b (L1, L5, L8 and L9), sharing similar heavy metal concentration trends.

Moreover, two principle components analysis used in Fig. 3.3 accounted for the ten sample locations and were based on analyzed metal concentrations. The principle component 1 (PC1) and principle components 2 (PC2) separated clearly three groups (A1, A2 and A3). These results confirm the findings of the hierarchical cluster analysis. Group A1 is consisting of sampling locations (L1, L2, L3, L5, L6, L7, L8, and L9) that are characterized by similar heavy metal concentration profiles. Whereas, location L4 within group A2 was characterized by low concentrations of Cu, Cd, Zn, Pb, Fe, and Mn, and high concentrations of Ni and Co. (Fig. 3.2). Location (L10) was classified as a separate group A3 because it is characterized by high concentrations of Fe, Cd, Mn, Pb, and Co, and low concentrations of Cu, Ni, and Zn.

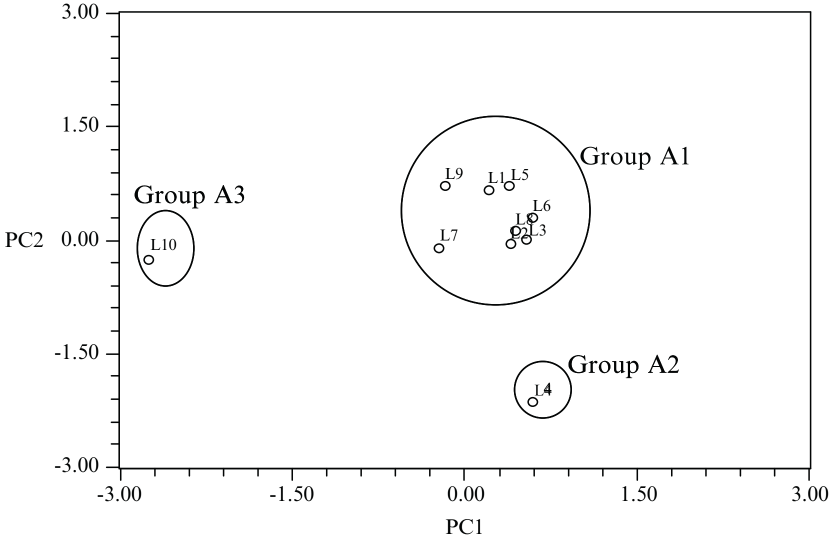

Fig. 3.3. Principle components analysis of sample locations (L1–L10) based on analyzed metal concentrations.

4. Conclusion

The amounts of heavy metals accumulated by lichens in Ohio metropolitan is mostly dependent on traffic density. Eight sampling locations showed similar accumulation trends, while two locations were found far away regarding the heavy metal concentration levels. This trend is pinpointing of traffic source. Coal burning power plant in the area did not have any influence on the heavy metals distribution.

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FARMING PRACTICES IN MOLDOVA FOR PREVENTING POLLUTION AND DEGRADATION OF THE ENVIRONMENT

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Abstract. Agriculture of Moldova is at a crossroad. The technological approach to farm intensification based on increased inputs of nonrenewable sources of energy (mineral fertilizers, especially nitrogen, and pesticides) accompanied by reduced biodiversity in agroecosystems has led to many negative consequences in agriculture. Agriculture needs systemic changes at the level of the landscape and individual farms. Evidence is presented from long-term experiments carried out in Moldova since the 1960s at the Research Institute of Field Crops. “Selecţia” These results show the energy intensive nature of our agroecosystems and their long-term impacts in depleting soil organic matter. The use of fertilizers has covered up negative effects associated with intensive rotations on the productivity of crops. Gains due to breeding intensive varieties winter wheat have been less than expected. The use of crop rotations that include perennial forages, organic + mineral fertilizers can reduce the need for intensive agrochemical inputs. Only such changes can help to prevent, but not to control pollution and degradation of the environment. The key for a new approach to an intensive agriculture on a sustainable basis is the recognition of the soil as being a living organism and the crucial role of enhanced rotations and soil organic matter management.

Keywords: farming intensification, mineral fertilizers, soil management, crop rotation.

1. Introduction

The industrial approach to farm intensification taken since the 1960’s in Moldova was based on increased inputs of nonrenewable sources of energy and their derivates (mineral fertilizers and pesticides). This development was supported by low prices for natural resources coupled with the lack of an economic mechanism for the evaluation of the negative consequences of human activity on the environment. Such consequences have aggravated the economic, ecological and social problems of our society. It neither possible to fully control such consequences without

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eradicating the causes of pollution and degradation of the environment, nor for the existing farming systems of Moldova to achieve sustainability without systemic changes. In order to make such changes in our agroecosystems we can choose to learn from natural ecosystems or, in other words, to use nature as a model. This means respecting a set of agricultural and ecological laws that have hitherto been largely ignored. A key issue for modern farming systems is to recognize soil as being a living organism and the significance of soil organic matter management and crop rotations. Soil revitalization programs would allow farmers to move toward more sustainable farming systems [1–5]. Experimental data obtained in the long term field experiments of the Research Institute of Field Crops "Selectia" (Balti, Republic of Moldova) has revealed some of the underlying principles of sustainability and the critical changes that are needed to transform our modern unsustainable farming systems.

2. Materials and methods

Research has been conducted in long-term field experiments with different crop rotations and permanent crops, with different systems of fertilization in crop rotation etc. on chernozem soils in the steppe region of Balti, located in the northern part of Moldova. These experiments have been conducted since 1962. They include eight, 10-field crop rotations which were unfolded in space and time. These crop rotations have a different level of saturation with row crops (from 40% up to 70%) including saturation by such crops as sugar beets (from 10% up to 30%), corn (from 20% up to 40%), and sunflowers (from 10% up to 20%). The size for each experimental plot in crop rotation is 283 sq. m. The plots under permanent crops are without replications. They have been conducted since 1965. The size of the experimental plots under permanent crops is 450 sq. m. The systems of fertilization and soil tillage are different for different crop rotation, because they take into consideration the structure of each crop rotation.

An additional set of long-term experiments has been conducted since 1966. Different systems of fertilization in a six field crop rotation are studied. These are: no fertilization, three systems of mineral fertilization using increased rates of mineral fertilizers, six systems of organic + mineral fertilization using 10 and 15 tons of manure per hectare combined with similar increased rates of mineral fertilizers; and only manure fertilization and the residual action of manure in crop rotation. More details regarding the design of the experiments and conditions of conducting researches in these experiments can be found in our previous publications [6, 7].

3. Results and discussion

Compared with natural systems the agroecosystems have a deficit in their balance of energy. The annual deficit of energy even for crop rotation with perennial leguminous crop is 39.2%, compared with permanent black fallow on unfertilized plots (Table 3.1).

Permanent crops reduce the deficit of energy relative to black fallow, fertilized and unfertilized plots, up to 64.6–64.8%, but, the deficit still remains substantial. The input of energy includes the content of energy in crop residues and farmyard manure. The output of energy includes the content of energy in the yield of crops removed from the fields and the content of energy in uncompensated mineralizational losses of soil organic matter.

Table 3.1. The annual balance of energy in long-term field experiment with crop rotation and permanent crops, Beltsy, Moldova, average for 30 years, thousands mdj/ha.

Variants		Output	Input	Balance	
				+/–, mdj/ha	The annual deficit (%)
Crop rotation with perennial leguminous crop		109.7	66.7	–43.0	39.2
Permanent crop fertilized	Winter wheat	95.5	33.8	–61.7	64.6
	Corn for grain	157.8	55.5	–102.3	64.8
Permanent black fallow	Fertilized	26.9	4.4	–22.5	83.6
	unfertilized	32.7	–	–32.7	100

As a result, the annual uncompensated mineralization losses of soil organic matter remain also very high (Table 3.2).

Table 3.2. Annual losses of soil organic matter in the long-term field experiment of the Research Institute of Field Crops "Selectia", average for 30 years, 0–20 cm layer of soil, t/ha.

Variants		Annual losses of soil organic matter, t/ha
Crop rotation with 30% of perennial leguminous crops, fertilized plots		0.45
Permanent crops, fertilized plots	Winter wheat	0.66
	Corn for grain	0.73
Permanent black fallow	Fertilized	1.17
	Unfertilized	1.42

The highest uncompensated mineralization losses of soil organic matter are typical for permanent black fallow on unfertilized and fertilized plots – 1.42 and 1.17 t/ha, respectively. In black fallow mineralization losses predominate especially on unfertilized plots, because the input of fresh organic matter is very limited in the absence of crops, and soil is tilled by mold board plow and regularly by cultivation which stimulates the mineralization of soil organic matter. The lowest losses of soil organic matter are in a crop rotation with perennial leguminous crops (0.45 t/ha). On this plot the input of fresh crop residues was the highest, and the intensity of soil tillage was low. But even in crop rotation with 30% of perennial leguminous crop the losses of soil organic matter exceed the gains.

Monocultures have had an intermediate losses of 0.66 and 0.73 t/ha, respectively for winter wheat and corn for grain. It is important to mention that from the total annual mineralization losses of soil organic matter the share of fresh crop residues and animal manure consists in crop rotation with perennial leguminous crops – 89%, but in permanent black fallow on fertilized plots only 55%.

The quality of soil (agrophysical, agrochemical and biological properties of soil) is determined in great extent by the amount of fresh organic matter added to the soil.

Enriching soils regularly with fresh organic matter helps both to cover the deficit of soil organic matter, to improve the quality of soils and to increase the level of yields for majority of crops in our long-term field experiment. At one point we interrupted all the experiments and planted a crop of winter rye to examine residual effects of different rotations. We found a direct correlation between the content of labile fraction of soil organic matter and the level of yields for winter rye harvested for green mass for unfertilized plots [6, 7].

The longer is the crop rotation the higher the yields. The 10 field crop rotations yielded more than the seven field crop rotation and, especially more than the monocultures. In other words, the higher the diversity of crops in the crop rotation the higher the productivity of individual crops (Table 3.3).

The crops that are most receptive to increased diversity in rotations are winter wheat and sugar beets both on fertilized and unfertilized plots. Crops of corn for grain, winter barley and sunflower are less influenced by decreasing the diversity of crops in rotation both on unfertilized and, especially, on fertilized plots.

We determined “the rotation effect” (the difference in yields for crops in crop rotation and in permanent cropping) by using data from Table 3.3 (Table 3.4).

The highest rotational effect, both on fertilized and unfertilized plots, was noticed for winter wheat and sugar beets. The rotation effect is less on fertilized plots, but still significant for most crops.

By utilizing crop rotations it is possible to reduce or even avoid use of mineral fertilizers and pesticides, which will prevent soil and water pollution.

Table 3.3. The yield of crops (t/ha) under the influence of their diversity in crop rotation in the long-term field experiments of the Research Institute of Field Crops "Selectia", 1994–2006, Balti, Republic of Moldova.

Diversity of crops in crop rotations	Crops				
	Winter wheat	Sugar beets	Corn for grain	Winter barley	Sunflower
			Fertilized		
10 field crop rotation	5.3	44.6	5.8	4.1	2.1
7 field crop rotation	4.5	41.0	5.9	3.6	1.8
Permanent cropping	3.1	20.6	5.6	3.8	1.5
			Unfertilized		
10 field crop rotation	4.9	36.2	5.4	3.3	2.0
7 field crop rotation	4.0	26.9	5.3	2.5	1.5
Permanent cropping	2.2	10.2	3.9	2.0	1.5

Table 3.4. The "rotation effect" for different crops in the long-term field experiment of the Research Institute of Field Crops "Selectia", average for 1994–2006, t/ha and %.

Crops	Without fertilizers		With fertilizers	
	t/ha	%	t/ha	%
Winter wheat	2.7	122.7	2.2	71.0
Sugar beets	26.0	254.9	24.0	116.5
Corn for grain	1.5	38.5	0.2	3.6
Winter barley	1.3	65.0	0.3	7.9
Sunflower	0.5	33.3	0.6	40.0

By increasing the diversity of crops in crop rotation and, especially, by using perennial crops with higher ability to restore soil fertility, it becomes possible simultaneously to prevent soil degradation under the influence of water and wind erosion. Keeping soil under permanent cover of living or dead mulch, as well as maintaining a good structure of the soil by less disturbance through soil tillage, are also crucial for sustainable land management.

We have expected a higher level of yields in the era of "green revolution" by increasing the production of new, more productive varieties and hybrids. Figure 3.1 shows the yields of one of the oldest varieties of winter wheat Odessa 51 and new, more productive varieties of winter wheat grown in different periods of time since 1962. The winter wheat varieties were grown side-by-side in a crop rotation after an early harvested predecessor (alfalfa on the third year, after first cutting). Each year one half of the field was sown with the variety Odessa 51 and the other half of the field was sown with new varieties registered in the Republic of Moldova. The difference in yield is very small. The fluctuations of yields under the influence of weather conditions are considerable higher for both types of varieties than the difference in yields between varieties.

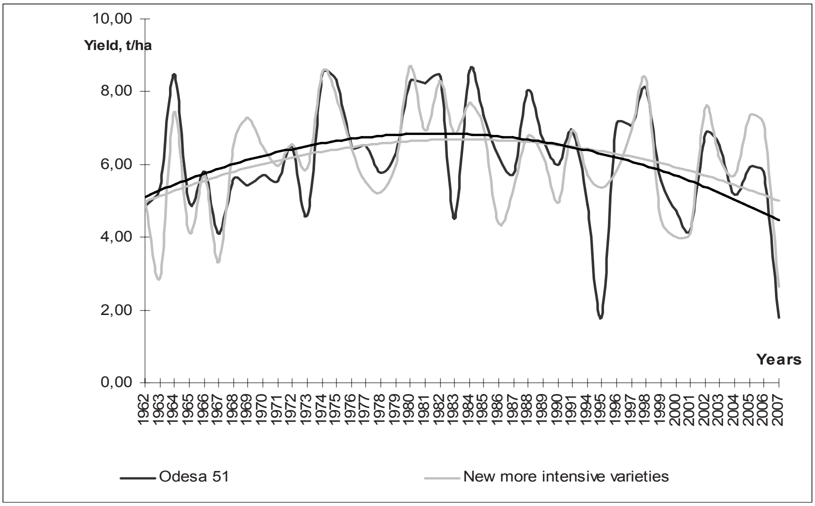

Fig. 3.1. The dynamics of yield for winter wheat (variety Odesa 51 and new more intensive varieties) in the long-term field experiment on crop rotations, 1962–2007, Research Institute of Field Crops "Selectia" Balti, Republic of Moldova (crop rotation N 5).

In another long-term field experiment with different systems of fertilization and crop rotations it was established that combined organic + mineral fertilization systems increased the yield of winter wheat by 1.5 t/ha, or 25–27% more yield than the control (Fig. 3.2). This means that 73–75% of the yield for winter wheat on the best fertilized plots was supported by basic soil fertility, mainly by mineralization of soil organic matter. On unfertilized plots 100% of the yield is derived from soil fertility. The fluctuations of yields under the influence of climatic conditions are significantly higher than the influence of fertilization.

These results show the importance of crop rotations and soil fertility for modern farming systems. Wise utilization of rotations and fertility would allow farmers not only to maintain and increase productivity of crops but also to cut the production expenditures, to prevent soil degradation and pollution of the environment.

Proper soil organic matter management can prevent also drought, which recently become a recurrent problem in the Republic of Moldova. Accomplishing this kind of change probably entails a change in mindset with a greater focus on sustaining a healthy, living soil through organic matter management and crop diversity.

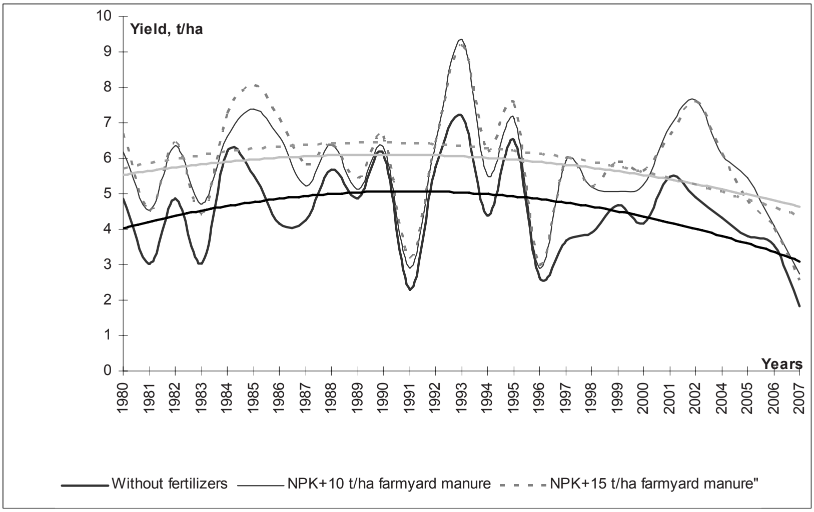

Fig. 3.2. The dynamics of yield for winter wheat (t/ha) in the long-term field experiment with different systems of fertilization, Research Institute of Field Crops "Selectia", 1980–2007.

4. Conclusions

The deficits of energy and soil organic matter associated with agroecosystems that include annual field crops and even perennial leguminous crop are very high. This makes these systems dependent on external inputs and vulnerable to unfavorable weather conditions.

The uncompensated annual losses of soil organic matter even in crop rotation with 30% of alfalfa consists in 0.5 t/ha. The higher the diversity of crops in crop rotation the higher the yields for the majority of crops.

"The rotation effect" is higher on unfertilized than on fertilized plots. Fertilization reduces the rotational effect, but it remain still high, especially for such crops as winter wheat, sugar beets and sunflower.

The share of basic soil fertility in yield formation on plots with optimal rates of organic + mineral fertilization on chernozem soils, is 73–75%.

The fluctuation of yields for winter wheat under the influence of climatic conditions are significantly higher than the influence of organic + mineral fertilization in crop rotation and especially more than the influence of new, more productive varieties of winter wheat.

Sustainable development of agriculture is possible only by restoring soil fertility and, in particular, soil organic matter as the integral index of soil fertility.

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THE ROLE OF SOIL ORGANIC MATTER IN LIMITING ORGANIC POLLUTION IN SOILS WITH FOCUS ON ENDOCRINE DISRUPTOR COMPOUNDS

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Abstract. The purpose of this presentation is to provide a general survey on the various phenomena that anthropogenic organic pollutants (EDCs) of various nature and origin are subjected in soils and on the specific role exerted by the most chemical-active fraction of soil organic matter, i.e., the humic substances, on these processes. The presentation will then focus on some representative examples of adsorption/desorption studies of an important class of organic pollutants, the endocrine disrupting compounds, onto soil humic acids. These compounds are hormone-like substances that are able to alter, i.e., disrupt, the normal endocrine functions in animals and humans, and may enter the soil mainly through disposal of urban and industrial effluents, sludges, and wastes. Adsorption/desorption processes play a very important role in the estrogenic risk of EDCs, which is generally related to their distribution and speciation in the various soil phases.

Keywords: soil humic substances, anthropogenic organic pollutants, interaction processes, endocrine disruptor compounds, adsorption, desorption.

1. Introduction

The purpose of this paper is to provide an introductory overview of the various phenomena that anthropogenic organic pollutants (AOPs) of various nature and origin are subjected in soils and on the specific role exerted by soil humic substances (HS) on these processes. Due to the limited space available, detailed references are not included but only some fundamental and comprehensive reviews and books are cited to which the interested reader may refer to for further details.

The paper will focus on adsorption/desorption of an important class of organic pollutants, i.e., endocrine disrupting compounds (EDCs), onto soil humic acids (HAs) that are the most abundant and chemical and biochemical active fractions of

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HS and soil organic matter. Adsorption/desorption of EDCs onto soil HAs is generally considered being one of the most important processes that controls EDC behavior, performances, and fate in soil, and the assessment of their potential environmental hazard.

2. Anthropogenic organic pollutants and their fate in soil

An "anthropogenic organic pollutant" may be defined as "any organic chemical that is foreign to the natural ecosystem and may adversely affect, either directly or indirectly, the natural physical, chemical, and biological equilibria and processes in the global environment or a portion of it", e.g., the soil.

Substantial amounts of AOPs can reach the soil either (a) by purpose, e.g., various types of pesticides, including herbicides, fungicides, insecticides, and nematicides, currently used in large amounts in common agricultural practices, and belonging to various classes of organic compounds of extremely variable physical and chemical properties; or (b) incidentally, e.g., by wet and dry atmospheric deposition and by application of municipal and industrial wastes, refuses, sludges, and effluents, which include chemicals of widely differing classes and properties such as polynuclear aromatic hydrocarbons, phthalic acid diesters and several organic solvents, detergents, and surfactants [2].

Once on soil surface, the parent AOPs and their degradation products may be subjected to various fates. They can be transported by soil runoff and/or erosion to surface waters, or undergo volatilization and/or photodecomposition, can enter the soil and be leached, eventually reaching the groundwater table, or be subjected to various phenomena including partial or total chemical decomposition and/or biological degradation, uptake by plant roots, and various physical and chemical interactions with soil inorganic and organic solids and colloidal components [2].

The behaviour and performance of AOPs on and in soil are controlled by several factors including the physical and chemical properties of the AOPs, the thickness, the hydrological status, the chemical and biological properties of soil, and the type and extent of interactions of the AOPs with the various mineral, organic and biological soil components. Most studies have suggested that AOPs show affinity for soil organic colloids greater than that for mineral colloids. Thus, the content and nature of soil organic matter, and especially its HS fractions, play a major role in determining the fate of AOPs in soil [2].

The risk assessment of AOPs in soil and the possible remediation measures to be undertaken require an extended and accurate evaluation and quantification of the soil response to AOPs. In particular, a key factor in AOPs fate in soil is considered to be the adsorption/desorption processes of AOPs onto soil organic and mineral components.

3. Soil humic substances

Approximately 60–70% of the total soil organic carbon occurs in HS, which are the most ubiquitous and widespread natural non-living organic materials in soils, as well as in all terrestrial and aquatic environments. Soil HS consist of a physical and chemical heterogeneous mixture of relatively high-molecular-mass, yellow-to-black colored organic compounds of mixed aliphatic and aromatic nature, formed by secondary synthesis reactions, i.e., humification of products of microbial and chemical decay and transformation and recalcitrant residues of biomolecules originated from organisms during life and after death [3].

In particular, HAs are defined as the HS fraction that is soluble in dilute alkaline solution and is precipitated upon acidification to pH 2 [3];. A "typical" model macromolecule of soil HA basically consists of aromatic, phenolic, quinoid and heterocyclic "building blocks" that are randomly condensed or linked by aliphatic, oxygen, nitrogen, or sulphur bridges. The macromolecule bears aliphatic, glucidic, aminoacidic and lipidic surface chains as well as chemically reactive functional groups of various nature (mainly carboxylic and phenolic but also alcoholic hydroxyls, carbonyls, etc.) which render acidic the HA polymer. HAs are rich in hydrophilic and hydrophobic sites, exhibit a polydisperse and polyelectrolyte character, possess surface activity, and present a relatively open, flexible, sponge-like structure rich of holes [3]. An additional typical feature of HS is the presence in their structure of highly reactive organic free radical moieties of prevalent semiquinoid nature [3]. All the above described properties qualify HAs as privileged natural organic compounds in the interaction with AOPs.

4. Interactions between humic substances and organic pollutants

The behavior, performance and fate of AOPs in soil have been shown to be greatly affected by the presence of HAs, with important implications in their persistence, immobilization and accumulation, mobility and transport, bioavailability and ecotoxicity, degradability, volatilization and leaching. In particular, HAs may interact with AOPs in several ways [2], which are shortly summarized below.

The solubilisation of low water-soluble, non-ionic AOPs, e.g., PAHs, PAEs, PCBs, DDT, n-alkanes, is favoured in the presence of HS, likely by AOP partitioning into HS and/or adsorption onto HS, or due to an overall increase in solvency. For example, water solubility of DDT and PCBs is enhanced in the presence of HA in the medium as a function of HA concentration, pH and temperature. At low HA concentrations, water solubility of DDT and some PCBs increases by a decrease of temperature, but decreases by a raise in pH.

Abiotic hydrolysis of some pesticides was shown to be catalysed positively or negatively by HAs, especially in the dissolved phase. For example, HAs are able to enhance the acid hydrolysis rate of the chloro-s-triazines like simazine, atrazine and propazine, whereas the alkaline hydrolysis rate of n-alkyl esters of 2,4-D (2,4-DOE) is decreased.

By absorbing sunlight, HAs as photosensitizers are able to act as initiators of photoreactions of some AOPs such as atrazine in the top layer of soil by accelerating, increasing or even determining light-induced transformation of AOPs. HAs have been shown to act mainly as precursors for the production of highly reactive, short-lived photo-reactants such as the solvated electron, e^-_{aq}, singlet oxygen, $^1O_2$, superoxide anion, $O_2^{-\cdot}$, peroxy radicals, $RO_2^{\cdot}$, hydrogen peroxide, H_2O_2, and redox-active species including photo-excited parent HA molecules and HA organic radicals. However, HAs can also act as scavengers of other photo-transient species such as the hydroxyl radical, OH. The physical and chemical properties of AOPs may be modified by photo-degradation, which will, in turn, affect significantly their fate and migration into the bulk soil.

The most important processes of interaction of AOPs with soil components, especially with HAs, are considered to be adsorption/desorption. The amount and physical and chemical nature and properties of both AOP and HA will affect the mechanism and extent of adsorption/desorption processes. These include: the molecular structure, the number and type of functional groups, the size, shape and configuration, polarity, polarizability and charge distribution, and solubility of both HA and AOP, and the acidic or basic or neutral, ionic or non-ionic, polar or non-polar nature of AOP. Further, adsorption/desorption of AOPs onto soil HAs are also affected in different way by some relevant parameters of the medium, such as pH, ionic strength, redox potential, amount of water, etc.

HAs can adsorb AOPs to various extent by a number of physical and chemical binding mechanisms and forces of different strength. The formation of ionic bonds is generally achieved by proton transfer from acidic, carboxylic and phenolic OH groups (proton donors) of HAs and basic groups (proton acceptors) of AOPs such as the pesticides diquat, paraquat, chlordimeform, phosphon, phenacridane chloride, s-triazines and amitrole. Hydrogen bonds can be formed between various O-/OH- and N-/NH- groups/sites available on the HA macromolecule and several AOPs including acidic pesticides, such as chlorophenoxyalkanoic acids and esters, asulam and dicamba, and several non-ionic polar pesticides, such as substituted ureas, phenylcarbamates, alachlor, metolachlor, cycloate, malathion and glyphosate. Electron donor-acceptor, or charge-transfer bonds can occur between electron-deficient structural moieties, such as quinones, or electron-rich moieties, such as diphenols, present in HA macromolecules and the complementary feature present in some AOPs. These include electron donor groups of s-triazines, substituted ureas, amitrole, or electron acceptor groups of paraquat, diquat, chlorodimeform, chloranyl, DDT, PCBs, and dioxins. Stable covalent bonds can be formed, often mediated by chemical, photochemical and enzymatic catalysts, between suitable functional groups of HA and AOPs such as chlorophenoxyalkanoic acids and esters, and their degradation products such as anilines, catechols and phenols. Ligand exchange is another binding mechanism by which HA can adsorb some AOPs such as s-triazines and anionic pesticides, e.g., pichloram, through the displacement of hydration water or other weak ligands partially holding a polyvalent metal ion associated to HA by a suitable functional group ligand of the AOP molecule. Binding by dipole-dipole and van der Waals forces is also ascertained to occur in AOP adsorption onto HAs, either in addition to stronger binding forces or, more important, in the adsorption of non-ionic and non-polar AOPs. Finally, another important non-specific mechanism is hydrophobic adsorption, or partitioning, occurring between HA hydrophobic active sites, such as aliphatic side chains and lipidic and aromatic structural moieties, and nonionic, non-polar AOPs that interact weakly with water, such as organochlorine insecticides including DDT, PAEs, PAHs, PCBs, etc.

Several possible adsorption mechanisms of those illustrated above may operate simultaneously and/or in sequence for any given AOP. For example, the AOP molecule may be initially adsorbed by HA sites providing the strongest binding, followed by progressively weaker sites as the stronger sites become filled. Once adsorbed, the AOP may be subject to further reactions becoming either covalently and irreversibly bound or only physically trapped into the HA matrix. Adsorption processes may thus vary from complete reversibility to total irreversibility, i.e., the adsorbed AOP may be easily desorbed, desorbed with various degrees of difficulty, or not at all. Further, the effect of adsorption on AOP migration in soil depends on whether the adsorption occurs on solid, immobilized or suspended, mobile fractions of HAs. Thus, HAs can either "attenuate" or "facilitate" AOP movement and transport in soil.

A comprehensive study of adsorption/desorption processes of pesticides onto HAs should include the evaluation of both quantitative aspects, through the measurement of adsorption/desorption kinetics and isotherms, and qualitative and molecular aspects through the determination of adsorption/desorption mechanisms of binding. More detailed information and discussion on the above topics can be found in several recent reviews (e.g., [2]).

5. Endocrine disruptor compounds

EDCs are hormone-like organic compounds of natural and anthropogenic origin that are able to alter or disrupt the development and functioning of the endocrine system in animals and humans either directly, by blocking or imitating natural hormones, or indirectly, by interfering with the synthesis, storage, secretion, transport, catabolism and activity of various natural hormones [1]. Compounds proven or suspected to act as EDCs include natural estrogens of human origin, pharmaceutical products like estrogenic compounds, several pesticides including herbicides, fungicides, insecticides and nematicides, various industrial chemicals like PCBs, PAEs, dioxins, and several products and by-products of the paper, paint, and plastic industries [1].

These compounds may enter the soil through current agricultural practices and/or application, discharge or disposal of urban and industrial effluents, sludges, and wastes. Despite the high inputs and potential toxicity of EDCs, and the increasing social concern for a reliable risk assessment of the actual exposure of animals and humans to EDCs, relatively few data are available on the types and amounts of EDCs introduced into soil and aquatic systems. Until now, the attention on this issue has mainly focused on water contamination, and very few information is available on soil contamination by EDCs.

The risk assessment of potential environmental hazards associated with the presence of EDCs in soil, as well as the definition of possible remediation measures, require an accurate evaluation and quantification of the soil response to these compounds, which is generally related to their distribution and speciation in the various soil phases. Depending on the strength and extent of interactions of EDCs with soil phases, they can either accumulate in the top soil layer or be moved down to deeper soil horizons and groundwater. In particular, adsorption/desorption of EDCs onto soil HAs are generally considered one of the most important processes that controls EDCs behavior, performances, and fate in soil, including mobility, transport, accumulation, bioavailability and toxicity, and the assessment of the potential environmental hazard associated with them.

In the following section some examples taken from the current literature are provided on the adsorption kinetics and adsorption and desorption isotherms of some representative EDCs onto some soil HAs.

6. Examples of EDCs adsorption/desorption processes onto soil

6.1. Methodology

Adsorption kinetics and adsorption/desorption isotherms and coefficients of any EDC onto any HA are generally determined using the slurry-type, batch equilibrium method, as reported in the current literature, and then measuring the non-adsorbed/desorbed EDC by high performance liquid chromatography (HPLC) using appropriate detectors, or gas chromatography (GC). Experimental adsorption data are then tentatively fitted into the current adsorption equations, linear and non-linear Freundlich:

$$x/m = K\,C_e^{1/n} \tag{1}$$

and Langmuir:

$$x/m = (KbC_e)/(1 + KC_e) \tag{2}$$

where x/m is the amount of EDC adsorbed in μg g^{-1}, and C_e is the equilibrium concentration of EDC in solution in μg mL^{-1}. The best fitting based on the best correlation coefficient is finally considered for interpretations. Generally, in desorption studies, the Freundlich equation is used for fitting the data in any case.

The magnitude of adsorption, i.e., the adsorption capacity of the HA substrate, is estimated by the values of the Freundlich constant, K, and the distribution coefficient, K_d, which is calculated at each equilibrium concentration as the mean value of the ratios of adsorbed concentration to the solution-phase concentration at equilibrium.

6.2. Results and interpretations

In general, adsorption of EDCs onto HAs occurs in two phases, a rapid one in the first few hours of contact, which corresponds to more than 90% of total adsorption, and a slow one that needs generally less than 24 h to be completed. One example of kinetic curves generally obtained is presented in Fig. 6.2.1 for atrazine.

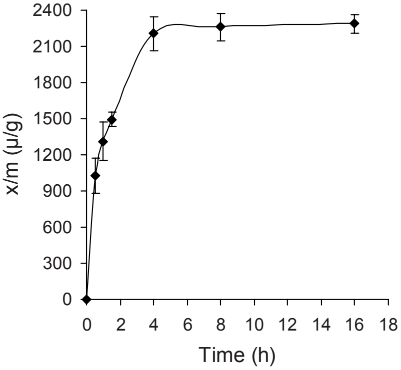

Fig. 6.2.1. Adsorption kinetics curve of atrazine at 10 mg L^{-1} onto AS-HA. The vertical line on each marker point indicates the standard error (n = 3).

Four examples taken from the literature for the four types of isotherms generally measured for EDCs adsorption onto HAs are provided in Fig. 6.2.2 (linear), Fig. 6.2.3 (Freundlich non-linear, L-shaped), Fig. 6.2.4 (Freundlich non-linear, S-shaped) and Fig. 6.2.5 (Langmuir), respectively, for octylphenol (OP), atrazine, *cis*- and *trans*-chlordane, and bisphenol A (BPA). As for OP, atrazine and *cis*- and *trans*-chlordane, no limiting adsorption is observed for several EDCs onto HAs over the concentration range tested, whereas a maximum adsorption, i.e., saturation, is reached by some EDCs like BPA.

As in the examples given in Table 6.2.1, in general, the adsorption capacity of HAs for the various EDCs varies in a large range of values as a function of the structural and chemical properties of both the EDC and the HA considered. Often the values of the Freundlich constant, K, and of the distribution coefficient, K_d, calculated from the experimental isotherms (Table 6.2.1) follow the same trend, but in some cases a different trend is obtained. This finding suggests that the use of K or K_d values, alone, as an index of adsorption capacity of EDC onto HA, may be misleading. Thus, in general it is advisable to use both parameters for a better evaluation of the adsorption capacity of EDCs onto HAs.

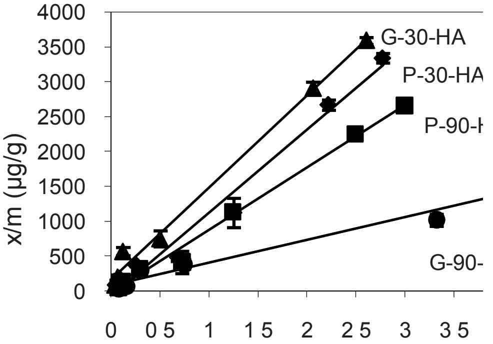

Fig. 6.2.2. Linear adsorption isotherms of OP onto four soil HAs. The vertical line on each marker point indicates the standard error (n = 3).

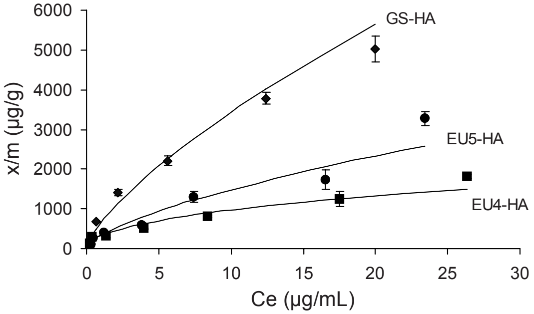

Fig. 6.2.3. Freundlich non-linear, L-shaped, adsorption isotherms of atrazine onto three soil HAs. The vertical line on each marker point indicates the standard error (n = 3).

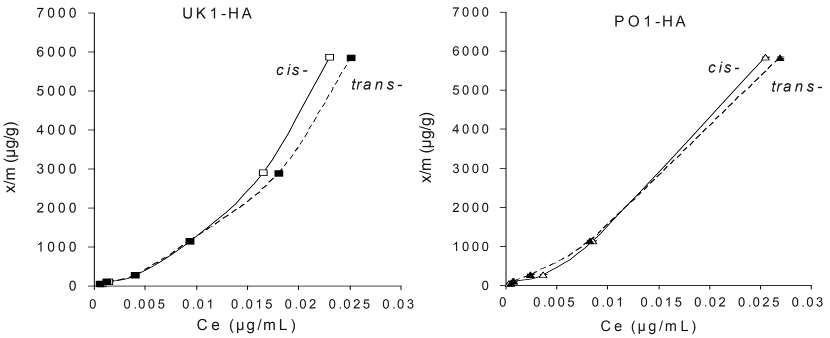

Fig. 6.2.4. Freundlich (S-type) adsorption isotherms of *cis*- and *trans*-chlordane onto the HA examined.

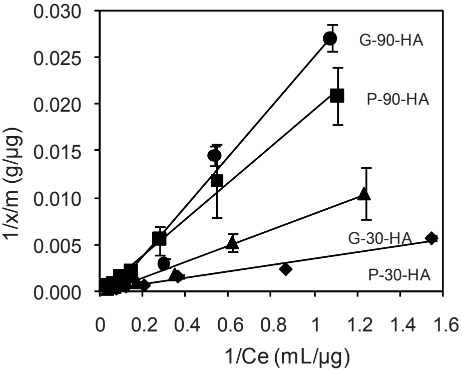

Fig. 6.2.5. Langmuir adsorption isotherms of BPA onto four soil HAs. The vertical line on each marker point indicates the standard error (n = 3).

Table 6.2.1. Correlation coefficients, r, adsorption parameters, K, 1/n, Kd, for a number of EDCs adsorbed onto various humic acids (HAs).

Origin of HA	r	K (L kg^{-1})	1/n	K_d (L kg^{-1})
Cis-chlordane				
UK1	0.978	562031	1.32	119356
PO1	0.975	155919	1.01	154608
Trans-chlordane				
UK1	0.976	298638	1.19	119932
PO1	0.989	174736	1.10	154381
Atrazine				
E4	0.989	257.8	0.56	122.9
E5	0.980	335.4	0.65	279.5
AS	0.988	646.1	0.72	592.9
BPA				
P30-HA	0.986	n.a.	n.a.	273
P90-HA	0.997	n.a.	n.a.	59
G30-HA	0.994	n.a.	n.a.	165
G90-HA	0.986	n.a.	n.a.	87
OP				
P30-HA	0.988	1158	n.a.	1341
P90-HA	0.992	889	n.a.	905
G30-HA	0.992	1398	n.a.	2326
G90-HA	0.975	351	n.a.	503

Adsorption/desorption studies performed for some EDCs onto some HAs yield very different results as a function of the involved species. In some cases, as for BPA (Fig. 6.2.6, left), adsorption shows to be completely or almost completely reversible, and desorption occurs quickly and almost completely after few desorption steps. In other cases, as for OP (Fig. 6.2.6, right), adsorption is partially reversible or mostly irreversible, with a partial desorption occurring slowly, and high amounts of EDC retained by HAs at the end of the experiment.

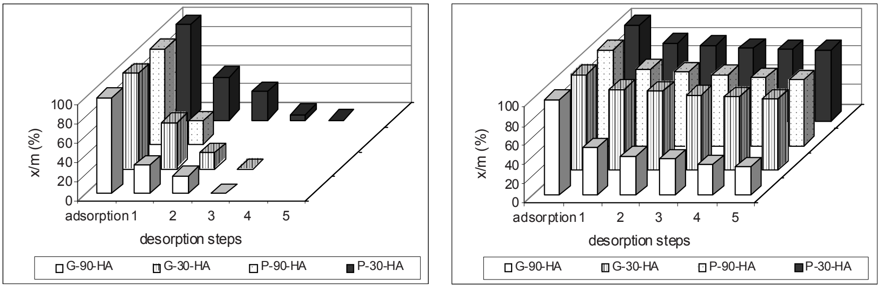

Fig. 6.2.6. Percentages (%) of initially adsorbed (100%) BPA (left) and OP (right) that remain adsorbed onto each humic acid (HA) after each desorption step.

7. Conclusions

In conclusion, different HAs are able to adsorb, generally by a rapid kinetics, variable amounts of EDCs according to different mechanisms as indicated by their adsorption isotherms and equations. The EDCs that are desorbed quickly and completely from HAs are expected to move easily down the soil profile, and possibly contaminate groundwater. On the contrary, the EDCs desorbed slowly and only partially are expected to remain mostly adsorbed by HAs, especially on the surface soil layer, with corresponding soil contamination but protection of groundwater.

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PART IV. WASTE MANAGEMENT

HUMIC SUBSTANCES IN MUNICIPAL REFUSE DISPOSED OF IN A LANDFILL

Composition, Functions, Fate

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Abstract. Disposal of municipal waste in a landfill can create environmental and hygienic problems due to leakage water, odour and other nuisances until the disposed material becomes biologically and chemically stabilized. The stabilization process includes both mineralization and transformation of the waste organic matter, which may include humification of organic substances. Humic-like substances (HS) have been isolated from fresh municipal waste, and especially from that one aged for several months in a landfill. The amounts and structural composition of waste-related HS resembled those from a low-in-quality soil such as podzol. The HS have been found capable of forming Cu^{2+} and Fe^{3+} and other metal complexes. In laboratory experiments, however, the HS extracted from landfilled waste underwent strong microbial decomposition, especially if serving as sole sources of carbon or nitrogen for soil microorganisms. Indirectly, the experimental data reported here find their verification also in a more recent research results obtained by other authors.

Keywords: municipal refuse, landfill, microbial activity, humic substances.

1. Introduction

In a world with limited energy and raw material resources, the production of waste should be avoided or at least minimized as much as possible. Nevertheless, in the Member States of the European Union (EU) alone, about two billion tones of wastes are produced every year, and this figure is rather rising. In general, there

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are two major ways of the solid wastes management: (i) utilization, and (ii) disposal in a landfill. Although a reintroduction of solid wastes into the product cycle should be preferred whenever ecologically possible and economically useful, their disposal in landfills remains widely spread. Therefore, the EU has laid down strict requirements for waste and landfills to prevent or reduce as far as possible the negative effects of the waste landfill on the environment, in particular on surface water, groundwater, soil, air, and human health [3]. Usually, a landfill can create some of these problems until biological and chemical stabilization of the disposed waste occurs. It has been widely documented, that in different natural environments refractory organic substances such as humic matter play an important role in stabilization processes [16, 25]. Rather less attention has been paid to humic substances eventually appearing in municipal refuse. In order to fill that gap experiments were performed some years ago [5, 7, 8, 10, 12–14, 24].

In this paper results of these investigations on the appearance, characteristics and fate of waste-related humic substances should be summarized. In addition, an actual development in the same field of applied science should be quoted.

2. Model landfill and material sampling

In a suburb of Braunschweig, Germany, big cylindrical containers of 40 m^3 in volume were constructed. The construction details of these thermally insulated and bottom-drained model landfills are described elsewhere [26]. Municipal waste originating from a domestic sector of the city was placed in the containers in amounts generated by some 5,000 people in a week. In some containers dewatered sludge was added, and waste was compacted mechanically. The top of containers remained open to the air but was covered with a soil layer. At intervals of 2 or 4 months, during a period of 20 months, samples of waste (1–2 kg) were taken using small openings in the container wall. Air-dried and finely milled samples were analyzed. For the description of analytical procedures, and other details refer to the original papers as cited in the paragraph 1 of this chapter.

3. Microbial counts and activities in municipal waste

Municipal waste delivered for disposal at the landfill was rich in different groups of microorganisms. The counts of aerobic bacteria capable of utilizing proteins for instance, was $2.5 \cdot 10^{12}$ g^{-1}. Figure 3.1 shows that the microbial counts were mostly reduced during the first weeks of the waste disposal. Later, the counts increased with maxima reached after 6 or 8 months. Simultaneously, the CO_2 release in samples of waste, which indicates the mineralization of decomposable organic matter, was reduced from 72 to 15 mg^{-1} $h^{-1} \cdot 100$ g (dw) in the course of disposal, i.e., between months 0 and 20. At the same time the addition of easily utilizable carbon (glucose), or carbon and nitrogen source (peptone) to the waste samples markedly enhanced CO_2 evolution. Thus, although rather stabilized after 20 months of disposal, the municipal refuse still contained microorganisms capable of mineralization activities. Probably, actinomycetes and fungi were strongly involved in these effects, since their numbers remained relatively stable in course of time in comparison to the counts of bacteria which were reduced from 100% to 0.1% after 20 months.

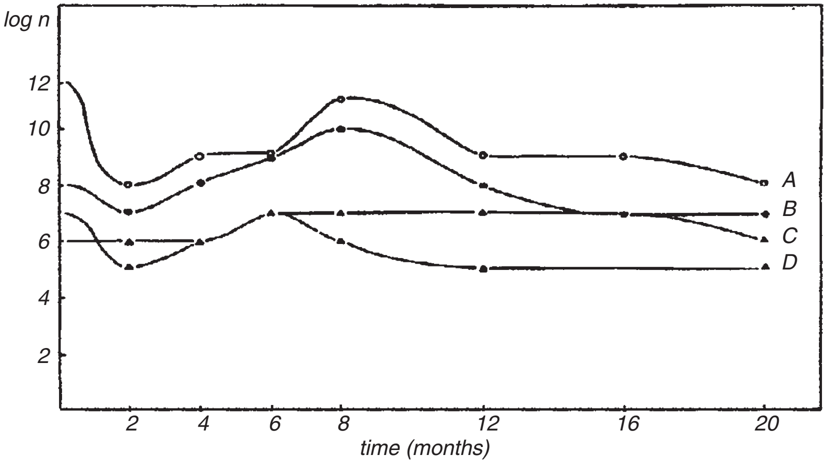


Fig. 3.1. Numbers of aerobic microorganisms in municipal waste disposed of in a landfill. A: aerobic proteolytic bacteria; B: anaerobic proteolytic bacteria; C: actinomycetes; D: microscopic fungi.

From earlier investigations it is known that different fungi and actinomycetes are capable of forming dark polymers that resemble humic substances in many respects [11, 18]. It was also possible to isolate numerous strains of microscopic fungi from municipal waste, which were capable of oxidizing simple phenolic compounds into dark coloured polymers. In the waste material they belonged to the complex microbial population. In individual experiments the ability of the waste-related microbial population was examined to produce humic-like polymers from two individual substrates which cannot be easily oxidized by microbial exoenzymes, i.e., casein (protein), and starch (carbohydrate). After a 2 months of aerobic incubation at 35°C, the cultures containing casein yielded a total amount of 830 mg C L^{-1} in humic-like substances. The adequate number for cultures containing starch was significantly lower (74 mg C L^{-1}). The cultures with starch, however, yielded 3.800 mg L^{-1} microbial biomass, whereas those enriched in casein yielded 1.800 mg C L^{-1}, and non-supplemented control cultures yielded only 33 mg biomass per liter. Since spectral characteristics indicated Because similarities in spectral characteristics between the microbially formed humic substances and groundwater-related humic acids could be observed, one can speculate about introduction of humic substances from a municipal landfill into groundwater aquifer, e.g., via landfill leachate, to occur.

4. Humic substances in municipal waste – their contents and characteristics

Humic substances were extracted from municipal refuse in a N_2-atmosphere using a mixture (1:1) of 0.1 M $Na_4P_2O_7$ and 0.1 M NaOH, and were allowed to precipitate 24 h at pH 1.5. The representative yields are shown in Table 4.1.

Table 4.1. Yields of humic substances from municipal waste (mg/l00 g waste).

	Period (months)				
Source	0	2	6	12	20
Compacted refuse	271	300	405	260	250
Uncompacted refuse enriched 2: 1 with sewage sludge	275	588	990	403	610
Compacted refuse enriched 2: 1 with sewage sludge	275	488	998	251	220

Evidently, humic substances were present even in fresh municipal waste, and their contents increased and decreased again during the disposal period. When compared with fresh waste, the maximum increase was reached after 6 months in waste disposed of with sewage sludge added. Later on, the content of humic substances decreased again, and finally, after 20 months, in compacted waste with or without sewage sludge added it was lower than in the fresh one.

In comparison with the soil humic acid from podzol or with a commercial humic acid (Fluka AG), the humic substances from municipal waste had a much lower optical density at first (Fig. 4.1. A, B). Later, however, the slopes of the extinction curves showed a strong increase in optical density, and this usually indicates a high degree of polymerization of the structural units in humic substances [2].

In order to obtain a better insight with respect to their structure, humic substances were analyzed by IR spectroscopy. Figure 4.2 shows the IR spectra of humic substances extracted from samples taken in three different layers of the waste disposed in a landfill. Apparently, all the waste-related humic substances, and especially those extracted from the middle layer, demonstrate structural similarity with soil humic acid.

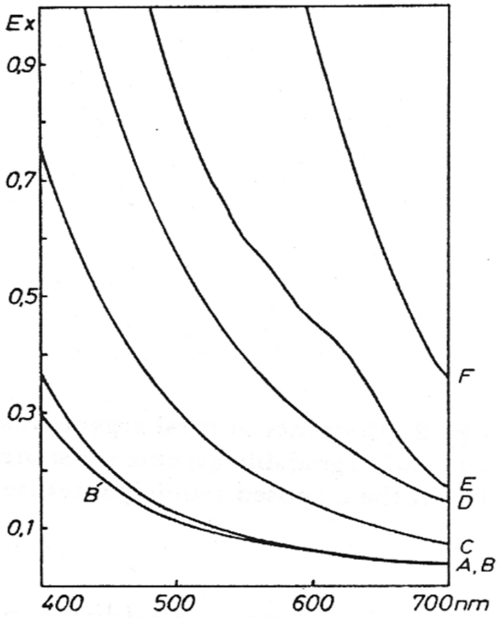


Fig. 4.1. Visible spectra of waste-related humic substances (HS), and reference humic acids. A: HS from fresh waste; B: HS from waste disposed of for 2 months; C: HS from waste disposed of for 6 months; D: HS from waste disposed of for 12 months; E: humic acid from podzol soil; F: commercial humic acid (Fluka AG).

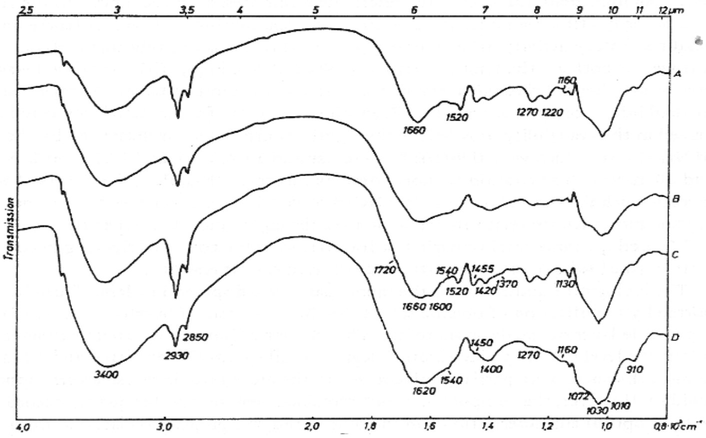


Fig. 4.2. IR spectra of humic substances (HS) from the municipal waste disposed of for 12 months, and a soil humic acid. A: HS from a bottom (60 cm) container layer; B: HS from a middle layer (120 cm); C: HS from an upper layer (180 cm); D: humic acid from podzol soil.

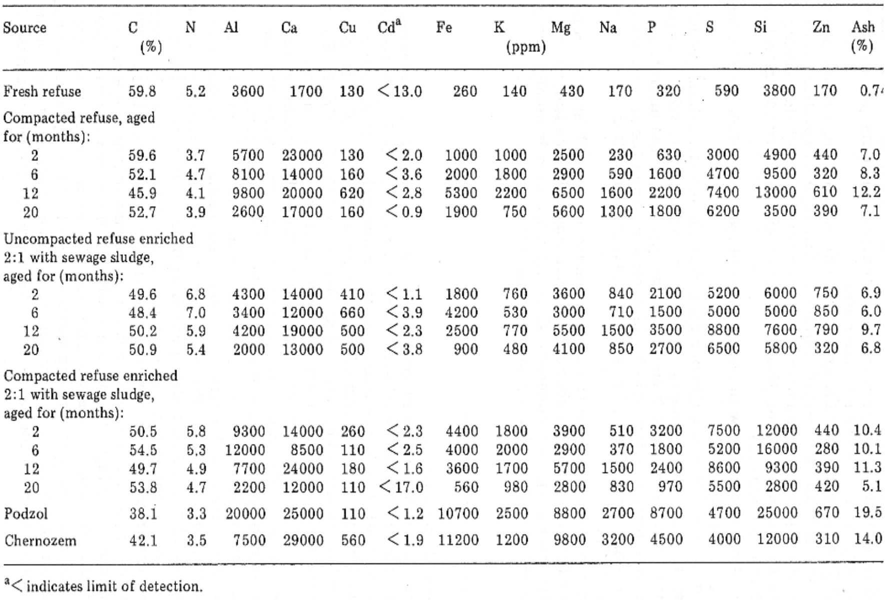
The NMR signals (not shown in Fig.) indicated the presence of chemical structures, which are likely to occur already in raw waste, such as proteins, lipids, carbohydrates and lignin-cellulose materials. With ageing of the waste in a landfill, the composition of humic substances changed. In particular, the concentration of proteinaceous material and lipids decreased, while the fraction of aromatic compounds increased.

The elemental composition of the waste-related and reference humic substances are compared in Table 4.2. The carbon and nitrogen contents of the waste humic substances were always higher than those of the soil humic acids.

For the carbon values at least, this is a reflection of the comparatively low ash contents. The soil humic acids contained much larger amounts of Fe, Mg, Na and P than waste humic substances, but similar amounts of Ca, Cu, Cd, K, S and Zn. According to Kerndorff and Schnitzer [19] high N and S contents of humic material appear to be the most valid indicators of a source material pollution, and this could be attributed also to municipal waste.

Metals are bound to humic substances usually as complexes, and therefore likely to be rather unavailable for organisms. Also, the concentration of Cu, Cd, Fe and Zn in the landfill drainage water was 10^2 to 10^3 times lower than in the humic substances [15]. This difference indicates that waste humic substances may play a role in retaining metal ions in the waste decomposing in a landfill if the complexes are stable enough.

Table 4.2. Elemental composition of waste-related humic substances and soil humic acids.



Source	C	N	Al	Ca	Cu	Cd[a]	Fe	K	Mg	Na	P	S	Si	Zn	Ash
	(%)							(ppm)							(%)
Fresh refuse	59.8	5.2	3600	1700	130	< 13.0	260	140	430	170	320	590	3800	170	0.7
Compacted refuse, aged for (months):															
2	59.6	3.7	5700	23000	130	< 2.0	1000	1000	2500	230	630	3000	4900	440	7.0
6	52.1	4.7	8100	14000	160	< 3.6	2000	1800	2900	590	1600	4700	9500	320	8.3
12	45.9	4.1	9800	20000	620	< 2.8	5300	2200	6500	1600	2200	7400	13000	610	12.2
20	52.7	3.9	2600	17000	160	< 0.9	1900	750	5600	1300	1800	6200	3500	390	7.1
Uncompacted refuse enriched 2:1 with sewage sludge, aged for (months):															
2	49.6	6.8	4300	14000	410	< 1.1	1800	760	3600	840	2100	5200	6000	750	6.9
6	48.4	7.0	3400	12000	660	< 3.9	4200	530	3000	710	1500	5000	5000	850	6.0
12	50.2	5.9	4200	19000	500	< 2.3	2500	770	5500	1500	3500	8800	7600	790	9.7
20	50.9	5.4	2000	13000	500	< 3.8	900	480	4100	850	2700	6500	5800	320	6.8
Compacted refuse enriched 2:1 with sewage sludge, aged for (months):															
2	50.5	5.8	9300	14000	260	< 2.3	4400	1800	3900	510	3200	7500	12000	440	10.4
6	54.5	5.3	12000	8500	110	< 2.5	4000	2000	2900	370	1800	5200	16000	280	10.1
12	49.7	4.9	7700	24000	180	< 1.6	3600	1700	5700	1500	2400	8600	9300	390	11.3
20	53.8	4.7	2200	12000	110	< 17.0	560	980	2800	830	970	5500	2800	420	5.1
Podzol	38.1	3.3	20000	25000	110	< 1.2	10700	2500	8800	2700	8700	4700	25000	670	19.5
Chernozem	42.1	3.5	7500	29000	560	< 1.9	11200	1200	9800	3200	4500	4000	12000	310	14.0

[a] < indicates limit of detection.

Because different heavy metals have been found to exert negative effects on microorganisms and their metabolic activities [6], the affinity of some health relevant bacteria to the presence of humic substances extracted from municipal waste was tested. Humic substances from a compacted municipal waste (anaerobic landfill) slightly inhibited the growth of *Pseudomonas aeruginosa,* and a strong inhibition was observed with a *Staphylococcus aureus* strain. Preparation extracted from a non-compacted mixture of waste and sewage sludge inhibited only the growth of *S. aureus*. The observed inhibition effects of waste-related humic substances were comparable to those obtained with a phenol solution (100–200 $\mu g \cdot mL^{-1}$).

As mentioned above, the municipal waste, which was disposed of in large-in-volume containers representing model landfills were covered with a soil layer. In some of them, thin soil layers also separated to individual 60 cm high layers of refuse. Since in soils, humic substances usually undergo a partial degradation by microbial activities [9], it was tested in laboratory experiments whether or not waste-related humic substances can be degraded and utilized under aerobic conditions as sources of nutrient by soil microorganisms. According to results obtained, up to 50% of humic substances were utilized as a supplementary source of nutrients in only 21 days. The microbial utilization was enhanced to over 80%, and for some preparations up to 98%, if the humic substances served as the sole source of carbon or nitrogen, respectively. Remaining humic substances which could be re-isolated from microbial cultures were lower in their carbon (up to 12%), and nitrogen (up to 2.3%) contents. Spectroscopic analyses (UV, Vis, FTIR) indicated losses, especially in aliphatic structural units, and a relative enhancement in aromatic structures.

5. Recent developments in the research on humic matter in solid wastes

In Germany and some other countries a mechanical-biological pre-treatment of residual municipal solid waste prior to land-filling became preferred in recent years in order to minimize different harmful emissions, some of which might contribute to the greenhouse effect [4, 20]. Such a procedure appears quite necessary because otherwise, under landfill conditions the refuse, which contains biological degradable matter, might need around 22–30 years to become fully settled and mineralized according to results obtained in China [29]. A fine black soil-resembling fraction, however, could be obtained from a typical refuse landfill in Shanghai also already after 8–10 years of disposal but still, the refuse contained a large and metabolically diverse population of microorganisms [30]. On the basis of simulation tests and a mathematical method, [27] suggested different stabilization indicators of semi-aerobic landfill such as chemical oxygen demand (COD) $\leq$ 400 mg L^{-1}, NH_3-N $\leq$ 15 mg L^{-1}, and biodegradable matter (BDM) $\leq$ 5 %. Similar to our previous investigations, which were discussed in the paragraph 4, even actually several authors utilized alkali extractable organic carbonaceous matter (humic substances) to evaluate the stability of disposed wastes. Wu and Ma [28] found the content of fulvic acids (FA) but not that of humic acids (HA) correlate with CO_2 evolution, and thus, the authors recommended a FA-based test for the evaluation of stability of the disposed waste. In experiments carried out by Mondini et al. [21], water-extracted organic C did not provide reliable information on the transformation of lingo-cellulosic wastes but in contrast, the alkali-extracted organic C reflected organic matter changes during the waste disposal. An increase of the amount of humic-like carbon has been observed between the 7th and 12th weeks. Also similar to our results, Adani and Spagnol [1] found differences in the stability of waste-related humic acids. HA from a more evolved waste compost and disposed of for 150 days contained a higher portion of recalcitrant fraction based on aromatic carbon and a lesser amount of more labile aliphatic carbon than HA from a raw waste or that one disposed of for 11 days only. Fuentes et al. [17] performed complex structural analyses of humic substances extracted from domestic and other wastes. They found the humification process to be associated with an increase of the aromatic character of the systems, with the presence of phenolic groups as principal constituents and the decrease of oxygen containing carboxylic or carbonyl groups. The content of larger molecular size fractions also increased. Recently, Montoneri et al. [22, 23] reported structural composition and physical-chemical characteristics of humic acid-like substances isolated from fresh and composted green urban wastes. From the results obtained the authors postulated that extracts of these wastes can served as bio-surfactants and other chemical auxiliary for fabric cleaning and dyeing, and also for the photo-degradation of different dyes.

6. Conclusions

Municipal wastes contain diverse and a large number of metabolic active microorganisms. Basically, many of these microorganisms are not only capable of decomposing organic matter but also of formation of humic substances from simply structured C and N containing breakdown products.

The waste-related humic substances usually appear in complexes with metal-ions. In the course of waste disposal, humic substances become a subject of microbial transformation and degradation, and thus, their role in a long-term stabilization of organic wastes disposed of in a landfill seems rather questionable.

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RECOVERY AND DISPOSAL OF PHOSPHATE SLUDGE FROM AUTOMOTIVE INDUSTRY

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Abstract. Turkish automotive sector constitutes one of the major powers of the Turkish Industry with its importance as one of the most-advanced branches of the Turkish manufacturer industry. There are 15 automotive main industry companies which manufacture trailers, trucks, light lorries, pick-ups, passenger cars, buses, minibuses, midibuses. Main hazardous waste originated from automotive industry is phosphate sludge. Phosphate sludge coming from automotive sector often contains heavy metals and a variety of other hazardous substances which can cause soil and ground water pollution. This sludge is classified as hazardous waste at the European Waste Catalogue as adopted in Council Decision 2000/532/CE. This work attempts to better understand the physical and chemical characteristics of these sludges, by studying on samples taken from automotive manufacture plant in Marmara Region of Turkey. Chemical composition and leaching characteristics are given, together with disposal and recovery methods.

Keywords: hazardous wastes, soil pollution, water pollution, wastes disposal.

1. Introduction

Phosphating and metal coloring operations are generally used to obtain a good substrate for further painting and deposition of organic agents in order to provide corrosion protection. For example, anodizing is an electrolytic process that converts the metal surface into an insoluble oxide coating, which confers corrosion protection [1, 2].

Phosphating is a chemical/electrochemical process, in which thin, microcrystalline and water insoluble phosphates are produced on metal surfaces from phosphoric acid solutions in a dipping or spraying process. Because they originate from a chemical reaction with the underlying metal, the pale to dark grey colored metal phosphate coatings are firmly anchored to the metal surface and have numerous

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cavities and capillaries. This property gives the phosphate layers an optimum absorption capacity for oils, waxes, coloring pigments, and paints, so that they have proved their worth as corrosion protection and as a good surface for coats of coloring and paint.

A further property of the phosphate coating is the ability to reduce friction (as arises for example in deformation, drawing or sliding processes). So, as well as an improvement in the surface properties of the peaces treated, in prolonged use of the tools the work rate can be fundamentally increased.

Phosphate sludges are often classified as hazardous wastes by environmental agencies (e.g., European Union Commission Decision 2001/573/EC). In the hazardous waste list, phosphate sludge is assigned as (11) "Wastes From Chemical Surface Treatment and Coating of Metals and other Materials; Non-Ferrous Hydrometallurgy", (11 01) "wastes from chemical surface treatment and coating of metals and other materials for example galvanic processes, zinc coating processes, pickling processes, etching, phosphating, alkaline degreasing, anodizing" *(11 01 08* phosphating sludges).*

The hazardous character and toxicity is related to the high concentration of leached species, such as heavy and/or transition metals, such as Zn and Ni. Removal of those species depends on their ultimate equilibrium form and, particularly, on the pH values of the surrounding environment [3]. Here, toxicity characteristics are assessed from leaching tests. Leaching tests in distilled water (DIN 38414-S4) indicate that the leaching levels of Ni and Zn are not directly predictable by the solubility of corresponding hydroxides, since the mobility is mainly related to the composition of the residue [4].

2. Characterization

Samples were dried at 105°C to constant mass before eluting and the water content determined.

The heavy metal composition of dried samples was determined by X-ray fluorescence spectroscopy.

Leaching tests were performed according to DIN-38414-S4 (EN 12457) in order to determine pollutants' mobility under neutral conditions at the beginning using distilled water over 24 h. The liquid (water)/solid ratio was 10 L/kg. Pictures were taken as dimension of 1 μm and 100 nm by using Scanning Electron Microscope and given Fig. 2.1.

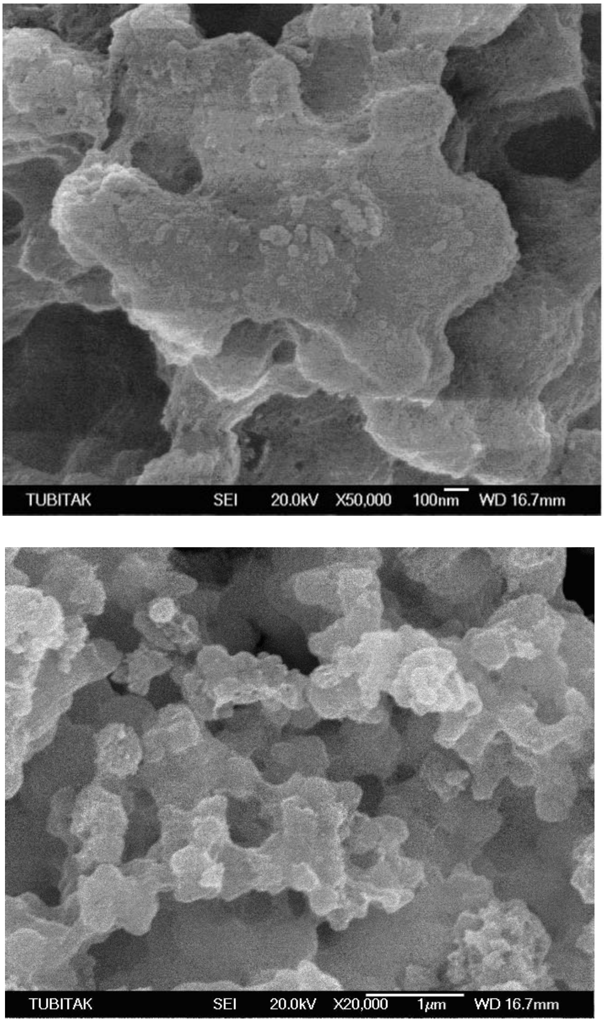

Fig. 2.1. Pictures of phosphating sludge by using SEM.

Chemical composition and leaching characteristics are given Tables 2.1 and 2.2.

Table 2.1. Chemical composition of phosphating sludge determined by XRF.

Elements					
Fe	Na	Ni	Zn	P	O
22.552	0.008	0.85	12.30	20.93	41.28

Table 2.2. Concentration of phosphate sludge of eluate.

Eluate criteria L/S = 10 L/kg	Phosphate sludge (mg/L)	Wastes to be processed as inert waste (mg/L)	Wastes to be processed as non-hazardous waste (mg/L)	Wastes to be processed as hazardous waste (mg/L)
As (Arsenic)	0.142	≤0.05	0.05–0.2	<0.2–2.5
Ba (Barium)	0.026	≤2	2–10	<10–30
Cd (Cadmium)	0.002	≤0.004	0.004–0.1	<0.1–0.5
Cr (Chromium)	<0.001	≤0.05	0.05–1	<1–7
Cu (Copper)	0.04	≤0.2	0.2–5	<5–10
Hg (Mercury)	<0.0005	≤0.001	0.001–0.02	<0.02–0.2
Mo (Molybdenum)	0.0027	≤0.05	0.05–1	<1–3
Ni (Nickel)	120	≤0.04	0.04–1	<1–4
Pb (Lead)	0.097	≤0.05	0.05–1	<1–5
Sb (Antimony)	0.016	≤0.006	0.006–0.07	<0.07–0.5
Se (Selenium)	0.058	≤0.01	0.01–0.05	<0.05–0.7
Zn (Zinc)	650	≤0.4	0.4–5	<5–20
Chloride	133	≤80	80–1,500	<1,500–500
Fluoride	134	≤1	1-15	<15–50
Sulphate	115	≤100	100–2,000	<2,000-5,000
DOC (Dissolved Organic Carbon)	24	≤50	50–80	<80-100
TDS (Total Dissolved Solids)	7,250	≤400	400–6,000	<6,000–10,000
Phenol Index	<0.05	≤0.1		
Criteria for original sample		(mg/kg)	(mg/kg)	(mg/kg)
TOC (Total Organic Carbon)	3,250	≤30,000 (3%)	50,000 (5%)– pH ≥ 6	60,000 (6%)
BTEX (Benzene, toluene, ethylbenzene and xylenes)	1.6	6		
PCBs	<0.01	1		
Mineral oil	7,200	500		
LOI (Loss of Ignition)	24			10,000 (10%)

Particle size distribution is given in Fig. 2.2.

Table 2.3 shows the main mineralogical phases in sludge after calcination at 950°C. Structure of the sample before calcinations was mostly amorphous. SHIMADZU XRD-6000 instrument coupled with Cu-X Ray tube (л = 1.5405 Angstrom) was used for determination of components.

Table 2.4 gives the relevant physical characteristics of the sludge. As expected, sludge has very high moisture concentration as 65% and the particle size distribution is mainly varied between 2–50 µm and average particle size is 10 µm (Fig. 2.2).

Chemical composition of phosphating sludge determined by means of Atomic Absorption Spectrometry is given in Table 2.5. Concentrations of Ni, Zn, Fe, and Na are 7,415 mg/kg, 94,000 mg/kg, 186,000 mg/kg, and 27,000 mg/kg, respectively.

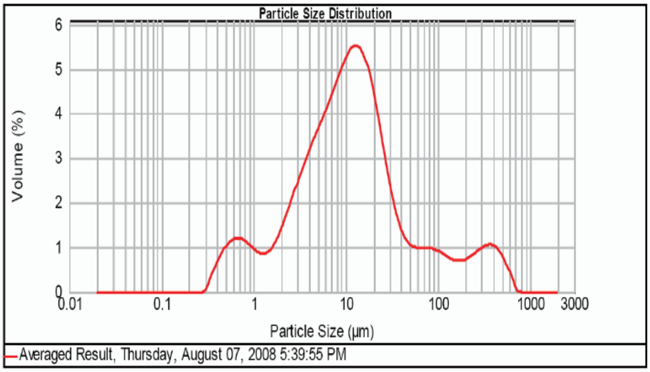

Fig. 2.2. Particle size distribution of phosphating sludge.

Table 2.3. Main mineralogical phases in sludge after calcination.

Compounds	Formulation of compounds	Composition rate (%)	Dust diffraction number
Iron Phosphate	$Fe_7(PO_4)_6$	44	49–1088
Zinc Phosphate	$Zn_2P_2O_7$	50	34–1275
Sodium Iron Phosphate	$NaFeP_2O_7$	6	36–1454

Table 2.4. Physical characteristics of the sludges.

	Particle size distribution (%)		
Moisture Content (%)	0.3–2 (µm)	2–50 (µm)	50–1,000 (µm)
65	10	80	10

Table 2.5. Chemical composition of sludge.

Composition (mg/kg)				
Ni	Zn	Fe	Na	Total P
7,415	94,000	186,000	27,000	150,400

3. Stabilization/solidification of phosphating sludge

With ever-increasing emphasis on the environment and the decrease in available landfill capacities as well as within the frame of harmonization of EU directives with Turkish regulations, the generation and disposal of phosphate sludge has become a challenge in automotive industry in Turkey. The general application for waste disposal in Turkey is landfilling due to economical considerations. Eluate concentration of pollutants after the Hazardous Waste Control Regulation should not be exceeded in order to dispose of the waste on landfill sites. But, eluate concentrations of Ni and Zn in the leaching test of phosphating sludge exceed the limits set in the Regulation. For this reason, another opportunity for recovery and disposal of phosphating sludge is stabilization and solidification processes before landfilling. The solidification/stabilization technology can be applied to the phosphating sludge classified as hazardous wastes. In the process, some binders and additives such as cement, zeolite, and bentonite can be used, which are non-hazardous and inexpensive in Turkey.

An effective procedure for stabilization/solidification of phosphating sludge was developed and verified. The sludges containing some toxic heavy metals are detoxified and made non-hazardous by solidification/stabilization technology.

After S/S process using cement, zeolite and bentonite as binder, the product is analyzed by using SEM, XRF and XRD in order to determine the structure and composition of the material. S/S process is realized by mixing of binders and additives in different proportions. According to the result, the properties of the material can well define whether it is hazardous or non-hazardous. The solidified materials are also analyzed by using elute and extract procedures, and the hazard characteristics of the waste are determined based on the regulation by means of leaching test methods (DIN 38414-S4 Test).

A solidification/stabilization process was realized by mixing of binders and additives as cement, sand and sludge in different proportions. Twenty-eight days retention time was applied for maturation of concrete. The leaching test was realized by using distilled water according to standard method. Ni and Zn are analyzed by means of standard methods after receiving extract and eluate. Results of leaching tests are given in Figs. 3.1 and 3.2.

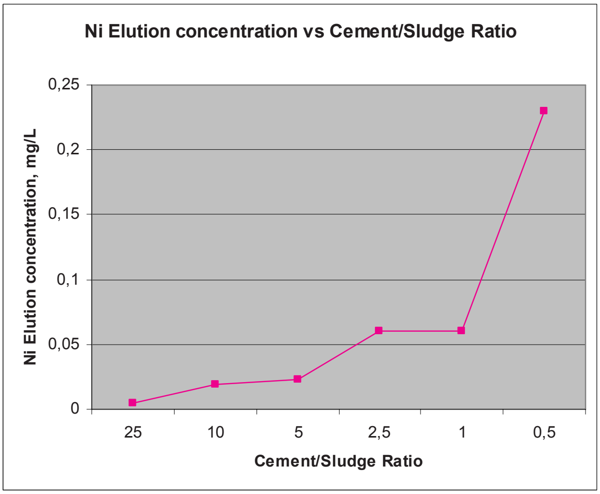

Fig. 3.1. Ni elution concentration of solidified sludge.

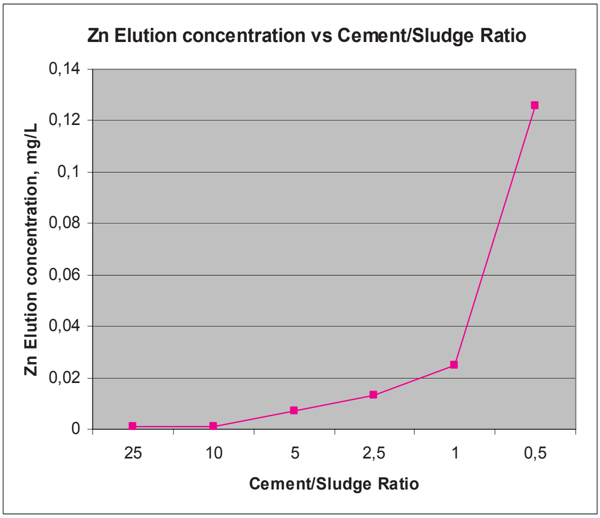

Fig. 3.2. Zn elution concentration of solidified sludge.

According to the results, Ni concentration of elution was reduced from 120 mg/L (original sample) to 0.005, 0.019, 0.023, 0.06, 0.06, 0.23 mg/L by mixing ratio of cement/sludge 25, 10, 5, 2.5, 1, 0.5 , respectively. Zn concentration of elution varied from 650 mg/L (original sample) to 0.001, 0.001, 0.007, 0.013, 0.025, 0.126 mg/L by mixing ratio of cement/sludge 25, 10, 5, 2.5, 1, 0.5, respectively (Table 3.1). Increasing the cement content of the mixtures decreases the elution rates of the heavy metals.

Table 3.1. Leaching test result according to sludge and cement mixing ratio.

Sample no.	Sludge (%)	Cement (%)	Sand (%)	Elution concentration of Ni (mg/L)	Elution concentration of Zn (mg/L)
1	100	–	–	120	650
2	50	25	25	0.230	0.126
3	25	25	50	0.060	0.025
4	10	25	65	0.060	0.013
5	5	25	70	0.023	0.007
6	2.5	25	72.5	0.019	0.001
7	1	25	74	0.005	0.001

Additionally, compressive strength tests should also be conducted in order to determine the usability of solidified concrete waste as bricks or other construction materials.

4. Conclusion

The automotive sector manufacturing vehicles and its spare parts is called as 'the locomotive' of the economy in industrialized countries. It is labeled as the locomotive sector because of its close relations with many industrial branches and other sectors of the economy.

Turkish automotive sector represents one of the major powers of the Turkish Industry with its importance as one of the most-advanced branches of the Turkish manufacturer industry. In Turkey, the automotive sector presents a rapid-rising performance inside the general Turkish economy.

As a recovery and disposal methods, solidification and stabilization processes are very important considering the limited number of hazardous waste disposal sites.

Additionally, economical consideration is also very important to encourage the Turkish industry especially automotive industry by improving feasible disposal and recovery processes. In that point, to find both technical and economical feasible disposal method for phosphating sludge originated from automotive industry and to implement this method to all automotive industry in Turkey is essential to encourage them and to eliminate one of the environmental problems that can be a challenge for the development of this sector.

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PROCESSING AND VALORIZATION OF SECONDARY WINERY PRODUCTS

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Abstract. The information regarding the composition of secondary winery products (mark, yeasts, vinasse, grape seeds, superior fractions obtained at wine distillation, waste waters, etc.) and several complex technologies of processing these products are presented, such as: production technologies for tartaric acid and its derivatives; technologies of synthesis of medicinal and agricultural preparations obtained on the basis of the biologically active compound ENOXIL, extracted from grape seeds; technologies of grape seeds processing for the production of oil of various quality, of food powder and combined forages; technologies of production of anthocyanin concentrate production from grape seeds and also technologies for winery waste waters and mark treatment to enhance biogas generation and utilization of wastes as natural fertilizers.

Keywords: secondary winery products, tartaric acid, biologically active compound, grape seeds, anthocyanin concentrate, winery waste waters.

Abbreviations:

SWP – secondary winery products
TA – tartaric acid
GS – grape seeds
SUM – State University of Moldova

1. Introduction

Winemaking industry in the Republic of Moldova has a potential of grapes processing of up to 1 million tones per year, at 125 factories, which only process around 300–400 thousands tones of grapes annualy due to the lack of raw material.

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Besides the basic production, 25% of secondary winery products are obtained: mark, yeasts, vinase, waste waters, etc. All of these products are on one hand, a source for the production of other valuable compounds, and on the other, a tremendous source of environmental pollution [1].

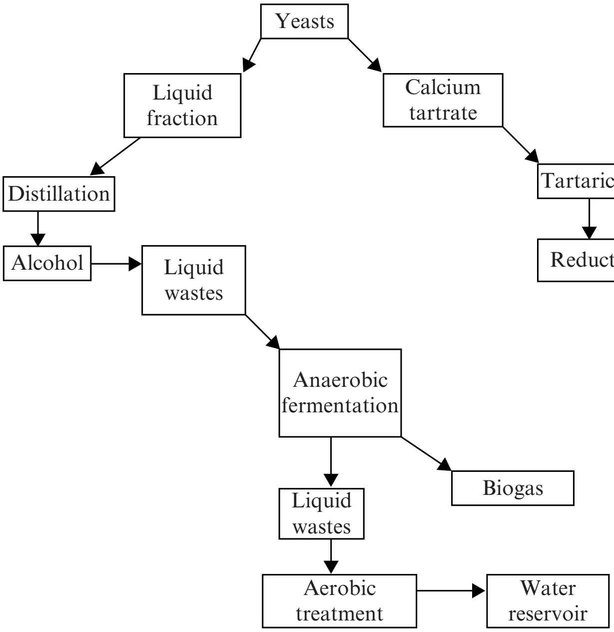


Fig. 1.1. Proposed scheme of winery yeasts processing in the RM.

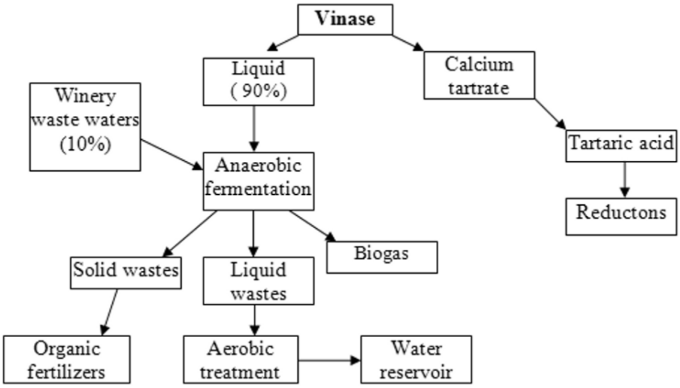


Fig. 1.2. Proposed scheme of complex processing of vinasse in the RM.

Therefore, it is important to implement technological procedures for the processing of SWP in order to obtain a various range of valuable compounds with specific properties, which cannot be obtained by means of synthetic chemistry and are widely used in various industrial fields (Figs. 1.1–1.3): tartaric acid, vitamin E, grape seeds oil, polyphenols, colorants, tannins, medicinal preparations, etc.

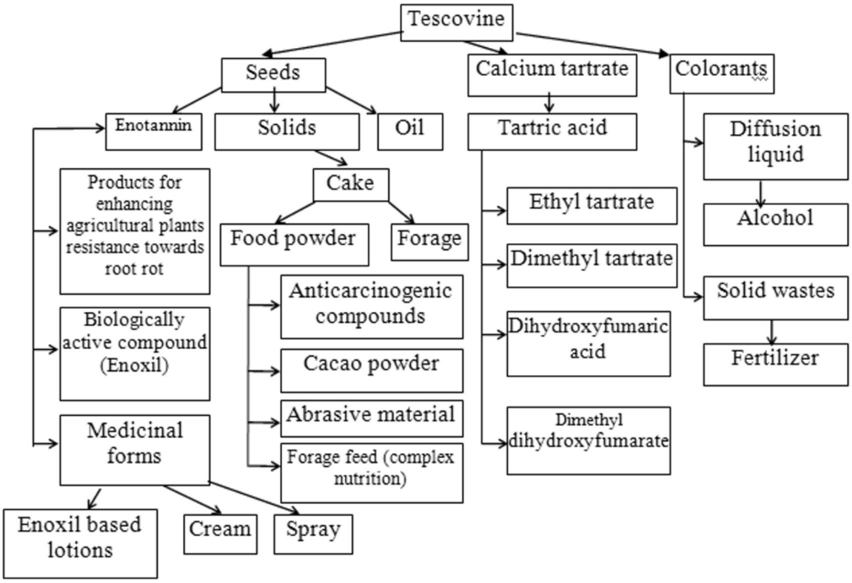


Fig. 1.3. Proposed scheme of complex processing of marc in the RM.

2. Analysis and discussion

2.1. Production of tartaric acid and its derivatives

During the years 1980–1990, the Republic of Moldova exported the tartaric raw material (calcium tartrate, calcaric sediments) to the countries, which directly produced TA (Ukraine, Odessa; Armenia, Erevan; Georgia, Tbilisi; Italy, etc.) [2].

Still, these acids are not currently produced in the country, even if large amounts of raw material are present and around 100–350 tones of tartaric acid could be produced each year.

On the basis of TA, a series of reductones (dihydroxyfumaric acid, esters of tartaric and dihydroxyfumaric acids, diethyl tartrates, etc. [3–5]) can be synthesized, with potential applications in pharmaceutics and cosmetics.

A new and easier procedure for tartaric acid obtaining has been elaborated. This procedure broadens the utilization of local raw material which contains tartaric compounds, increases the purity of the final product, assures a reduced consumption of chemical reagents and comprises two know-how elements: (i) *reactive extraction of TA;* (ii) *TA crystallization by azeotrope mixture distillation.*

In order to demonstrate the high efficiency of the elaborated procedure, the technologies of TA obtained from vinasse and wine yeasts using the ion exchange method have been optimized [6–8].

As opposed to the classical procedure, the new technology does not contain the calcium tartrate stage due to the utilization of the reactive extraction step, which assures the selective extraction of TA from the aqueous solution using an extractant, which can be an anionic resin such as *Amberlite LA-2* dissolved in an organic solvent like *butyl acetate*, thus, allowing the increase of the extraction rate and the purity of the final product.

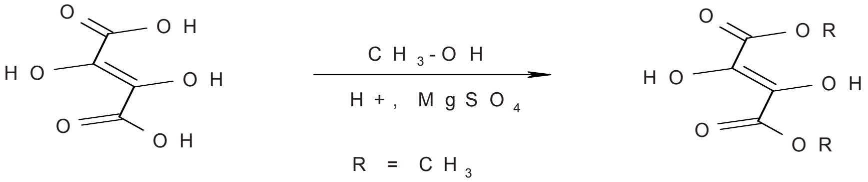
The crystallization of TA from the azeotrope mixture, which is formed when an organic solvent (in which TA is almost insoluble) is introduced into the aqueous solution, takes place at the same time with the distillation of the water from the mixture, thus decreasing the crystallization time and leading to the formation of a higher purity final product (85–90%) [9].

The elaborated technological procedure is represented in the pilot installation in Fig. 2.1.1, which presents the reactor for raw material dissolution, a Nutsche filter, an extraction column, a distiller of the azeotrope mixture and an installation for vacuum drying of TA with organic solvent trapping for its subsequent recycling as well as basic devices, such as: vacuum pumps, centrifuge pumps, collecting vessels, etc.

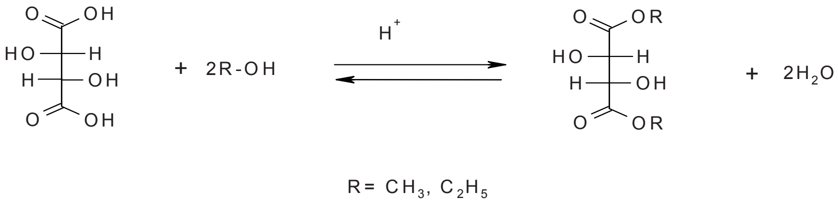
In order to obtain several derivatives of TA, the procedures of obtaining of dialkyl tartrates and dihydroxyfumaric acid derivatives were optimized.

Fig. 2.1.1. Pilot installation for TA production.

The 2,3-dihydroxyfumaric acid is an unsaturated hydroxy acid, therefore, the esterification reaction requires mild conditions. The synthesis of dihydroxyfumaric acid esters was performed at room temperature by the interaction of the 2,3-dihydroxyfumaric acid with alcohols, in the presence of mineral acids:



The optimization of TA esterification processes with methanol or ethanol at heating in the presence of КУ-2-8 cation exchanger was performed.



It has been found that the rate of the synthesis increases the yield by 15–30% in the case of ester extraction with chloroform after distillation of excessive methanol, as compared to the reaction where the product is extracted from the mixture (35–66%) and is the highest in the presence of gaseous HCl.

The synthesized TA derivatives were tested as additives in various cosmetic preparations. Interesting results were obtained when diethyl tartrate was used as additive in cosmetic creams. The rheological properties were compared to the blank sample (a cream with lanoline substrate) according to the following parameters: viscosity, adhesion, etc. The obtained results are presented in Fig. 2.1.2.

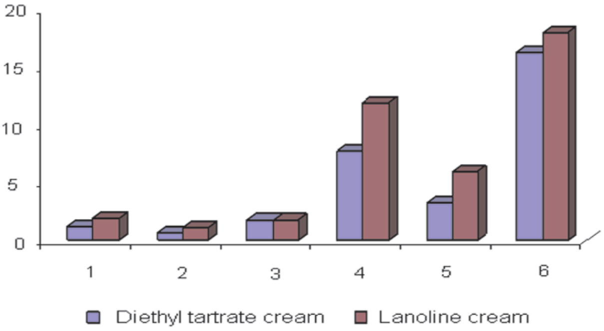


Fig. 2.1.2. Variation of the values of rheological structural parameters during 6 month.

The comparative stability of the creams was tested by the artificial oxidation in rigid conditions. Figure 2.1.3 presents the variation of the peroxide index during the oxidation of the lanoline containing cream, and Fig. 2.1.4 – the variation of the peroxide index during the oxidation of the diethyl tartrate containing cream. The data presented in these figures show that oxidation of the substrate is better inhibited by the diethyl tartrate containing cream.

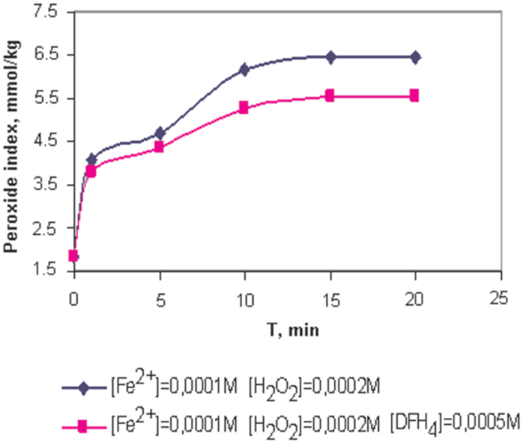


Fig. 2.1.3. Variation of the peroxide index at the oxidation of the lanoline containing cream.

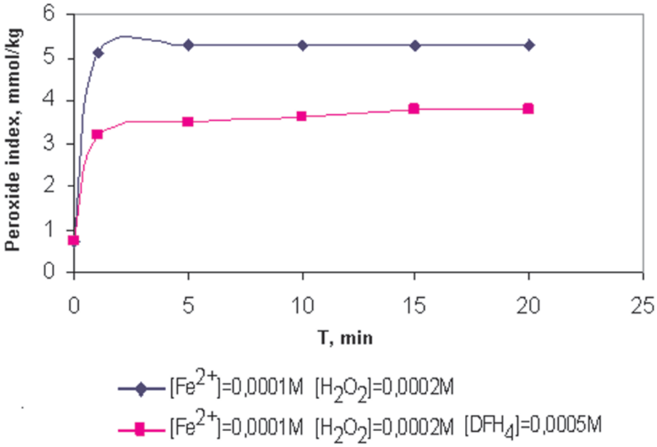


Fig. 2.1.4. Variation of the peroxide index at the oxidation of the diethyl tartrate containing cream.

2.2. Production of oil from grape seeds

The content of seeds in a tone of grapes constitutes up to 7% of the total mass (Fig. 2.2.1).

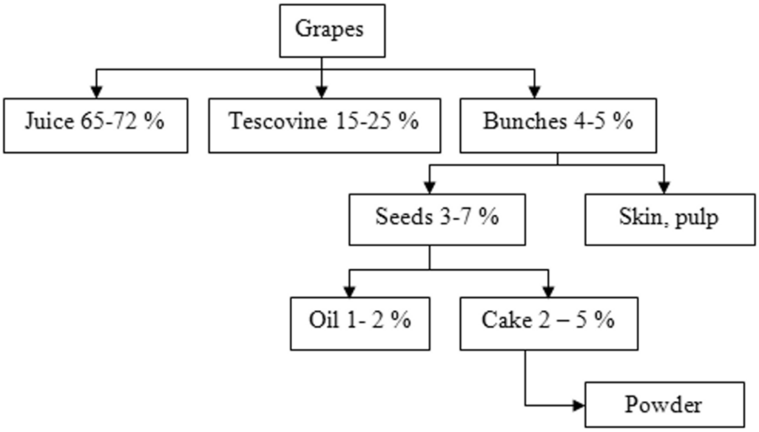


Fig. 2.2.1. Obtaining of oils and food additives from grape seeds.

Obtaining and conditioning of seeds is a complicated technological process [10]. During 1982–1986 around 10,000 tones were annually produced in the Republic of Moldova, and subsequently transferred to the cities of Tighina (oil factory), Odessa, Armavir (Krasnodar region), Tbilisi (Georgia) and Cocand (Uzbekistan) for processing.

Depending on the type and the region where the vines are grown, the content of oil in the grape seeds (dry mass) varies from 9.5% up to 20.0%.

A standardizing documentation has been elaborated and approved for grape seeds and grape seeds oil as well as for the procedure of production of oils and food additives from SWP (Fig. 2.2.2), used as additives in the “Romanita” muffins, in pastry, in cosmetics. The GS cake was successfully used as an additive in animal foodstuff.

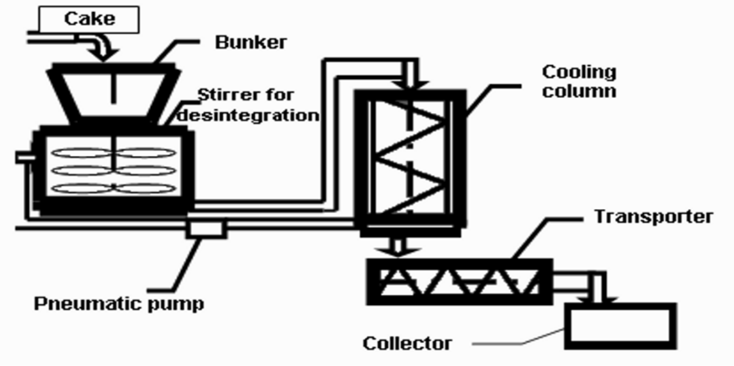


Fig. 2.2.2. Unit-scheme of the disintegration installation with the production of powder.

For the processing of GS for various oil production has been mounted an installation (Fig. 2.2.3).

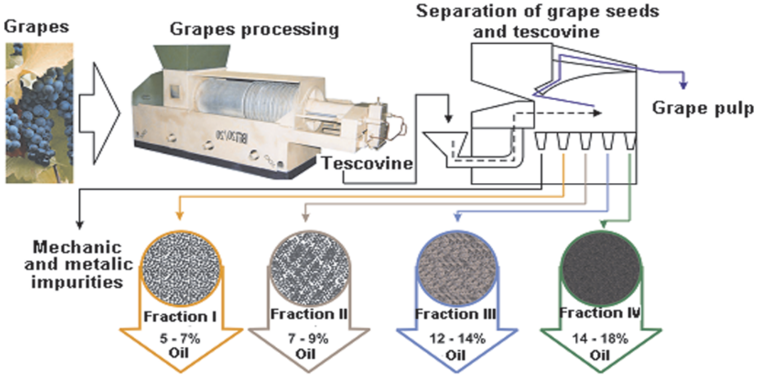


Fig. 2.2.3. Operation scheme of grapes processing.

The extraction of oil from the grapes is performed using double pressing of seeds mass, which was prior thermally treated at moderate temperatures.

The proposed procedure of GS processing allows: decreasing the oil cost; obtaining of ecological energy sources at a lower cost; obtaining of qualitative raw material for the production of biologically active additives; obtaining a qualitative cake.

2.3. Production of the natural colorant

One of the most important problems of our civilization is the deficiency of vitamins in adults as well as in children, including those possessing antioxidant properties (C, E, A, P and β-carotene).

For implementation purposes a new technology was proposed for the production of the colorant from SWP, with significant advantages, the preservation of anthocyanins in their native form and the production expenses. This technology includes the utilization of low energy consuming systems on the basis of semipermeable membranes. The technological installation for the production of anthocyanin concentrate from grapes has been mounted (Fig. 2.3.1). This includes a pilot installation for ultra filtration and reverse osmosis.

The process of concentration is performed in semi periodical regime, at a pressure of 2.0 MPa up to 4.0 MPa, until the concentration of the colored compounds reaches the concentration of 20–25 g/kg and is efficient until the colored compounds concentration in the product reaches 25 g/kg. The concentration limit is correlated with membranes specificity: membranes require a sudden increase of the pressure, which causes the loss of colored compounds.

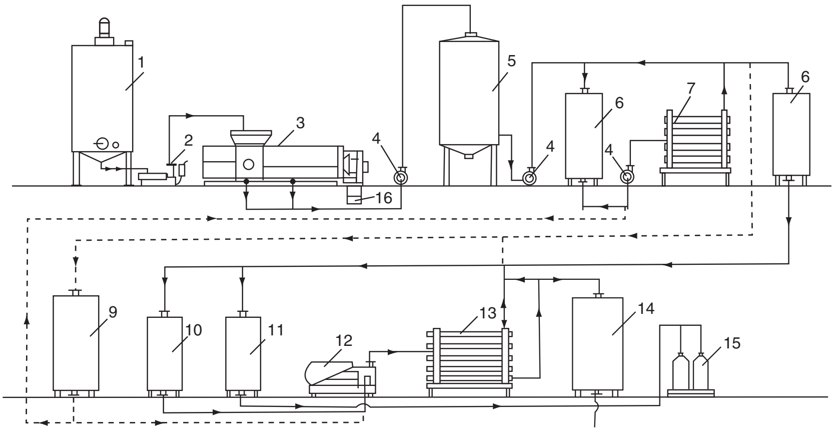


Fig. 2.3.1. Technologies of the production of anthocyanin concentrate from grapes: 1 – fermentation reactor; 2 – helicoid pump; 3 – press VPO; 4 – centrifuge pump; 5 – clarifying reservoir; 6 – recycling reservoir; 7 – ultra filtration installation; 8 – filtered extract reservoir; 9 – regeneration solution reservoir; 10 – recycling reservoir; 11 – concentrate reservoir; 12 – pump with 3 pistons; 13 – reverse osmosis installation; 14 – filtrate reservoir; 15 – vessels for anthocyanin preservation; 16 – transporter.

2.4. Production of medicinal preparations on the basis of enotannins

There is a large number of human diseases initiated by fungi and bacteria in the Republic of Moldova. The diseases of Vitis vinifera and fruit trees, induced by various fungi, represent another major problem in our country. Considering the fact that enotannins content in grapes accounts for 8%, it could be possible to obtain around 2–2.5 thousand tons of enotannins annually [2]. Preliminary research demonstrated that the rate of enotannins solubilization is about 65–70%. Therefore, some 1.2–1.3 thousand tons of active compound could be obtained, inducing modifications for the production of preparations with applications in medicine, veterinary, agriculture and other areas.

Moldavian researchers obtained new preparations from GS, with potential use in medicine, veterinary and agriculture [5].

A new procedure of enotannins solubilization in water has been elaborated, based on its oxidation with hydrogen peroxide. As a result of the chemical process, a mixture of water-soluble compounds is formed. The assays performed for the estimation of antifungal and antimicrobial activity of the novel preparation on fungi and bacteria pathogenic for humans and on those pathogenic for plants showed that the active compound ENOXIL can serve as a source for obtaining biologically active compounds and medicinal preparations. ENOXIL is produced by simple modifications of enotannins obtained from GS.

Enoxil has an evident antagonist action on the development of Botrytis cinerea Pers. in vines. Applications of 0.2% Enoxil solution on the gray rot of grapes demonstrated a 2-fold decrease of the attack of the disease as compared to the untreated vines. Research demonstrates that after further investigations related to Enoxil, it could be used for treating gray rot in vines, representing an alternative non-polluting method of obtaining pure products, which can be used together with the utilization of chemical agents and partial defoliation of the vine.

2.5. Treatment of winery waste waters with biogas production

Organic wastes represent one of the sources, which are formed continuously, and can be used for the production of biogas and its subsequent transformation into thermal and electric energy. This biotechnology helps solving environmental burden, allows obtaining of protein, vitamin and mineral additives for zootechnics, as well as of fertilizers for agriculture [11].

The level of pollution of waste waters increases abruptly during such periods due to the increase of the amount of concentrated marc formed as a result of wine alcohol distillation. Thus the COD values of these waters range between 3000 and 22,000 mg O_2/L, and it is quite clear that the efficiency of aerobic treatment will be very low, taking into consideration that COD of waste waters should be around 1000–1200 mg O_2/L before aerobic treatment. Currently, the wastewaters are disposed of in aquatic reservoirs close to the treatment station. This is not a solution of the problem as the accumulation of organic matter in aquatic reservoir takes place despite the evaporation and infiltration in soil.

Currently, there are no sufficient data regarding the industrial utilization of anaerobic biotechnologies for marc treatment. However, considering the published literature and the results of many experiments performed by Moldavian researchers, the effective implementation of this technology is possible from both the economical and technical points of view [2,8].

3. Conclusion

The primary objective now is to attract investments to implement technological approaches for the processing of SWP in order to obtain a various range of valuable compounds with specific properties, which cannot be obtained by means of synthetic chemistry and are widely used in various industrial fields.

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FATE AND BEHAVIOR OF TOXIC ORGANIC POLLUTANTS IN PLANT, SOIL AND IRRADIATED SEWAGE SLUDGE

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Abstract. This study was conducted to determine the toxic organic pollutants, Polycyclic Aromatic Hydrocarbons (PAH) and Polychlorinated Biphenyls (PCB) in Navel orange fruits, soil, and sewage sludge. The fruits were collected from 20 years old trees grown at three different farms at El-Gabal El-Asfar. The three farms received sewage water for irrigation for different periods of time: 20, 50, 90 years. The control farm is located in Anshas area, which received canal water for irrigation. The soil samples were collected from the same locations as for the fruits. The raw sludge samples were colleted from the drying beds of El-Gabal El-Asfar farm, whereas the digested sludge samples were collected from the drying beds of El-Gabal El-Asfar Wastewater Treatment Plant. The results indicated that long-term irrigation with sewage water induced the accumulation of toxic organic pollutants (PAHs and PCBs) in the Navel orange fruits and soil. The accumulation of PAHs in the fruits is less than PCBs due to their lower water solubility and hence uptake by the plant roots. The same pollutants tend to accumulate more in the top soil layer (0–20 cm) and decrease with the soil depth. Gamma irradiation (dose = 6 kGy) of raw sludge showed degradation effect on several PAHs and PCBs congeners. However, the extend of the degradation vary between the different compounds. In the digested sludge the PAHs and PCBs concentrations stay more or less similar for irradiated and non-irradiated samples indicating the lower degradation effect of gamma irradiation on the digested sludge than on the raw sludge.

Keywords: PCBs, PAH, irrigation, pollutant's uptake.

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1. Introduction

Sewage wastewater and sludge are used for irrigation and fertilization of agricultural soils. They contain several toxic organic pollutants that are harmful to human health and the environment. The legislative control of the environmental contaminants, which enter the food chain, is of a great concern to the public. Thus, it is important to investigate the fate and behavior of such pollutants in plant, soil, and sewage sludge.

The main organic pollutants that exist in the sewage sludge and sewage water are polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The organic pollutants accumulation in soil varies between the different group of compounds, PAHs or PCBs, and between the specific congeners within each group. The accumulation increase gradually in the order: PCBs > CB (chlorinated benzenes) > PAHs > PCDD/F [11].

PCBs are one of the most important xenobiotics and persistent organic pollutants in the environment [2]. There is a relationship between the metabolism and the structural properties of PCBs [9]. Chlorination grade, substitution, and molecular configuration play an important role in PCBs metabolism in plants. The lower the chlorination grade the higher is the metabolic rate in plants [14]. The solubility of these compounds decrease as the number of rings increase. Plant uptake of PCBs can occur through two pathways, the root system or atmospheric deposition [15].

PAHs are non-polar (hydrophobic), soluble in organic solvents, and difficult to mobilize due to their low water solubility. Their water solubility decreases with increasing molecular weight, whereas the resistance to oxidation, reduction, and vaporization increases. They are lipophilic and accumulate in soils by binding to the organic matter [11]. The lower molecular weight PAHs of two or three ring groups such as naphthalene, fluorene, phenanthrene, and anthracene are toxic, their toxicity tends to decrease with increasing molecular weight. There is a concern about PAH existence in the environment due to the fact that the higher molecular weights PAHs cause cancer to human beings. Pyrene is a product of incomplete combustion of fossil fuels and has been identified in surface and drinking water, numerous foods, and ambient air [10, 12, 13]. Polycyclic aromatic hydrocarbons – although non-polar – can be assimilated by intact plants [9].

Information is lacking on toxic organic pollutants' transfer and fate in plants and soils under sewage water irrigation regime. Also, the effect of gamma irradiation on their fate in sewage sludge needs to be studied. The ultimate goal of this study is to ensure the safe utilization of sewage water and sludge in agricultural soils.

2. Materials and methods

This study was conducted to determine the toxic organic pollutants on the Navel orange fruits and soils from four different farms. In addition, two different kinds of sewage sludge were analyzed for their PAHs and PCBs content. The four farms used different kinds of water, canal water and sewage water, for irrigation. One farm received canal water, the other three farms received sewage water for different periods of time: 20, 50, 90 years. The kinds of sludges used were raw sludge collected from El-Gabal El-Asfar farm and digested sludge collected from El-Gabal El-Asfar Wastewater Treatment Plant, both are located North -East of Cairo city.

The raw sludge from El-Gabal El-Asfar Farm was originated from the domestic sewage water and received no treatment. At El-Gabal El-Asfar WWTP the domestic sewage water received primary (sedimentation) and secondary (biological) treatments in addition to anaerobic digestion process at 35°C for 27 days in digesters.

2.1. Sludge irradiation treatment

The sludge samples were divided into two equal portions. One portion was sent to the National Center for Research and Radiation Technology, Atomic Energy Authority, for irradiation treatment. The samples received the radiation dose of 6 kGy at a dose rate of 5.6 kGy h^{-1}.

2.2. Determination of PAHs and PCBs in fruits, soil and sludge

This method was developed and conducted at the Institute National de la Recherche Agronomique (INRA), Laboratoire d'analyses des sols, Arras (France) as follows.

2.2.1. Extraction

PAHs and PCBs in soil [6,7] and sludge [3] were extracted using Pressure Liquid Extraction with an Accelerated Solvent Extractor (DIONEX ASE 200).

Twenty gram of soil or 2 g of sludge was weighed and added to 5 g of celite. The mixture was placed in a metallic cell of ASE 200, which was filled with pure sand. Each cell prepared was carried in the ASE 200 sampler and extracted at three types of conditions: temperature 150°C, pressure 103,4 Bar and organic solvent mixture acetone/hexane/dichloromethane (50/25/25; v/v). About 40 ml of extract was obtained in a glass tube and transferred in a graduated flask in order to adjust the final volume at 50 ml with pure acetone. Two 20 ml-volumes of final extract were transferred in two different conical flasks. The first flask was called PAH extract and the second PCB extract. 0.5 ml n-dodecane at 1% in hexane was added as keeper in each conical flask containing the PAH and PCB extracts.

PAHs and PCBs were extracted from fruits using Liquid–Liquid Extraction (LLE) [4, 5]. Twenty millilitre of fruit juice and 3 g of sodium chloride (NaCl) were measured and added in a glass conical funnel of 250 ml for LLE. The mixture was shaken first for 15 min and, after addition of 100 ml of dichloromethane, shaken for another 30 min. The conical funnels were left at vertical position in order to perform the decantation of the mixture. The lower chlorinated phase was transferred into a glass conical flask of 250 ml through a funnel filled with glass wool and anhydrous sodium sulfate.

The residual aqueous phase was extracted another time with 100 ml of hexane and shaken for 30 min. The mixture was left in vertical position for decantation. The lower aqueous phase was discarded and the hexane phase was transferred in the same conical funnel (which contained the chlorinated extract) through the same funnel. The volume of the final extract was adjusted to 250 ml in a graduated glass flask and this extract was divided in two equal volumes measured with a graduated glass test tube and distributed in two different glass flasks. The PAH and PCB extracts were then obtained. 0.5 ml n-dodecane at 1% in hexane was added as keeper in each conical flask containing the PAH and PCB extracts.

2.2.2. Purification and Determination of PAHs

The PAH extract was reduced partially in a rotary evaporator and then to dryness with a low flow of nitrogen. Then 2 ml of methyl alcohol was added to the conical flask to dissolve the dried residue. After a contact time between 30 and 45 min, the extract was filtered through a fritted disk (0.45µm of porosity). The sample was kept in a small vial for PAHs determination. PAH solution mixture “Accu – Standard Inc.” and High Pressure Liquid Chromatograph (Varian) equipped with Fluorescence Detector (FD) were used for measurement.

2.2.3. Purification and Determination of PCBs

The PCB extract was reduced partially in a rotary evaporator and then to dryness with a low flow of nitrogen. 4 ml of hexane was added and left in contact between 30 and 45 min to dissolve the dried residue. The extract was purified using a glass filtration system which consists of 50 cm narrow tube with a tape in the bottom and a piece of glass wool, 5 g of magnesium silicate, 2 g of anhydrous sodium sulfate and filled with hexane. The extract was put on the column and purified through the sorbent with 80 ml of hexane. The filtrate was received into conical flask~~s~~. It was evaporated partially to 5 ml using rotary evaporator. 20 ml sulfuric acid was added to the 5 ml extract in the conical flask. The mixture was transferred into a separation funnel, shaken for 5 min and left some time to obtain the separated layers. The lower aqueous layer was discarded. The upper layer was received in a conical flask after passing through anhydrous sodium sulfate to purify it from sulfuric acid residue. Copper wire was added till it covers the sample~~s~~ and left for 15 min in contact without shaking. The mixture was filtered on glass wool to separate hexane solution and copper wire, which was rinsed with a few volume of hexane. The hexane phase was evaporated partially using rotary evaporator and then to dryness with a low flow of nitrogen. The dried residue was dissolved with

2 ml of internal standard (PCB 202 in hexane at 50 µg/l). The contact time was between 30 and 45 min before transferring the extract into small vial (2 ml).

Quantitative determination of PCBs was performed using PCB standard "Accu Standard Inc." and a gas chromatograph (GC 3400, Varian) equipped with an Electron Capture Detector (ECD).

3. Results and discussion

3.1. Plant

The concentrations of PAHs in Navel orange fruits were 9.9, 16.3, 21.4, 26.5 µg·kg^{-1} for canal water, 20, 50 and 90 years of irrigation using sewage water, respectively. Whereas, the concentrations of PCBs in Navel orange fruits were 165.8, 255.8, 282.0, 455.3 µg·kg^{-1} for fresh water, 20, 50 and 90 years of irrigation using sewage water, respectively. It was noticed that the longer the irrigation period the higher were the concentrations of these pollutants in the fruits. PAHs concentration in fruit is less corresponding to PCBs. This implies that there is little uptake and transport of PAHs through the plant. The results agree with [11]. This could be due to their low water solubility, which prevents their uptake by plant roots. In addition, PAHs are lipophilic, which make them immobile by bounding to soil organic matter in the upper soil layers [11].

The average PAHs and PCBs concentrations in the two top soil layers (0–20 and 20–40 cm) are shown in Table 3.1.1. These two layers represent the soil where most of the active root system exists.

Table 3.1.1. Average of total PAHs and PCBs in the top soil layer (0-40) mg kg^{-1}.

	F.W.	20 years	50 years	90 years
PAHs	0.11	0.26	0.52	2.68
PCBs	6.1	21.9	37.1	120.1

The percent recoveries of PAHs and PCBs by orange fruits are shown in the Table 3.1.2. Both compounds showed reduction in the percent of recovery as the irrigation period increased. This indicates that, in the long term, there is a substantial accumulation of these compounds in the soil relative to their concentrations in plants. The highest recovery was under the fresh water irrigation regime. This could be due to the low concentrations of the organic pollutants in the soil relative to their concentration in plants. On the contrary, under high soil concentrations of these compounds, as a result of prolonged irrigation with sewage water, the recovery by plant was low.

Table 3.1.2. Recovery of PAHs and PCBs by fruit.

Compounds	F.W. (%)	20 years (%)	50 years (%)	90 years (%)
PAHs	9.4	6.3	4.1	1.0
PCBs	2.7	1.2	0.8	0.4

3.2. Soil

The concentration of PAHs and PCBs congeners varies according to the type of irrigation water, the irrigation period and the soil depth. The data given in Tables 3.2.1 and 3.2.2. indicate that, the longer the irrigation period the higher the concentrations of all congeners are. The soil irrigated with canal water exhibited the lowest congener's concentrations in all soils layers. The concentrations of all congeners are higher at the surface soil layer (0–20 cm) and decrease with the soil depth. Some transport of PAHs and PCBs from the upper soil layer into the lower layers was observed. The reason for being concentrated at the soil upper layer is that, the prolonged application of sewage water at El-Gabal El-Asfar Farm has increased the organic matter content particularly at the surface soil layer. Organic matter is the major sorptive material of organic pollutants in the soil [8], which explain their accumulation in the surface soil layer. The distribution of the different compounds in the soil indicated that, the total PCBs were much higher than the total PAHs in all soil layers.

The higher molecular weight of the congeners (Benzo(a)anthracene ‘230.27’, Benzo(k)fluoranthene ‘252.32’, Benzo(ghi)perylene ‘252.31’) revealed higher concentrations, indicating more persistence relative to the lower molecular weight congeners (Naphthalene ‘128.17’, Acenaphthene ‘154.21’, Fluorene ‘166.22’). The data reveal the long-term effects of sewage water on PAHs and PCBs contents in the soil. The long term (90 years) application of sewage water to the soil showed 22 and 20 time increase in the top soil layer (0–20 cm) of PAHs and PCBs, respectively, relative to the control.

Table 3.2.1. Total soil PAHs as affected by the kind of water and irrigation period ($mg \cdot kg^{-1}$).

Soil depth (cm)	F.W.	20 years	50 years	90 years
0–20	0.13	0.33	0.59	2.91
20–40	0.08	0.19	0.46	2.45
40–60	0.07	0.15	0.29	0.80
60–80	0.05	0.11	0.21	0.47
80–100	0.04	0.09	0.16	0.29

Table 3.2.2. Total soil PCBs as affected by the kind of water and irrigation period (mg·kg^{-1}).

Soil depth (cm)	F.W.	20 years	50 years	90 years
0–20	6.5	28.8	44.1	131.8
20–40	5.7	15.1	30.0	108.5
40–60	4.4	10.5	13.0	55.0
60–80	2.9	6.1	8.3	37.6
80–100	1.8	4.7	5.5	20.7

It is obvious from the data in the Table 3.2.3 that percent transport of PCBs congeners varies according to their chlorination grade and substitution pattern. As for the chlorination grade, after 90 years of irrigation, almost 50% of the top soil (0–20 cm) concentration of 2,4-dichlorobiphenyl was transported to the lower soil layer (80–100 cm), whereas, for the 2,2,4,5,5-pentachlorobiphenyl congener no translocation (0.0%) was recorded to the lower soil layer (80–100 cm). Regarding the substitution, the 2,3,4,4,5-pentachlorobiphenyl congener recorded 25% translocation to the lower layer (80–100 cm) comparing with 0.0% of the 2,2,4,5,5-pentachlorobiphenyl.

Table 3.2.3. Concentrations of some soil PCBs congeners as affected by the kind water, irrigation period and the depth of the soil profile (mg·kg^{-1}).

Depth (cm)	2,4 Dichlorobiphenyl				2,2,4,5,5-Pentachlorobiphenyl				2,3,4,4,5-Pentachorobiphenyl			
	C.W.	20 years	50 years	90 years	C.W.	20 years	50 years	90 years	C.W.	20 years	50 years	90 years
0–20	4.1	8.1	10.0	20.4	0.0	7.3	11.6	25.8	0.0	0.4	1.4	8.2
20–40	3.1	6.3	7.4	15.9	0.0	1.3	8.5	22.6	0.0	0.3	0.9	8.1
40–60	3.0	6.3	6.5	12.4	0.0	0.0	0.0	2.3	0.0	0.0	0.0	4.3
60–80	2.4	4.4	5.5	10.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.3
80–100	1.6	3.6	4.2	9.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.1

3.3. Sewage sludge

3.3.1. PAHs

The data in the Table 3.3.1.1 show that PAHs congeners (fluorine, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)pyrene) are dominant in the raw sludge, whereas, in the digested sludge the dominant congeners are naphthalene, acenaphtene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene. Chrysene and pyrene exhibited the highest concentration in raw sludge and digested sludge, respectively. Anthracene and benzo(a)pyrene exhibited the lowest concentrations in raw and digested sludge, respectively. Most congeners recorded higher concentrations in the digested sludge than in the raw sludge.

The effects of gamma radiation treatment on organic pollutants vary according to the compound. The concentrations of some compounds stay the same after irradiation, whereas the concentrations of other compounds were reduced. . Several compounds in raw sludge such as phenanthrene, fluoranthene, pyrene, and chrysene exhibited higher concentrations in non-irradiated sludge than in irradiated sludge. The results indicate the degradation effect of gamma irradiation on these compounds. The results agree with former findings in the literature [1]. However, the different compounds showed differences in the magnitude of degradation in response to 6 kGy of gamma irradiation. In raw sludge, the reductions were as follows: 25% for phenanthrene, 22% for fluoranthene, 51% for pyrene, and 17% for chrysene. In the digested sludge, the concentrations of these compounds were more or less similar in irradiated and non-irradiated sludge. This indicates that the digestion processes have caused some degradation of PAHs during the processes of methane gas formation, thus no further significant degradation could occur by radiation.

Table 3.3.1.1. Toxic organic pollutants (PAHs) in different kinds of irradiated and non-irradiated sludges ($\mu g \cdot kg^{-1}$).

Compounds	Raw sludge		Digested sludge	
	PAHs		PAHs	
	Irradiated	Non-irradiated	Irradiated	Non-irradiated
Naphthalene	<LOD*	<LOD*	350	330
Acenaphthene	<LOD*	<LOD*	520	500
Fluorene	130	<LOD*	670	640
Phenanthrene	860	1,150	1,310	1,300
Anthracene	110	110	410	430
Fluoranthene	460	590	550	570
Pyrene	301	630	2,450	2610
Benzo(a)anthracene	<LOD**	<LOD**	<LOD**	<LOD**
Chrysene	2,710	3,250	2,070	1,460
Benzo(b)fluoranthene	<LOD*	180	320	330
Benzo(k)fluoranthene	<LOD*	<LOD*	<LOD*	<LOD*
Benzo(a pyrene	270	280	190	230
Dibenzo(ah)anthracene	560	<LOD**	<LOD**	<LOD**
Benzo(ghi)perylene	<LOD**	990	<LOD**	<LOD**
Indeno(123 cd)pyrene	<LOD**	<LOD**	<LOD**	<LOD**
Total	5,410	7,180	8,840	8,400

*LOD = 0.11.

**LOD = 0.54.

3.3.2. PCBs

The data in the Table 3.3.2.1 show that PCBs congeners (PCB 77, PCB 101, PCB 52) are dominant in the raw sludge, whereas, in the digested sludge the dominant congeners are PCB 77, PCB 153, PCB 101, PCB 118, and PCB 66. The congener PCB 77 exhibited the highest concentrations in both raw and digested sludge. However, it recorded higher value in digested than in raw sludge, whereas PCB 101 recorded higher value in raw than in digested sludge.

The different compounds showed differences in the magnitude of degradation in response to 6 kGy of gamma irradiation and the kind of sludge. PCBs congeners exhibited higher concentrations in non-irradiated than in irradiated raw sludge. The results indicate the degradation effect of gamma irradiation on these compounds. However, PCBs congeners exhibited almost similar concentrations in

Table 3.3.2.1. Toxic organic pollutants (PCBs) in different kinds of irradiated and non-irradiated sludges ($\mu g \cdot kg^{-1}$).

Compounds	Raw sludge		Digested sludge	
	PCBs		PCBs	
	Irr	Non-irr	Irr	Non-irr
PCB 8 (2,4 Dichlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 18 (2,2,5-Trichlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 28 (2,4,4-Trichlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 52 (Tetrachlorobiphenyl)	10.9	22.4	<LOD	16.0
PCB 44 (2,2,3,5-Tetrachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 66 (2,3,4,4-Tetrachlorobiphenyl)	<LOD	<LOD	7.0	6.5
PCB 101 (2,2,4,5,5-Pentachlorobiphenyl)	37.5	41.5	12.5	10.0
PCB 77 (3,3,4,4-Tetrachlorobiphenyl)	38.7	40.8	46.4	44.1
PCB 118 (2,3,4,4,5-Pentachlorobiphenyl)	<LOD	<LOD	7.8	7.0
PCB 153 (2,2,4,4,5,5-Hexachlorobiphenyl)	<LOD	<LOD	20.3	16.6
PCB 105 (2,3,3,4,4-Pentachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 138 (2,2,3,4,4,5-Hexachlorobiphenyl)	<LOD	<LOD	21.9	16.0
PCB 126 (3,3,4,4,5-Pentachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 187 (2,2,3,4,5,5,6-Heptachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 128 (2,2,3,3,4,4-Hexachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 180 (2,2,3,4,4,5,5-Heptachlorobiphenyl)	<LOD	<LOD	11.1	6.5
PCB 170 (2,2,3,3,4,4,5-Heptachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 195 (2,2,3,3,4,4,5,6-Octachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 206 (2,2,3,3,4,4,5,5,6-Nonachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
PCB 209 (2,2,3,3,4,4,5,5,6,6-Decachlorobiphenyl)	<LOD	<LOD	<LOD	<LOD
Total	87.1	104.7	127.0	138.7

LOD = 5.4.

non-irradiated and irradiated digested sludge. This indicates that the digestion processes caused the degradation of the most PCBs congeners thus no further significant degradation could occur by irradiation. Gamma irradiation seems to have pronounced effect on PCB 52; it reduces the initial concentration by 50% in raw sludge and by 100% in digested sludge.

Several PAHs and PCBs congeners were not detected as they are below the limit of detection (LOD < 0.11 $\mu g \cdot kg^{-1}$ and < 0.54 $\mu g \cdot kg^{-1}$) for PAHs and (LOD < 5.4 $\mu g \cdot kg^{-1}$) for PCBs.

4. Conclusion

Precaution must be taken when applying sewage water and sludge to agricultural soils due to their content of organic and inorganic contaminants. These contaminants, even at low concentrations, represent a negative impact on crop quality, human health, and the environment.

Lower concentrations of PAHs were recorded in orange fruits and soils than of PCBs. PAHs are hydrophobic compounds, which are difficult to mobilize (uptake) due to their low water solubility. The existence of these compounds in the fruits indicates their transfer into the food chain and the subsequent harmful effects on human health. Their persistence in soil can result in the pollution of the ecosystem. Gamma irradiation of sewage sludge could be a useful tool to reduce the levels of sludge contamination with toxic organic pollutants.

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NEW ENVIRONMENTALLY SAFE AND EFFICIENT WAY FOR DESTRUCTION OF TOXIC CHEMICALS

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Abstract. Reductive hydrodechlorination was used as a base reaction for the destruction of toxic chlorinated compounds including chlorobenzenes and polychlorinated biphenyls. Very effective catalytic systems for this process have been developed. They include new Pd and Ni containing catalysts supported on carbon and oxide supports prepared by unusual method of laser electrodispersion. Metal content in these catalysts is extremely low, but activity of each metal atom is extremely high due to inter-cluster interaction in comparison with the catalysts prepared by impregnation or deposition-precipitation. The effect of inter-cluster interaction is discussed. Another prospective system includes metals supported on ultradispersed diamond. Scheme of the process of multi-phase hydrodechlorination of high-boiling wastes is presented. New approaches could be valuable for the development of prospective catalytic systems for different catalytic processes.

Keywords: chlorobenzenes, polychlorinated biphenyls, PCB, hydrodechlorination, Pd catalysts, Ni catalysts, laser electrodispersion.

1. Introduction

The problem of utilization of chlorinated compounds is of great concern from ecological point of view. Nowadays, the production of many chlorinated organic compounds is limited, but due to their unique properties they are still widely used in the industry as plastics, insecticides, solvents for resins and adhesives, disinfectors for leather, etc. The production of chlorinated chemicals is very dirty. A rich variety of persistent toxic wastes are formed during their production and utilization. Risks

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from the use polychlorinated substances arise from their wide spreading and high stability to biodegradation, their bioaccumulation in food chains and high toxicity resulting in cancer, decrease of immunity, gene mutation, disruption of reproductive function, etc. Every year, two to three thousand tons of such wastes are produced only in Russia, and more than hundred thousand tons of early accumulated polychlorinated wastes have to be processed.

There are two main ways for the destruction of chlorinated wastes based on oxidation or reduction. At present, mainly the oxidative methods are used in industry. Weak points of oxidative methods are high technological expenditures, control difficulties, environmental risks due to formation of highly toxic dioxins during oxidation under uncontrolled conditions.

The second way, based on catalytic reduction is environmentally more safe. The formation of toxic by-products such as dioxins is totally excluded. Reductive methods are energy saving because hydrodechlorination proceeds under mild conditions. However, catalysts for this process include noble metals, so they are expensive and often unstable versus chlorination under reaction conditions [1–4].

The aim of this work was to develop new catalysts for reductive dechlorination, which are stable under the reaction conditions, and to improve the economics of the catalysts by the reduction of noble metal content and substitution of noble metals by not-noble ones. New catalysts were prepared by laser electrodispersion (LED) technique and compared with the catalysts prepared by conventional methods, for example, impregnation of carbon support by metal salt.

Recently, new catalysts supported on ultra dispersed diamond (UDD) have been developed. Crystallinity of the support, the absence of small pores, and possibly the presence of various defects on the surface make it possible to stabilize small metal particles on this support. In comparison with commercially available 5% Pd/Fluka 0.5–5% Pd/UDD demonstrated much better catalytic activities in hydrodechlorination (HDC) of 1,3,5-trichlorobenzene and hexachlorobenzene under multiphase conditions [5]. The HDC activity of UDD supported catalysts improves as the particle size decreases. This effect is the most evident in the case of chlorobenzene (CB) transformations.

2. Experimental

2.1. *Catalysts preparation*

LED technique has been described in [6]. This method is based on a cascade fission of liquid metal drops in a laser torch plasma. The process stops sharply when all drops become uniformly small. These small charged drops are further deposited on a support under the electric field. Different types of flat and granulated, dielectric and conducting materials can be used as supports. Special modification of LED technique that includes oscillating plate was used to prepare Pd and Ni catalyst on granulated carbon support Sibunit [7, 8] (0.6–3 mm in diameter). Si (chemically polished silicon (100) wafers covered by thin natural oxide) and SiO_2/Si (thermally oxidized silicon wafers covered by thick layer of thermal oxide) supports were also used for Pd loading. The scheme of catalyst preparation is shown in Fig. 2.1.1. This method results in the formation of amorphous spherical metal nanoparticles of well-defined size on the support surface. The amounts of deposited metals and particle surface density were controlled by deposition time.

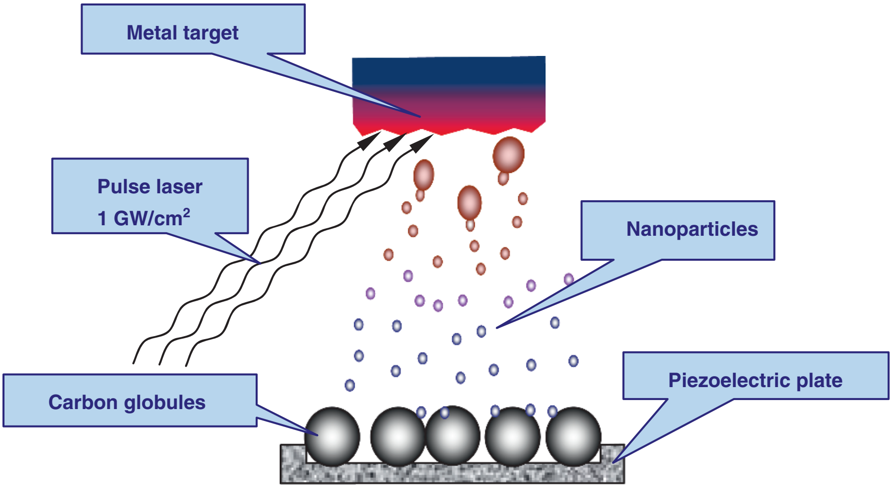

Fig. 2.1.1. Scheme for laser electrodispersion method for the preparation of Pd and Ni catalysts on granulated carbon support Sibunit.

Control catalysts Pd/UDD and Ni/UDD were prepared by wet impregnation of UDD powder using nitrates of corresponding metal solutions followed by calcination and reduction. Also commercially available 5% Pd/C by Fluka was used for comparison purposes. The metal content in catalysts varied over a wide range between 10^{-4} and 5% mass.

2.2. Catalytic experiments

Chlorobenzene HDC was performed by different methods. First, a fixed-bed flow reactor with 0,05 g of the catalyst at 150–250°C at atmospheric pressure was used. Flow rates were 3 h^{-1} (chlorobenzene) and 3.5 h^{-1} (hydrogen).

Multi-phase system for hydrodechlorination includes hydrocarbon solvent (e.g., heptane or i-octane), aqueous solution of KOH (0.89 M/l), H_2 and solid catalyst, and optionally some surfactant, which serves as phase-transfer catalyst (e.g., ammonium salts having long chain hydrocarbon moieties – so called quats).

Another system on the base of trickle-bed reactor was used for catalytic transformation of tetrachlorobiphenyl. The solution of NaOH (0.29 M/l) in methanol - water mixture (9:1) was used as reaction media. Tetrachlorobiphenyl's initial concentration was 0.063 M/l, reaction temperature 86°C, and reaction pressure 10 bar, reaction mixture flow rate 3.2 h^{-1}, H_2 flow rate 10.7 h^{-1}, catalyst loading 40 g.

The products were analyzed by gas chromatography (DBWAX column, 30 m, FID, carrier gas N_2, 35–200°C). Quantitative composition of reaction mixture was determined using internal standard technique. For this reason, calibration was made for each component by plotting the ratios of component/standard GC peak areas versus the ratios of known concentrations. Catalytic activities were calculated as moles of CB converted per mole of metal per hour. To estimate the activity of catalysts in PCB hydrodechlorination the conversion of PCB into less chlorinated products was compared as the function on time-on-stream.

2.3. Catalysts characterization

The amount of deposited metals was estimated by means of atom-absorption spectrometry using atom-absorption spectrometer Perkin Elmer 3030Z. Transmission electron spectroscopy (TEM) was used to investigate structure, particle size distribution, and arrangement in the deposited films. TEM images were obtained using Philips EM-42 (resolution of ~0.34 nm) and JEM 2100F (ultrahigh resolution of ~0.1 nm) transmission electron microscopes. Samples for TEM examinations were prepared by deposition of Pd nanoparticles onto standard grids using the laser electrodeposition method. The electron beam current was minimized to avoid the transformation (annealing) of the structure during imaging. The results obtained by both methods are in good agreement.

3. Results and discussion

Recently, it was found that catalytic activity of nano-structured catalysts depends not only on the particle size but also on an average intercluster distance or surface particle density [9, 10]. New approaches to catalyst design based on this phenomenon and associated with effect of intercluster interactions give us the instrument for multiple augmentation of catalytic activity of nano-structured catalysts [11–13]. Based on this effect the amount of noble metal in catalyst can be reduced in two to three orders in comparison with known supported catalysts.

Effects associated with electron exchange between nearby clusters are most pronounced with aggregates or ensembles of small clusters deposited on dielectric support and isolated from each other or with self-assembled catalysts [9, 10]. As a result of thermally activated electron tunneling between closely located clusters within a neutral ensemble nearly half of all clusters become charging at temperature above 400 K and dielectric permittivity $\varepsilon \geq 10$. The calculated lifetime of charge distribution is at least two orders longer compared to the typical time of catalytic reaction. The participation of these charged particles in the electron exchange with reagent may essentially reduce the activation energy of chlorohydrocarbon reactions, and this may be a reason for the high catalytic activity of self-assembled catalysts. In another case, when catalyst consists of separated clusters, only electron exchange between supported cluster and conducting support is possible. An average cluster charge resulting from the contact potential difference between supported particle and support should strongly depend on support type and metal loading [14]. There are no such effects in highly loaded metal films. By this means, when catalytic reactions are sensitive to the charge state of a catalyst, one can expect that the catalytic activity will depend on the surface particle density or intercluster distance.

Some theoretical and experimental results providing support for this idea have been viewed previously [9–14]. They were obtained for monodispersed nanostructured catalysts prepared by the unconventional method of laser electrodispersion [6]. Coulomb interaction of charged particles on the support under certain deposition time or surface particle density leads to the formation of self-assembling films which are conductive due to electron tunneling. TEM images of typical supported metal catalysts prepared by this method are shown in Fig. 3.1. All metal clusters are uniform in shape and size (about 2.0 nm for Pd and 2.5 nm for Ni) at the very narrow size dispersion less than 10%. The nanoparticles deposited on dielectric SiO_2/Si are uniformly distributed on a support surface as separated granules or small aggregates of granules depending on deposition time. Absolutely different picture was observed when metal clusters were deposited on conducting support Au/C. In this case nickel clusters form very long chains on support steps.

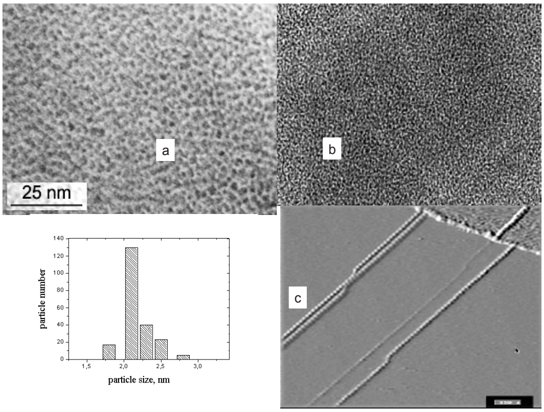

Fig. 3.1. TEM images for $Pd/SiO_2/Si$ (a), Ni/SiO2/Si (b) and Ni/Au/C (c) catalysts prepared by means of LED; particle size distribution for $Pd/SiO_2/Si$.

Metal clusters prepared by this means are amorphous, because during deposition they are cooled down extremely quickly, and they are unusually stable to oxidation. These specific features provided a possibility to study the role of inter-cluster interactions in catalysis and to produce unusually effective catalysts based on these effects.

Experimental evidences of the impact of cluster interaction on the charge state and catalytic properties of small supported clusters were obtained taking model reactions of chlorinated hydrocarbons and hydrogenation as examples. The following unusual experimental facts observed for a number of different reactions [5, 6, 9–12] provided support for the idea of the role of charged particles in catalysis:

- The unusually high catalytic activity of self-assembled catalysts based on Cu, Ni and Pd nanoparticles with size 5, 2.5 and 2 nm, respectively. For all reactions studied the activity of novel catalysts produced by means of laser electrodispersion technique with extremely low metal content was two to three orders of magnitude higher than that of known supported catalysts prepared by traditional methods.
- The sensitivity of self-assembled catalysts to solvent polarity in contrast to catalyst which includes separated clusters or highly loaded metal films.
- The correlation between catalytic properties and catalyst conductivity. For all reactions the catalytic activity increased when catalyst became conducting due to electron tunneling.
- Strong dependencies of catalytic activity of nano-structured catalysts on the surface particle density and the conductivity type of a support.

When two types of silicon with dielectric (SiO_2/Si) or semiconductor (Si) properties were used as supports for the deposition of absolutely similar clusters of Cu or Ni the strong extreme dependence of catalytic activity on the surface particle density was observed only for catalysts prepared on dielectric support [9, 10]. The highest activity in all cases corresponded to the catalysts consisting of ensembles of clusters. For the semiconductor support the catalytic activity only slightly increased with the decrease of metal loading. In this case, inter-cluster interactions become less important as a consequence of electron exchange between supported cluster and support [14].

These results were applied to design novel, highly effective and stable catalysts for the HDC of chlorinated organic compounds:

$$\text{R-Cl} + H_2 \rightarrow \text{R-H} + HCl$$
$$HCl + NaOH \rightarrow NaCl + H_2O$$

This process serves as a basis for the environmentally save destruction of polychlorinated wastes. It proceeds in vapor or liquid phase without formation of toxic by-products. In the latter case, the presence of alkali is necessary. Carbon supports are the most appropriate for the catalyst preparation due to their chemical stability. In the vapor-phase HDC catalysts on oxide supports that are stable to HCl can be used, too.

Figure 3.2 demonstrates that the catalytic activity of new Pd and Ni catalysts with extremely low metal content, prepared by means of laser electrodispersion technique in vapor phase, chlorobenzene HDC is many times higher than that of usual supported catalysts. Different types of surface particle density dependencies of the catalytic activity were also observed in this process for catalyst prepared on dielectric and conducting supports (Fig. 3.3). The highest catalytic activity corresponds to the films consisting of ensembles of clusters. Results of comparison studies of the catalytic activity of catalysts prepared by different methods are summarized in Table 3.1. One can see from these data that catalysts produced by usual methods also become more active with the decrease of metal content in the catalyst. Therefore, it can be proposed that effect associated with inter-cluster interactions is not a specific feature of catalysts prepared by means of laser electrodispersion. But it should be pointed out that in the case of usual supported catalysts the particle size as a rule increases with the growth of metal loading, and this fact may also cause the catalytic activity to change. It is also clearly seen that Pd catalysts are much more active than Ni ones, but Ni catalysts prepared by LED technique are better than Pd catalysts, prepared both by impregnation and deposition-precipitation, as well as commercially available catalyst by Fluka.

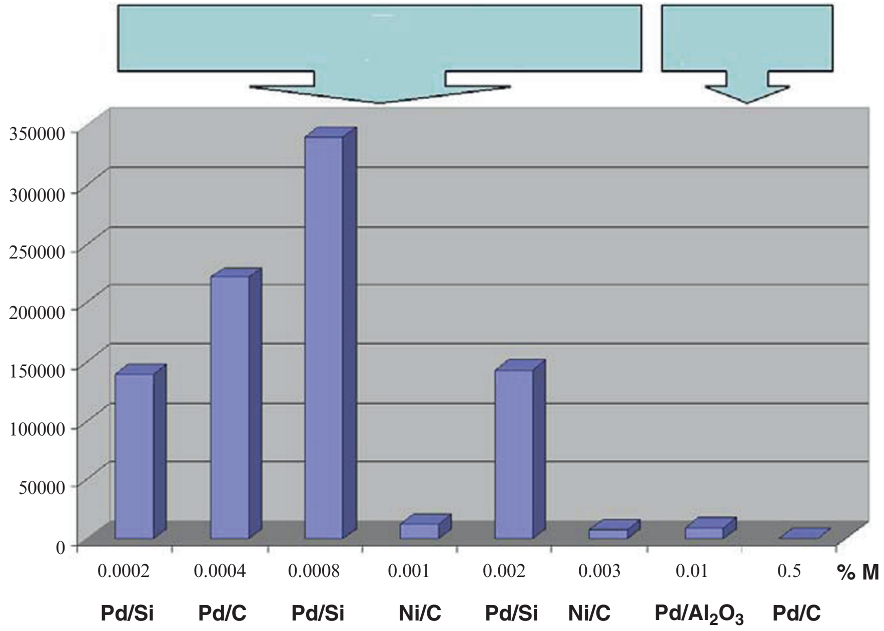

Fig. 3.2. A comparison of the catalytic activity of Pd and Ni catalysts prepared by LED and traditional methods in vapor phase hydrodechlorination of chlorobenzene at 150°C.

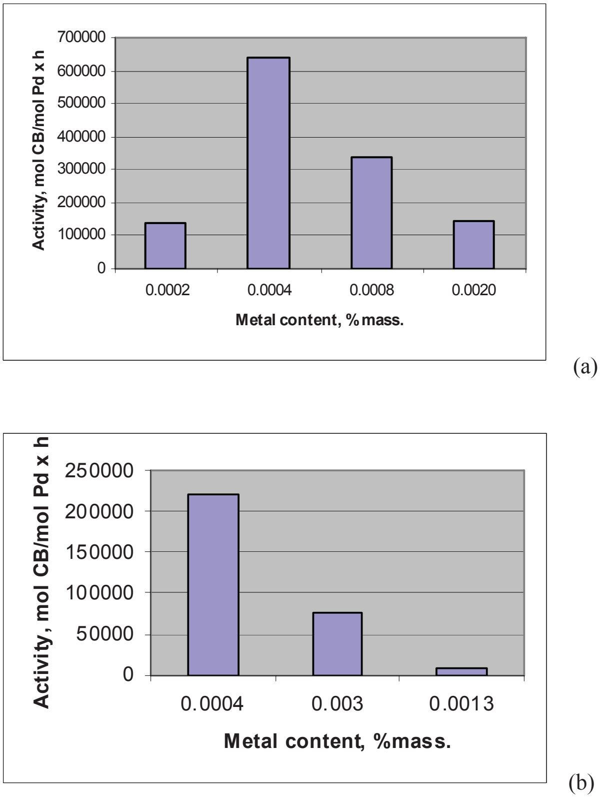

Fig. 3.3. Catalytic activity dependencies on Pd loading for catalysts on different supports in vapor phase chlorobenzene (CB) hydrodechlorination at 150°C: (a) Pd/SiO_2/Si; (b) Pd/C.

Liquid phase process is only suited for the HDC of real industrial wastes including high-boiling and solid compounds. As one can see from Fig. 3.4, novel Pd catalysts prepared by means of laser electrodispersion technique are also extremely active in multi-phase transformation of o-dichlorobenzene. These catalysts were also active in HDC of real technological wastes containing C_2Cl_6, C_4Cl_6, C_6Cl_6 and polychlorinated biphenyl which are the main components of electro-technical liquids.

Another important advantage of new catalysts is their unusual stability against chlorination. They keep the high activity for at least 7 h time-on-stream (Table 3.1). In accordance with X-ray photoelectron spectroscopy (XPS) data catalysts include Pd only in the metallic state even after long-term HDC [13]. The unusual fact of such high stability to chlorination is very important for this process.

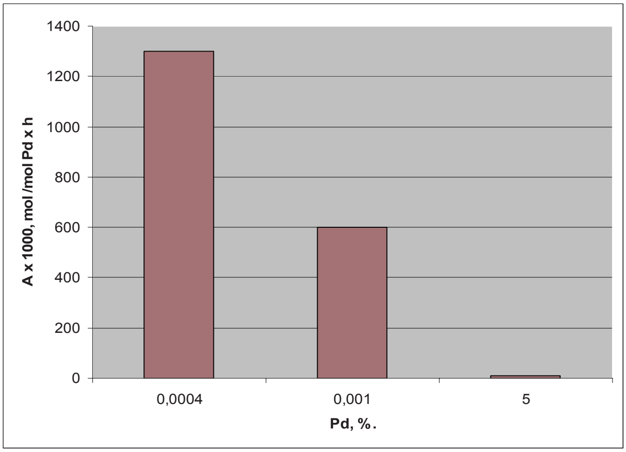

Fig. 3.4. A comparison of the catalytic activity of Pd catalysts prepared by LED with metal content ≤0.001% and known 5% Pd/C (Nippon) in multi-phase hydrodechlorination of o-dichlorobenzene.

Table 3.1. Comparison of the catalysts in chlorobenzene hydrodechlorination.

Catalyst	Production method	Pd (% mass.)	T (°C)	Time-on-stream[a] (min)	CB conversion (%)	Activity[a] (mol/mol Pd·h)
Pd/C	LED, granule size 2.5–3.0 mm	0.0004	150	120	33	230,000
			200	410	86	610,000
Pd/C	LED, granule size 1.6–2.0 mm	0.0004	200	240	53	620,000
				360	84	
				440	88	
Pd/C	LED, granule size 0.63–1.25 mm	0.001	150	120	35	97,000
			200	290	65	260,000
				350	85	
				420	89	
				450	91	
$Pd/SiO_2/Si$	LED	0.0002	200	228	29	410,000
		0.0004	150	60	96	680,000
			200	288	92	650,000
				370	92	
		0.0008	150	60	100	350,000
		0.002	150	420	100	140,000
Pd/UDD	Impregnation	0.5	200	180	100	554
Pd/C	Fluka	5	100	60	90	50
			150	60	100	55
			200	60	100	55
Pd/Al_2O_3	Deposition – precipitation	0.01	200	70	60	15,000
Ni/C	LED	0.001	200	220	37	42,000
		0.003	200	140	14	9,500
Ni/Al_2O_3	Impregnation	0.03	200	100	28	1,460
Ni/UDD	Impregnation	5.0	200	90	22	18

[a] If the conversion is constant during some period, the duration of such period is given in the column; if the conversion changes, there are some values of conversion at the moments of time.

In flow type HDC of tetrachlorobiphenyl under increased pressure (Fig. 3.5) high stability of the Pd/C in combination with high conversion was observed. One of the reasons of such a good performance was the use of reaction medium that includes methanol. There are some evidences that alcohols can participate in HDC

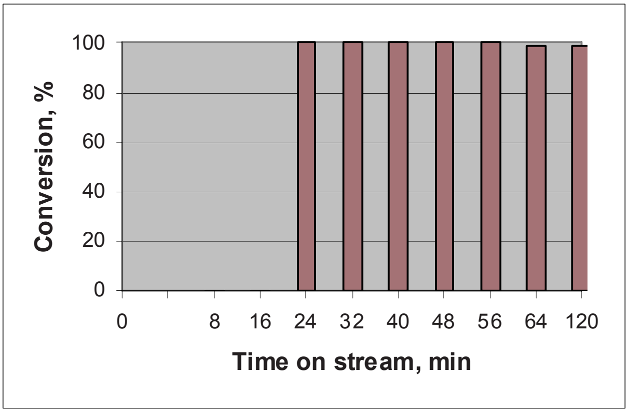

Fig. 3.5. Tetrachlorobiphenyl transformation on Pd/C in water-methanol mixture in flow-type system.

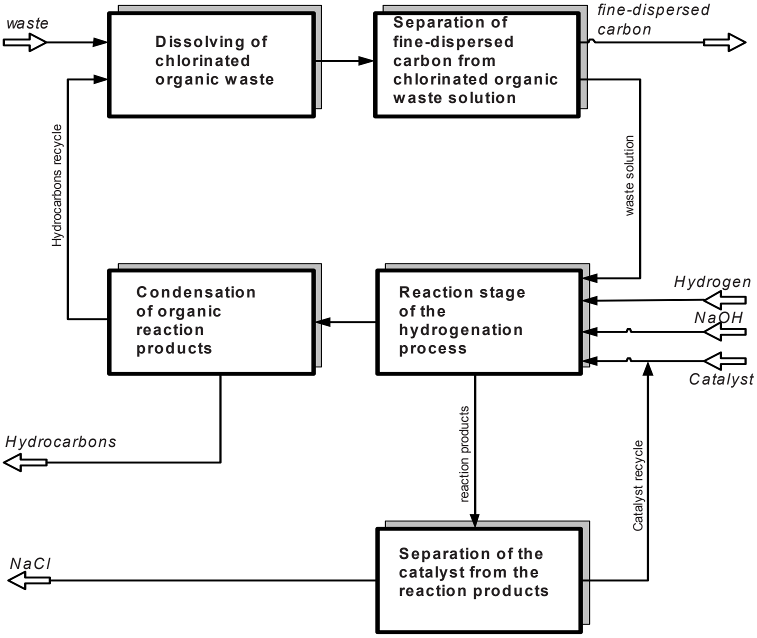

Fig. 3.6. Scheme of the process of multi-phase hydrodechlorination of high-boiling wastes.

process as hydrogen donors [15]. Also very efficient was Pd/UDD catalysts in hydrodechlorination of hexachlorobenzene in multi-phase system [5]. Full conversion of hexachlorobenzene to benzene was performed just within 60 min at 50°C.

Advantages of new catalysts associated with low metal content and high stability were used to work out the scheme of real technological process of multiphase hydrodechlorination of high-boiling polychlorinated shown in Fig. 3.6. This scheme includes the following stages: dissolving of chlorinated organic compounds, removal of fine dispersed carbon from solution, catalytic reaction, condensation of hydrocarbons produced in the process, catalyst separation and recycling.

4. Conclusions

The use of effect of inter-cluster interactions resulting in cluster charging let design highly efficient catalysts based on ensembles of clusters for ecologically safe destruction of polychlorinated compounds. Extremely low metal content in these catalysts reduces significantly the cost of catalysts based on Pd. Even Ni catalysts prepared by this means surpass known supported Pd catalyst in activity. Economic and environmentally effective process for polychlorinated wastes destruction is developed based on this approach.

It can be expected that such effects associated with electron exchange between nearby clusters on dielectric support or between supported cluster and conducting support should be important in all cases when catalysts contain small clusters with an optimum particle sizes between 1 and 5 nm at low metal loading or low surface particle density. The use of such effects may be of advantage to reduce metal content in different types of catalysts for other chemical processes.

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ELECTROCATALYSIS OF A MAJOR POLLUTANT, CO_2, TRANSFORMATION INTO USEFUL ORGANIC MATTER – FUNDAMENTAL AND APPLIED CONTRIBUTIONS

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Abstract. Metal nanorod arrays and nanotubes are expected to exhibit unusual and interesting properties for possible application in electrocatalysis and fuel cell. This work is divided into four main parts:

- Elaboration of the template nanostructure metals (Cu and Cu-Ni)
- Structural characterization (SEM, SEM-EDX) depending on experimental parameters
- Electrochemical characterization of the deposits towards test reaction (oxygen reduction)
- Preliminary data on the electroreduction of CO_2 on these metal nanorods

On Cu nanorods in bicarbonate solution the main reduction product of carbon dioxide is formic acid;on $(Cu\text{-}Ni)_{nano}$ more hydrogen and traces of methane have been obtained.

Keywords: nanocrystalline metals, template electrodeposition, electrocatalytic activity.

1. Introduction

There is significant interest and ongoing research in the preparation and application of nanometer sized materials. The physical and chemical properties of these materials are quite different from those of the bulk phase due to the high surface area to volume ratio [1].

A.M. Bahadir and G. Duca (eds.), *The Role of Ecological Chemistry in Pollution Research and Sustainable Development*,

Nanostructures shaped like long sticks or dowels with a diameter in the nanoscale but having a length that is much longer, from 1 to 200 nm. They may be synthesized on metals or semiconducting materials [1].

Metal nanoparticles are of interest due to their special properties in many aspects, such as catalysis [2–4], template for assembly of nano-sized materials [5], etc. Their properties and applications are strongly dependent on their shapes [6, 7]. Of all the methodologies developed for the production of metal nanoparticles, on either a physical or chemical basis, the electrochemical method [8–10] offers a simple alternative means for high yield production of nanoparticles.

Copper tubes having diameters between about 100 and about 200 nm have been fabricated by electrodeposition of copper into the pores of alumina nanopore membrane. Copper nanotubes are under consideration as alternatives to copper nanorods and nanowires for applications involving thermal and/or electrical contacts, wherein the greater specific areas of nanotubes could afford lower effective thermal and/or electrical resistivities.

The oxygen reduction reaction is very important in many processes, such as electrochemical energy conversion/storage, metal corrosion, fuel cell and electrocatalysis [11–14]. Different materials have been proposed as electrocatalysts for oxygen reduction and the mechanism of electrochemical reduction of molecular oxygen at such electrode materials has been extensively studied [12–14]. The kinetics of oxygen reduction is very important and it could be a measure for the electrocatalytic activity of different electrodes.

In this work we present the preparation and characterization of copper and Cu-Ni nanostructure onto a copper coin by deposition through an alumina membrane that is later dissolved.

The electrochemical reduction of carbon dioxide on metallic electrodes, has been a topic of great interest due to the build up of CO_2 in the atmosphere caused by oxidation of carbon compounds. On the other hand, CO_2 represents a possible potential source for carbon in the manufacturing of chemicals.

2. Experimental section

2.1. Reagents and solution preparation

Copper foil about 0.1mm thickness (Merck, Germany) was used in the process of electrodeposition of the copper nanorods. $CuSO_4 \cdot 5H_2O$ with purity greater than 99% (Remed Prodimpex SRL, Romania), $(NH_4)_2SO_4$ with purity greater than 99% (Aldrich, Germany), diethylene-tri-amine with purity greater than 97% (Fluka, Switzerland), $NaH_2PO_4 \cdot H_2O$ (monobasic) with purity greater than 99% (Fluka, Switzerland), $Na_2HPO_4 \cdot 2H_2O$ (dibasic) with purity greater than 99% (Fluka, Switzerland), NaOH with purity greater than 98% (Lachema, Czech Republic) were used to prepare the solutions with desirable concentration for the experiments in this study. Distilled water was used to prepare the aqueous solutions. All the treated substances were used without further purification.

2.2. Methods

Voltametric measurements were made using a potentiostat-galvanostat system – AUTOLAB PG-STAT12, Eco Chemie, Netherlands, with the specific software GPES 4.9 and a classic three electrode electrochemical cell. The experimental design consist of a platinum plate auxiliary electrode, an Ag/AgCl, KCl reference electrode, and the working electrodes were copper foil and Cu_{nano} with 2.075 cm^2 active surface.

Nanostructured copper particles were deposited electrochemically on copper foil through an alumina membrane using a deaerated solution of 100g L^{-1} $CuSO_4$ and a phosphate buffer solution (PBS), pH 7, under different applied potentials. Better electrocatalytic activity could be achieved when Cu_{nano} was electrodeposited at 0.4 V at a charge of 50 C. Prior to each experiment, the electrodes were rinsed with deionizer water and sonicated in a water bath for 15 min in ethyl alcohol.

The electrolysis cell consisted of a large (4.15 cm^2) and thin (150 μm) cathode copper current collector foil together with a thick copper anode (500 μm) surrounded by 60 μm thick Anodized Alumina Oxide (AAO) membrane, a porous cellulose separator has been placed in order to avoid the short circuit of the cell. A constant pressure was applied to the stack by means of two stainless steel clamps. The electrolyte bath was consisting of $CuSO_4{\cdot}5H_2O$ 100 gL^{-1}, $(NH_4)_2SO_4$ 20 gL^{-1} and diethyl-tri-amine (DETA) 80 mL L^{-1}. Electrolysis was carried out under pulsed cathodic current, representing a repeated sequence of 300 ms comporting two steps. Initially, a low current density of 2–4 $mA{\cdot}cm^{-2}$ is applied to the copper cathode for 200 ms followed by a 30 $mA{\cdot}cm^{-2}$ current density for 50 ms (type A Cu_{nano} electrode) or a low current density of 5 $mA{\cdot}cm^{-2}$ for 150 ms followed by a 30 $mA{\cdot}cm^{-2}$ current density for 50 ms (type B Cu_{nano} electrode). The same procedure has been applied for a mixture of 1:1 ($CuSO_4{\cdot}5H_2O$ 50 gL^{-1} and $NiSO_4{\cdot}7H_2O$ 50 gL^{-1}).

The time of electrolysis was 50 min for the type A electrode and 55 min for the type B electrode after which the alumina membrane was dissolved in 1M NaOH for 2 min at 80°C. Finally, the copper foil was washed with distilled water and dried at room temperature.

The electrodeposited $Metal_{nano}$ was characterized by SEM (Scanning Electron Microscopy, JEOL JEM 5510LV) and the composition has been determined by EDX.

The electrocatalytic activity of nanostructured copper particles (represented as type A and type B Cu_{nano}) has been assessed in comparison to the classical Cu electrode, in sodium buffer phosphate solution, pH 7.

3. Results and discussion

3.1. *Cu*$_{\mathbf{nano}}$ *electrode structure*

Typical SEM morphologies of the products are shown in Fig. 3.1.1. It can be seen that the products mainly consist of rod-like structures.

Figure 3.1.1 shows nanorods obtained under a controlled current of 2 mA cm^{-2} (type A electrode) and 5 mA·cm^{-2} (type B electrode). The mean transverse diameter of a Cu nanorod is about 30 nm, while the mean longitudinal length varies from 400 to 1nm. A higher yield of nanorods was obtained at a current density of 5 mA·cm^{-2}. The shape of the nanorods obtained at this current density are different from those obtained at a current density of 2 mA·cm^{-2}. There is evidence that the current applied during electrodeposition is of great importance for the structure of Cu$_{\text{nano}}$.

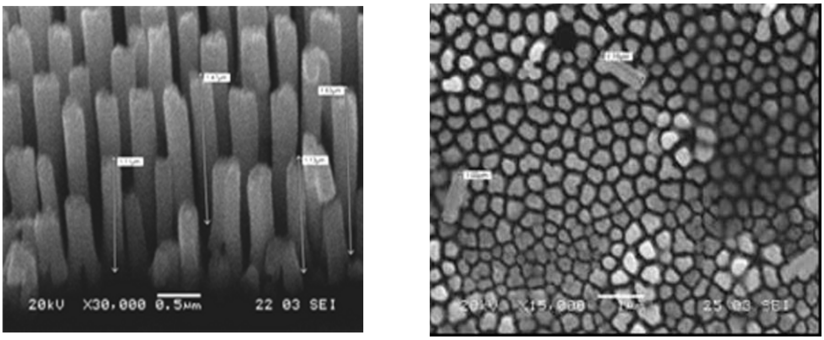


Fig. 3.1.1. SEMs for Cu $_{\text{nano}}$ (Scanning microscope JEOL JEM 5510LV).

3.2. *(Cu-Ni)*$_{\mathbf{nano}}$ *electrode structure*

From the mixture of Cu-Ni electrolytes, both the homogeneity, structure and stability of Cu-Ni nanorods is affected, Fig. 3.2.1 (a–c); in some experiments, Ni dendrites were obtained on initial copper nanorods, Fig. 3.2.1 (d).

This fact can be explained by the difference between the kinetic characteristics of fast copper and slower nickel electrodeposition.

The morphology of nanorods can be explained according to the one of accepted growing mechanism [15], of primary nucleation of Cu on the surface of AAO membrane and subsequant qrowing of (Cu-Ni)$_{\text{nano}}$ along the pore wall. Figure 3.2.2 shows the SEM images of (Cu-Ni)$_{\text{nano}}$ electrodeposited by method A, from electroytes containing a mixture of 1:1 ($CuSO_4 \cdot 5H_2O$ 50 gL^{-1} and $NiSO_4 \cdot 7H_2O$ 50 gL^{-1}).

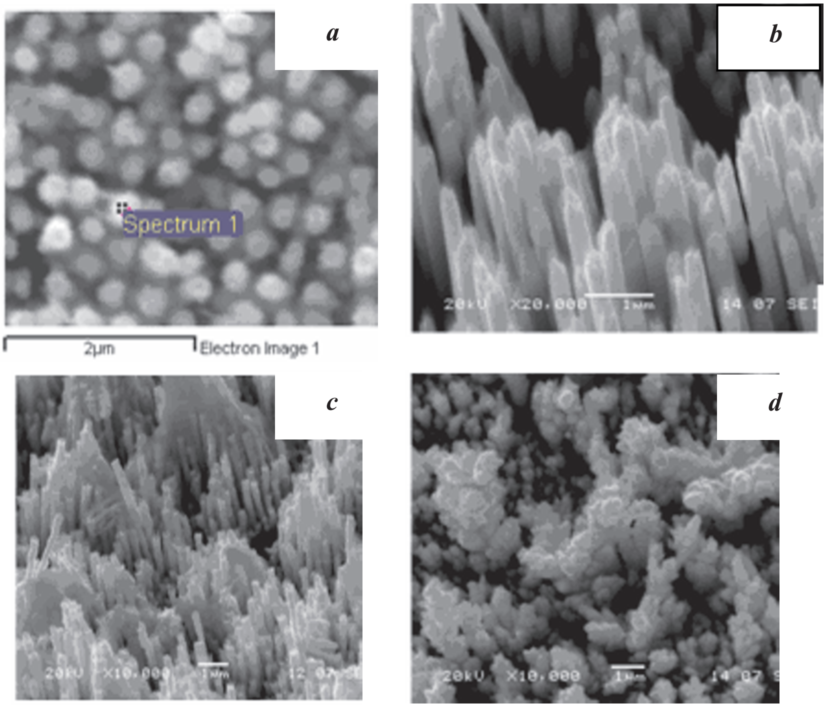


Fig. 3.2.1. SEMs for $(Cu\text{-}Ni)_{nano}$ (a–c) and dendrites formation (d).

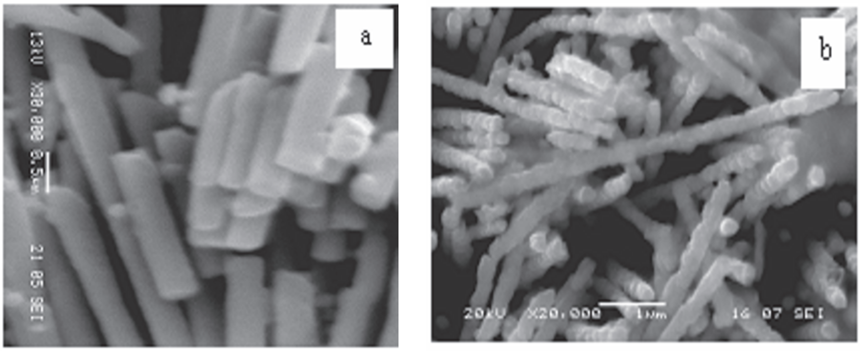


Fig. 3.2.2. SEMs for $(Cu\text{-}B)_{nano}$ (a) and $(Cu_{6.3}Ni_1)_{nano}$ (b).

The nanorods arrays have the length of 1.0–1.6 µm and the diameter of 217–290 nm, depending on the experimental parameters. The measured diameter of nanorods is controlled by pore diameter in AAO membrane.

The quantitative EDX analysis of (Ni-Cu)$_{\text{nano}}$ gives information about the composition of final nanostructures, Table 3.2.1. Starting from 1:1 copper and nickel ions in the electrolyte, different Cu-Ni composition from $Cu_{5.28}\,Ni_1$ to $Cu_{11.09}\,Ni_1$ are obtained.

According to these experiments, it is not possible to perform the advanced post treatment of (Cu-Ni)$_{\text{nano}}$ (AAO dissolving and washing) without affecting the nanorods structure. The remaining aluminum 0–6.3%, oxygen 1–19% and carbon 0–15.7%, proceeded, respectively, from AAO membrane and organic surfactant (DETA) in electrolyte. On the other hand, (DETA) is important to stabilize the nanorods.

Table 3.2.1. Quantitative EDX analysis of (Cu-Ni)$_{\text{nano}}$.

Sample	% (weight)					Discussion
	Cu	Ni	Al	O	C	
Cu-A	95.5	–	–	1.1	3.3	–
Cu-B	100	–	–	–	–	See Fig. 3.2.2a: pure Cu$_{\text{nanorods}}$ well washed, but pushed of the Cu coin
(Ni-Cu)$_1$	72.5	11.8	5.7	9.9	–	$Cu_{6.14}Ni_1$
(Ni-Cu)$_2$	75.2	14.3			10.5	$Cu_{5.28}\,Ni_1$
(Ni-Cu)$_3$	78.5	7.3	4.7	9.5	–	$Cu_{10.75}\,Ni_1$
(Ni-Cu)$_4$	58.8	5.3	6.3	19.2	10.4	$Cu_{11.09}\,Ni_1$
(Ni-Cu)$_5$	72.8	11.4	1.0	3.3	11.5	See Fig. 3.2.2b:$Cu_{6.3}\,Ni_1$ containing high quantities of unwashed (DETA)
Ni	–	80.2	1.0	3.1	15.7	High level of unwashed (DETA)

In this study, some nanostructures were used for oxygen and carbon dioxide electro reduction.

3.3. *Electrocatalytic activity of Cu$_{\text{nano}}$ for oxygen reduction*

The O_2 reduction peak current in PBS at pH 7 is taken as the measure of Metal$_{\text{nano}}$ electrochemical reactivity. In the presence of dissolved oxygen in PBS a reduction peak was observed in the cyclic voltammogram as shown in Fig. 3.3.1, comparing to the electrochemical answer on Cu foil.

The dissolved oxygen reduction peak was observed at –1.2 V/Ag,AgCl V at Cu electrode. At type B Cu$_{\text{nano}}$ structured electrode oxygen reduction occurs at -0.82 V with a strong decrease in over potential ($\Delta E = 380$ mV) when compared to Cu foil electrode whereas at type A Cu$_{\text{nano}}$ structures the results suggests that the electroreduction of oxygen takes place at about –0.65 V. Cu$_{\text{nano}}$ electrode can be used for catalytic oxygen reduction in neutral solution. This shift of potential is more important for Cu$_{\text{nano}}$ obtained according to (B) procedure, the one obtained at a low current density of 5 mA·cm^{-2} for 150 ms followed by a 30 mA·cm^{-2} current density for 50 ms.

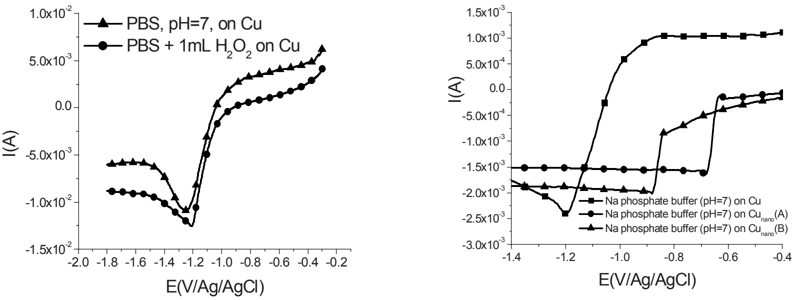

(a) (b)

Fig. 3.3.1. Cyclic voltammograms recorded for oxygen reduction at Cu (a) and Cu_{nano} (b) electrodes in PBS in the presence of dissolved oxygen and of oxygenated water.

In the presence of important quantities of H_2O_2 the reduction potential of the oxygen is displaced to 0.9 V. This value is close to the reduction potential of oxygen saturated PBS.

Different forms of Cu_{nano} were deposited on Cu foil at different applied potentials (E_{app}) by electro-deposition and used for oxygen reduction. Figure 3.3.2(a) shows the effect of applied potentials on the oxygen reduction peak currents. The oxygen reduction peak current increased at more negative potentials and reached a maximum at –0.4 V (Fig. 3.3.2 (a)). The difference in the electrochemical behavior of the Cu_{nano} electrode is due to the partially charged copper nanorods (Cu^0 and Cu^+) monolayer formed around 0 to –0.2 V. The partially charged copper nanostructures attributes in some cases to the poor performance for oxygen reduction at Cu_{nano} electrode.

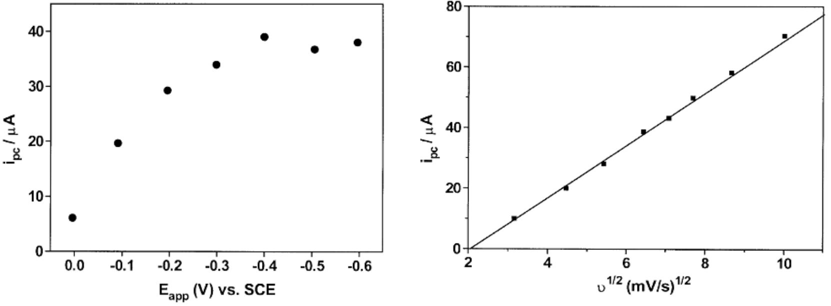
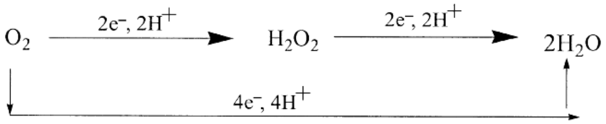

(a) (b)

Fig. 3.3.2. Effect of different applied potentials on the formation of Cu_{nano} particles onto alumina/ Cu electrode (a); plot of electrocatalytic oxygen reduction peak current (*i*pc) as a function of square root of scan rate observed for oxygen reduction at Cu_{nano} electrode in the presence of oxygen- dissolved in 0.1 M PBS (b).

The linear plot indicates that the oxygen reduction at Cu_{nano} electrode follows diffusion-controlled process, Fig. 3.3.2 (b). This means that the Faradaic current (*ip*) whose magnitude is controlled by the rate at which a reactant in an electrochemical process diffuses toward an electrode/solution interface (and, sometimes, by the rate at which a product diffuses away from that interface) is controlled by diffusion of the analytes.

$(Cu\text{-}Ni)_{nano}$ is also a high-active oxygen reduction electrocatalyst, having the oxygen reduction potential in the same region. But these results were not reproducible so far, probably due to a complex structure of template co-deposited Ni. Further investigations are necessary in order to establish and to confirm the oxygen reduction potential for this structure.

It should be noted that the cathodic peak current observed during oxygen reduction includes the current due to the reduction of metal oxides, if any, to metal (0). It is impossible to separate these two contributions accurately. However, the cathodic limiting currents observed during oxygen reduction at the Cu_{nano} electrodes were much larger than that of the peak currents observed for the cuprous oxide reduction, which was confirmed from the cathodic peak currents observed in the deaerated solution. Thus, it is reasonable to conclude that the major con tribution to the peak current comes from the catalytic oxygen reduction reaction, (Scheme 1).



Scheme 3.3.1. Oxygen reduction to H_2O by two pathways.

3.4. Preliminary data on carbon dioxide electroreduction

The Cu_{nano} (A), Cu_{nano} (B) and $(Ni\text{-}Cu)_2$ from the Table 3.2.1 were used for carbon dioxide reduction in aqueous medium (0.2 M K_2CO_3) under CO_2 atmosphere (14–25)°C. The electro-reduction of CO_2 was performed in a laboratory divided bench-scale reactor (V = 200 ml; Nafion 424 membrane), equipped with specified cathodes ($S = 2.2\ cm^2$) and Pt anode. The faradic efficiencies of formation for the main products were calculated from the total charge passed during batch electrolyses, which was set to 50 coulombs.

During the preparative electrolysis, 5 mL electrolyte samples were taken (in 30 min periods) These samples were studied with respect to form formic acid. Gas chromatography [16] and TOC analyses have been applied.

The best results (64% faradic efficiency) was obtained on Cu_{nano} (B) at 14°C; whereas on $(Ni\text{-}Cu)_2$ cathode 59% average faradic efficiency was observed for the formation of formic acid at the same temperature.

4. Conclusions

During these experiments, the most important problem was the reproducibility and homogeneity of the Cu_{nano} and $(Cu\text{-}Ni)_{nano}$ deposits and the oxidation stability of the nanostructures obtained. Accordingly, freshly obtained Me_{nano} electrodes were used for each experiment.

The difference in the electrochemical behavior of the Cu_{nano} and $(Cu\text{-}Ni)_{nano}$ electrode for the electrochemical dissolved oxygen reduction is due to the applied current and the partially charged metal nanostructures (Me^0 and Cu^+), formed around 0 to –0.2 V. The oxygen reduction at Cu_{nano} electrode follows diffusion-controlled process.

The current efficiency for main product formation in solution (formate) depended on the current density and was found to be up to 64% at high negative potential (–1.7 V/SCE) decreasing with operating time and increasing temperature: 59–64% at 14°C and 45–50% at 25°C.

The future objective is to obtain more stable nanostructures in order to obtain data on the electrocatalytic activity over time.

From the ecological point of view, carbon dioxide transformation in useful organic matter will be of great interest in the future. In this connection, the electrochemical reduction of CO_2 using the reported nanostructures and requiring only an additional input of water and electrical energy, appears an attractive possibility to prepare formic acid and hydrocarbons.

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WASTE MANAGEMENT IN LOW INCOME AND EMERGING COUNTRIES

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Abstract. Waste management situation in low income and emerging countries is mostly on a poor level, yet. The major reasons for the little progress during the last decades are significant demands in technical knowledge and political commitment, what generally outcomes in a crucial under financing of waste management activities. To achieve significant improvements it is essential to develop effective, reasonable technical solutions and to balance them with the financial means. Technical measures should aim on optimizing both environmental and economic benefits. Most recent developments proved that additional revenues may be obtained most likely from advanced recycling activities, from appropriate waste treatment techniques like MBT and from CDM. Useful measures in those three fields of waste management will be addressed in this paper.

Keywords: waste management, environmental benefits, material recycling.

1. Introduction

The approach for the sustainable usage of natural resources should lead to improved resource efficiency at the same time as a decrease of the negative ecological consequences of resource usage [1]. Following this approach, the instruments of waste management are also to be subject to a critical examination – this applies to highly developed countries as well as to developing countries to the same extent. In this document, classifications of various waste management instruments are planned with respect to a sustainable use of resources and consequences for waste management measures in developing and emerging countries are developed.

A.M. Bahadir and G. Duca (eds.), *The Role of Ecological Chemistry in Pollution Research and Sustainable Development*,

2. Sustainability of different recycling methods

2.1. Main recycling methods

A high degree of importance is to be awarded to the judgement of the principally applied recycling with respect to a sustainable use of resources. Fundamentally, according to European nomenclature, two forms of recycling can be defined: material recycling and energy recycling.

Material recycling is the substitution of raw materials through the gaining of material from waste, the use of the material characteristics of waste for the original purpose or for other purposes with the exception of the direct energy recovery. Under this we subsume material recycling, raw material recycling and biological recycling with composting (aerobic process) and fermentation (anaerobic process).

For the *energy recycling* of waste, the main purpose of the measure has to lie in the use of the waste. As a rule in energy recycling, waste products are utilized which are transferred by preceding mechanical pretreatment steps into high-value products, characterized by high heating values and low pollutant contents.

2.2. Assessment of the utilization options

The sustainability of waste management strategies is to be judged via the topics:

- Resource efficiency
- Damage to the environment

For resource efficiency and damage to the environment, the cumulative consumption/yield and damage to the environment are to be considered – from the cradle to the grave. Whereby not only the direct consumption of resources and yields or damage to the environment of the various recycling processes including the measures necessary for record keeping are to be considered. The effects which result from the use of primary raw materials compared to secondary raw materials during the creation of new products are also to be included in the observations.

To judge the material and energy recycling processes for recycling, the resource energy with the consequences of its use is to be categorized as a main indicator. As a rule, climatic effectiveness can also be categorized here.

The judgement of various recycling strategies in relation to a sustainable use of natural resources is of particular relevance in the waste fractions of paper and cardboard as well plastics and metals. The question about the type of recycling for metals is asked against the background of whether and with which quantity and quality the various metals can be separated from the waste stream and recycled.

2.2.1. Paper/Cardboard

The cumulated energy (Table 2.2.1.1.) demand for the production of fresh fibre paper of northern origin (e.g., Norway, Finland) amounts to approx. 39 MJ/kg [11]. According to the latest details from the paper industry, it was possible to somewhat reduce the energy demand for the production of fresh fibre paper. The cumulated energy demand for the production of fibre from recycled paper comes to approx. 15 MJ/kg. During the energy recycling of waste and secondary fuels in waste incineration plants and specially constructed power plants with energy efficiency factors of approx. 21% (pure electricity generation) up to approx. 76% (pure steam generation, steam use or combined heat and power (CHP) can be reached.

Table 2.2.1.1. Cumulated energy demand during the production of paper on the basis of fresh fibres and recycled paper fibres as well as energy savings during material and energy recycling at different energy efficiency factors – declaration of values according to the framework conditions in Germany.

Cumulated energy demand (CED) fresh fibre paper production	Cumulated energy demand (CED) fibre production from recycled paper	Energy saving using fibres from recycling paper compared to fresh fibres	Combustion enthalpy/ calorific value of paper in MSW	Energy saving using energy recycling with energy efficiency of 21%	Energy saving using energy recycling with energy efficiency of 39%	Energy saving using energy recycling with energy efficiency of 76%
39 MJ/kg	15 MJ/kg	24 MJ/kg	13.2 MJ/kg	10 MJ/kg	5.2 MJ/kg	2.8 MJ/kg

Together with the energy efficiency of the material recycling compared to the energy recycling which is clearly better, the climatologically effects of material recycling are also to be categorized more favourably [11, 15, 20]. Other environmental benefits of material recycling are:

- Significant reduction of demand for processed water of approx. 20 m^3/t paper compared to the production of fresh fibre paper with a demand of approx. 50 m^3/t paper
- Reduction of the amount of waste water
- Lower contribution to acidification through lower content of sulphur in the waste lye

The indicators shown in the sector resource efficiency demonstrate – for the resources of energy and water – significant advantages of material recycling compared to energy recycling of the Paper/cardboard fraction. Also in the sector on damage to the environment, advantages are to be listed, especially in the air emissions (climate relevance) and water pollution.

2.2.2. Plastics

Kindler and Nikles [14] investigated the energy demand for the production and processing of plastics. Despite the age of these studies, the energy demanded ought to differ only insignificantly from the consumption which is usual today. Kindler and Nikles calculated, e.g. an energy demand of 51 MJ/kg for PVC. A current study by PlasticEurope from 2008 [16] estimates a value of 55 MJ/kg. For polypropylene (PP) this value is at 72 MJ/kg, for Polyamide-6 even 166 MJ/kg. Per tonne of plastic produced, between 1.5 and 4 times of crude oil equivalent are consumed. Energy demands for the preparation of polymers (finished products) are not yet included in the values cited on polymer production.

The combustion enthalpy demonstrates large ranges for the different polymers, such as, e.g., PE and PP 43 MJ/kg, PVC 18 MJ/kg. Our own analyses of plastic waste from MSW, performed in the framework of analyses of MSW, resulted in an average calorific value of 23.2 MJ/kg for films and 26.7 MJ/kg for high-density (HD) plastics. The relatively low calorific values resulted from residuals of various waste components (organic, mineral, water) as well as the remains of liquids in the containers.

The following table shows the relationship of the energy demand required for the production of various polymers to the achievable energy yield through energy recycling at different energy efficiency factors. The differences between cumulated energy demand for the production of the different polymers and of the usable potential for energy recycling show that energy recycling in general demonstrates a limited potential for energy saving. Whether an advantage to the benefit of material recycling will arise from this is initially dependant on whether the individual polymers are used in a high value material recycling. Polymers, such as polyethylene (PE), polypropylene (PP), polyethylenterephthalat (PET) and polyvinylchloride (PVC), which form the vast majority of the elements in plastic packaging, are basically suitable for high value material recycling.

The energy demand influences recording Collection, transport, sorting and refining (granulate/powder) as well as transport to the processor. For these process steps, the energy demands are clearly under 1 MJ/kg. Depending of the sorting intensity and the plastic product [9] indicate energy demands of 0.3–3.2 MJ/kg. The material-related energy losses are of prime importance. These are essentially caused by non- recoverable plastics in the sorting facility and qualitatively low value plastic fractions (polymer purity, contamination) in the output of the sorting and refining facility.

The indicators shown in the sector on resource efficiency demonstrate the advantages of material recycling compared to energy recycling for the resource energy, this applies particularly to packaging plastic with large parts. The advantages of material recycling are also predominant [9] in the sector on damage to the environment.

2.2.3. Metals

The significance of metal recycling for the resource of energy is explained using the examples of steel, aluminium and copper, the predominant metals in MSW. In household and commercial waste, the metals fraction demonstrates the highest specific potential for saving energy and protecting the environment [9,;13,15]. The achieved separation of ferrous material by using magnetic separator and nonferrous material by using eddy current separation has a considerable influence on energy and resource saving. For sorting plants, the separation of ferrous metals is estimated to be up to 98%, and up to 84.7% for nonferrous separation (Al) [9]. The estimated ferrous separation is characterized as extraordinarily high according to the authors. The authors' own mass balances in mechanical processing steps of MBT facilities, gave values of up to a maximum of 86% for ferrous separation [7]. The ferrous and nonferrous separation from slag is fundamentally the best available technology available [12, 18]. Data about describe the efficiency of separation efficiency from slag is rarely available. The shortage of data available especially for nonferrous metals is, among other things, due to slag processing as a rule not taking place at the waste incineration facility. Tin plate and aluminium films are crushed during the incineration process and to fine grain and agglomerated with the slag according to Urban (spoken communication, 2008). Separation by means of the eddy current separation is, if at all, thus only possible to a very limited extent. According to [9] it is to be assumed that proportions of nonferrous metals – depending on the thickness of the film – are oxidized during the incineration process. IFEU [12] states a value of 66% for the ferrous- coverage rate. For ferrous metals, energy recycling performs only minimally more unfavourably than separate collections and/or sorting from raw waste, under the condition that there is a high ferrous covering rate via ferrous separation from slag (Tables and 2.2.3.1 and 2.2.3.2).

Table 2.2.3.1 Cumulated energy demand in the production of polymers on the basis of primary raw products and plastics out of waste as well as energy savings in the material and energy recycling at different energy efficiency factors.

Cumulated energy demand (CED) polymer generation [14][a]	Cumulated energy demand (CED) polymers of recycling plastics	Energy saving using polymers out of Waste compared to primary raw materials	Combustion enthalpy/ calorific value of diverse plastics[a]	Energy saving using energy recycling with energy efficiency of 21%	Energy saving using energy recycling with energy efficiency of 39%	Energy saving using energy recycling with energy efficiency of 76%
LD-PE 68 MJ/kg	Up to 15 MJ/kg	53 MJ/kg	43 MJ/kg	32.7 MJ/kg	16.8 MJ/kg	9.0 MJ/kg
PVC 51 MJ/kg	up to 15 MJ/kg	38 MJ/kg	18 MJ/kg	13.7 MJ/kg	7.0 MJ/kg	3.8 MJ/kg

[a] Without energy demand for the production of the finished (consumer) product.

Table 2.2.3.2. Comparison of the cumulated energy demand in producing selected metals from primary and secondary raw materials.

Metal	Energy demand steel production		Energy saving through recycling
	Primary raw material	Secondary raw materials	
Crude steel [13]	16.2 MJ/kg	6.1 MJ/kg (steel: recycling old cars)	62%
Oxygen steel [13]	20.4 MJ/kg	6.5 MJ/kg (tin plate: packaging)	68%
Aluminium [13]	211.8 MJ/kg	17.9 mean value	
		15.3 MJ/kg (recycling old cars)	93%
		16.4 MJ/kg from (recycling packaging)	94%
Copper	Pipes 32.1 MJ/kg [4]		
	Sheets 31.8 MJ/kg [4]	3.4–9.2 MJ/kg	80–92%
	Wire 50.4 MJ/kg [4]		
	Mean v. 46 MJ/kg [18]		

3. Market development and revenue situation of selected secondary resources

In recent years a clear price increase of secondary resources has been recorded. This applies in particular to metallic materials. This development is attributed to the rise in the demand for resources in the Asian market, coupled with the growing cost of resource development and production – caused by the massive rise in the cost of energy (Table 3.1).

Table 3.1. Revenue for selected secondary resources stemming from waste.

Secondary resources	Revenues
Mixed paper	55–70 €/t
Cardboard	85–100 €/t
LDPE plastics (granulate, natural)	350–450 €/t
LDPE plastics (films, bale)	320–400 €/t
PVC foil (mixed, bale)	60–100 €/t
PET (light blue, bale)	150–210 €/t
PET (coloured, bale)	20–40 €/t
Steel scrap	180–245 €/t
Copper	7,000–8,000 €/t
Aluminium	2,000–3,000 €/t

The improved revenue situation for recycled plastics or rather recycled polymers in particular, has created more favourable preconditions for high value material recycling. Increasing demand for crude oil at the same time as a shortage in its availability will also continue to drive up the price of crude oil in the medium and long term. The high energy demand for polymer production and the demand for crude oil as the base material will further improve the revenue situation for polymer secondary resources in the medium and long term. High energy demands for the generation of paper fibres and massive competition for the use of the raw material wood due to its function as a regenerative energy source, allow similar developments to be expected for paper and cardboard, as they have been shown for polymers.

The usage of FE metals in the packaging sector is strongly declining. The average revenue for steel scrap (Variety 2) came to 395 €/t in August 2008 – an increase of almost 400% compared to 2003. Aluminium is the most frequently used metal after steel worldwide. Due to its quantity, the consumption sector of packaging material (films and thin tapes, small containers and screw-on lids; food tins and drinks cans, tubes and aerosol cans) is of relevance for household and commercial waste. The consumption of aluminium in the packaging sector is strongly declining, as is the case for tin plate. The price of aluminium scrap has risen by approx. 30% compared to 2003 and is thus moderate in its rate of increase in comparison to ferrous and copper scrap. Following iron and aluminium, copper is utilized the most frequently. The range of resources is indicated at 32 years by Gerling and Wellmer (2005). The decrease of copper mining is predicted from 2008 onwards. Copper is one of the materials, which can be recycled without any loss of quality. Industry's demand for copper is increasingly being met from recycled material. Currently, around 12–13% of copper is produced from copper scrap worldwide, in the industrialized countries even up to 50% (Germany 35% – data from 2005). Copper existing in construction, machinery, equipment and various wastes, which can be used for recycling and recovery, is the largest and most economic copper mine in the world. In old waste disposal sites, using the most modern methods, copper has recently been processed in Switzerland. These disposal sites contain a copper content about twice as high as the average natural copper deposits. In particular deposited slag from waste incineration plants contains high copper levels. In the medium and long term, because of the very high energy demand in producing copper, in conjunction with its shortage, increasing revenue for copper scrap is to be expected in the medium and long term.

4. Consequences for waste management

The recycling of material in the material groups of paper and cardboard as well as plastic products has clear advantages over thermal recycling processes in the energy efficiency sector. Coupled with this as a rule, the climate change effect is also to be classified as lower. The same applies to the glass fraction. Also the covering rate of metals from raw waste is classed as high value compared to that from slag from the view of resource efficiency, as higher covering rate are gained in separate collecting and/or sorting of metals from raw waste than in removal from slag; this applies particularly for the nonferrous metals fraction (Fricke et al. 2008).

Which consequences can be drawn from these facts for waste management in developing countries?

Material recycling must be intensified to include the above-mentioned groups of material. For the material groups of paper/cardboard, plastics, metals and glass its is apparent that material recycling can be massively increased through intensifying the separate collecting systems and making them more flexible, in conjunction with an intensive use of sorting technologies. Collection and sorting systems are to be coordinated with each other. The goal of the whole system must be the reaching of an optimum between covering rate which is as high as possible and a high quality of recyclable material.

Triggered by the market development for secondary resources, the status of the self-financing resource economy has been reached in Germany for the material groups of paper/cardboard and metals. In the medium term this will also be the case for plastics. The improved market conditions create clear guidelines for the orientation of waste management concepts for developing countries, too.

5. Intensifying separate collection

Despite the good economic conditions for separate collections and existing, adapted collection and transport systems, these are only practiced on a low scale – as a rule informally/by the informal sector and are therefore often badly organized, irregular and selective. The collection rate achieved, thus only reached values between 5% and 8%.

A well organized municipal or private separate collection system does not, in comparison, exist or only exists on a small scale. This is to be traced back to, among other things, the shortage of specific information at stakeholders and among the technical experts regarding:

- The market for secondary resources, e.g., revenues, quality requirements and demand
- Waste quantities and qualities
- Appropriate technologies for collection and transport, efficiency of existing collection systems
- Instruments for economic modeling of the various available waste management instruments

- Knowledge of the acceptance in the population of participating in separate collecting systems
- To increase separate collections, the following preparatory measures are necessary
- Qualification measures
- Making available data relevant to planning, among other things, waste amount/ waste quality, recyclable material revenue/requirement
- Required and existing collecting systems
- Extent of preparatory measures, e.g., evaluating amount and type spaces for drop off systems, publicity required
- Economic studies, e.g. comparison of varieties of different waste management systems, sensitivity analyses focus on recycling specific revenues

Following approximate studies and experience from developing countries, which are mainly available for urban areas, the following measures are to be classified as suitable, under economically favourable conditions high rates of collecting and recovering are to be realised:

- Support of the informal sector including long term guarantees of revenue, making collecting equipment available, training
- Integration of the informal sector into the total system of waste management
- Setting up systems of drop off points for paper and cardboard, glass, metals, HD-plastics
- Setting up systems of curbside collection (bins and/or bags
- Integration informal sector for separate collection

Setting up a curb-side collecting system with several refuse bins/bags is to be aimed at, but is - in most cases - not realisable in developing countries for reasons of cost. In a few municipalities, waste and recyclable material collections are practiced using curb-side collecting systems with several refuse bins. As a rule these are then the 2-refuse bin system with separate collections of dry and wet waste or compost and residual waste. In a well-known case, a collecting bin is alternately used for wet and dry waste. A sorting plant is obligatory when implementing a curb-side collecting system. Separating material leads to an improved sorting capability and, as a consequence, to increased utilization rates.

6. Establishing assorting facilities

Sorting the recyclable material left over in waste takes place in sorting plants, which are preferably integrated into or used prior plants for waste treatment before disposal, such as mechanical–biological pre-treatment (MBT) and thermal waste treatment (IP). The target fractions are paper and cardboard, plastics, glass, metals and wood.

Against the background of low personnel costs and the generally prevailing labour policy goal of creating jobs, waste processing and sorting plants are to be adapted to correspond to these conditions. Personnel intensive sorting concepts are to be preferred to automatic process technologies. Other premises ought to be in line with appropriate issue of health and safety at work. As is also the case for separate collecting, the informal sector is to be integrated, e.g., as sorting staff. Flat bunkers are to be preferred for deliveries. This delivery concept offers the possibility of storing specific qualities of waste temporarily in special bunker sections, in order to add them to the waste stream in a targeted manner or to be able to supply to special sectors of the sorting plant. Separating off impurities, contaminants and harmful substances as well as large pieces of recyclable material manually and by using loading devices is also possible. The transfer of the material to the processing and sorting stage can take place by means of wheel loaders or mobile excavators with polyp gribber. In the most simple plants with small processing capacities, a manual approach (shovel/pitch fork) is also practical. Before being handled on the sorting belt the mixture of material ought to be processed with an aggregate for the opening of the bags and agglomerates (bag opener) and a device to separate material (screening stage with sieving section of approx. 80–100 mm). The coarse grain, concentrated on waste packaging, is placed on the sorting belt and sorted manually. The fine grain and the remnants of the coarse grain are taken on to the residual waste treatment.

7. Waste treatment before landfill

7.1. Conceptions

Conventional waste disposal meets its limits throughout most of the world with increasing waste generation and rising proportions of packaging and toxic compounds in MSW. Landfilling of waste leads to pollutant emissions over long periods of time and requires sophisticated emission control and treatment methods. The consequences are long after-care periods for abandoned landfills. Furthermore, in many countries it is increasingly more difficult to find suitable locations for landfills which are accepted by the population. These circumstances are to be found all over the world and make new strategies for waste management necessary. The promotion of waste minimisation and recycling are important components of modern waste management strategies. Nevertheless, even when the minimisation and recycling potentials are fully exploited, there is still a residual fraction which has to be disposed of. The burdens resulting from landfilling can be minimised by pre-treating the waste and thus limiting its emission potential. Several options are available for residual waste treatment:

- Mechanical–biological pre-treatment (MBT) of residual waste
- Thermal waste treatment (IP)

The selection of a treatment process suitable in a specific case results from the financial and infrastructural framework conditions, the waste quantities and, above all, the waste composition. Due to the relatively low costs, the high flexibility of the process and the possibility of centralised and decentralised application, MBT processes are gaining importance also in developing and threshold countries. With waste treatment of MSW before landfilling, the following objectives can be attained:

- Minimisation of landfilled masses and volume (e.g., prolonged landfill life-span)
- Inactivation of biological and biochemical processes in order to avoid landfill-gas (Greenhouse Gases) and odour emissions
- At the same time landfill settlements are reduced
- Immobilisation of pollutants in order to reduce leachate contamination
- Recycling efforts, e.g., the separation of recyclable fractions, fractions with high calorific value or the production of landfill construction material could and should be integrated in the treatment process if there is a demand for these materials.

7.2. Climate-relevants

Methane is generated during final disposal of waste management as a consequence of anaerobic decay of organic waste components. Basically two options exist to avoid methane emissions: On one hand active degasification of the landfill with subsequent flaring of LFG (landfill gas). On the other hand the stabilization of organic compounds in a biological treatment facility prior to landfilling aiming on a significant reduction of long term decay processes. Both options vary in terms of efficiency, sustainability, costs and potential CDM-revenues (Figs. 7.2.1 and 7.2.2).

The landfill degasification requires significant less invest and shows lower operational costs. However, the effect regarding gas recovery is limited, common collection hardly rarely exceed 50%, while a significant portion of LFG disappeares via the landfill surface. Additionally, flaring meets a technical bottom line with decreasing methane concentrations. The entire system of LFG is poorly sustainable, because the source of methane generation, i.e., the degradable organic matter is not removed.

Biological pretreatment in MBTs and digesters is the alternative. By means of spending more financial efforts, organic components will be stabilized prior to landfilling, what applies the same way to incineration plants. Biological decay processes, which otherwise happen inside the landfill will be carried out in advance under controlled technical conditions and in significantly reduced time. Hence, the gas generating processes will be sustainably reduced or even entirely avoided. The difference in terms of climate relevance of both methods becomes obvious when evaluating the potential gas emissions from landfilling.

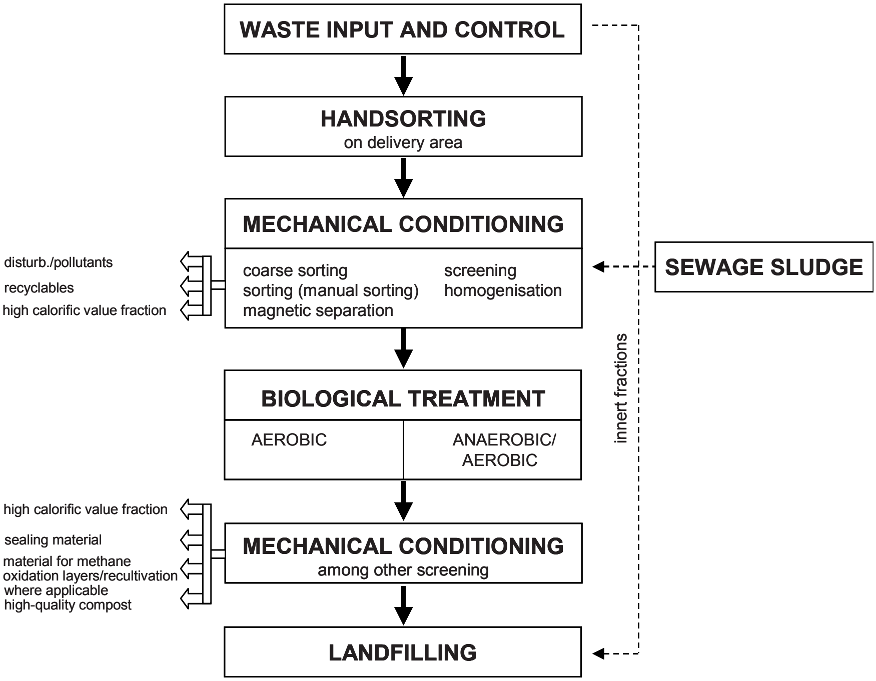

Fig. 7.2.1. A typical mechanical-biological waste treatment sequence.

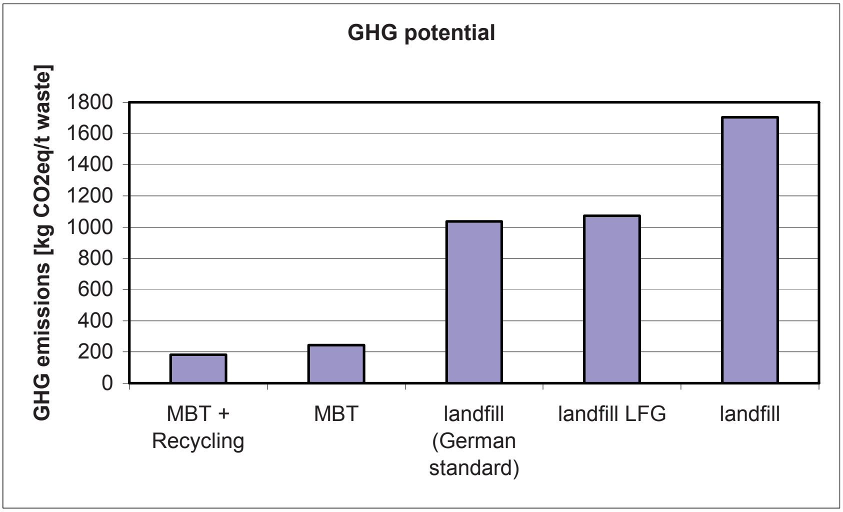

Fig. 7.2.2. GHG potentials by different waste management activities.

7.3. Clean development mechanism (CDM)

Generally waste management activities generate Greenhouse Gases, both methane (landfills) and CO_2. Therefore, improvements in waste management may result in significant reduction of GHGs. According to data from German Federal Ministry of Environment in former times 36% of total methane emissions in Germany are related to landfills. Between 1990 and 2004 numerous measures like landfill closures, reduction of waste for disposal and utilization of landfill gas have been implemented in Germany. In total methane generation has been reduced by 21 Mio. t CO_2eq, what is equal to 50% of the reduction goals of German industry between 1998 and 2012 (45 Mio. t). The ministry still has identified a reduction potential of another 12.4 Mio. t CO_2eq just in German waste management. Considering the poor technical level of the waste management systems in low income countries, it seems obvious that the potential for emission reduction is huge.

Climate relevant waste management projects may be registered as emission reduction projects, according to the regulations of the UN-Framework Convention on Climate Change. Beside the political-symbolic aspect this measure has also significant economic criteria. CERs (Certified Emission Reductions) are to be produced and sold to the international market, to lift the total profitability of the project over a critical investment threshold. The legal basis of Certified Emission Reduction (CER) trading is the Article 12 of the Kyoto Protocol, called the Clean Development Mechanism (CDM). The CDM mechanism allows industrial nations to meet their quantitative reduction goals for greenhouse gas emissions by carrying out emission reduction projects in developing countries. The trading market for the CERs is basically governed by European legislation and its conversion to the member states. Particularly the EU emission trading system with its participants from energy-intensive enterprises and power plants offer the opportunity to pool the CERs into the EU-system and to sell them to other participants. The Federal Republic of Germany administrates the national conversion of the EU guidelines by the Project-Mechanism-Law (ProMechG, Project-Mechanism-Law). The law permits operators of large power plants to cover up to 22% of the granted emission rights in the period 2008–2012 by emission certificates from Kyoto projects. That corresponds with approximately 90 million tons of CO_2-equivalents per year in Germany.

In accordance with Article 17 of the Kyoto protocol CERs from climate protection projects may be also subject to national purchase programs of countries, which may accomplish a part of their obligations to reduce greenhouse gas emissions. States like, e.g., the Netherlands, Austria, Japan or Spain are strongly involved with national purchase programs from CDM projects. Currently CERs from CDM projects are traded in the European Union market and in national purchase programs for approx. 8–10 €/ t CO_2-equivalent, on basis of future delivery obligations (*forward contracts*). A third option for carbon trade is provided by the voluntary market for the compensation of CO_2-emissions. By investing in emission certificates from climate protection projects, unavoidable emissions may be compensated and neutralized, like for flights, fair meetings or production enterprises. The price is self regulated by the market and reflects the quality of the projects and the demand of the market.

Within the validation process the emission reduction process will be monitored, validated and finally certified. For the approval as a climatic protection project it requires several steps involving various institutions. The process opens with compiling a draft report, the so called PDD (Project Design Document). The PDD explains how and in what amount the greenhouse gases are going to be reduced. Beyond the technical concept other project-relevant aspects such as additionality, sustainability, environmental impact and socio-economic benefits are addressed in the PDD. One important element of the PDD is the monitoring concept, which facilitates how real greenhouse gas reductions during the lifespan of the project later will be determined. The project presented in the PDD must be officially validated by an independent UN-accredited institution (a so called DOE, Designated Operational Entity). At the same time the host country is requested to approve the project. After the validation by the DOE and the "Kyoto permission" of the host country's authorities the project can be submitted for registration at the UNFCCC. A registration is finalized automatically after 8 weeks, if no veto is inserted by the expert panel of the CDM executive board.

Generally, CDM projects may be acknowledged and registered only in case the meet the so called additionality-criteria. In order to prevent from "stick-in effects", it must be ensured that the designed project faces certain barriers, which would not be overcome without the CDM implementation. The additionality can be proven economically (e.g., lack of profit) or by outlining technical barriers. After establishing the MBT-plant, the real avoided emissions will be measured and calculated as determined in the approved monitoring concept, then verified by a further DOE and registered as CERs at a temporary account of the UNFCCC. Then the CERs can be transferred to accounts of international buyers. In waste management are two large groups of potential CDM projects:

- Directly reduction of the generation of methane
- Improvements in energy efficiency

There are a number of measures to improve the energy efficiency of waste management activities, such as material recycling instead of energetic reutilization or substitution of fossil energy resources and so on. Compared to direct methane reduction those measures are technically more complex and economically less reasonable. Most activities take place in industrial countries. Direct reduction of methane generation or emission shows a significantly larger potential for CDM due to the poor present emission situation. Basically 4 different project activities may be attractive for CDM:

- Gas extraction and flaring/recovery for old, existing and new landfill sites
- Methane avoidance due to mechanical biological pre-treatment

- Methane avoidance due to composting activities
- Methane avoidance due to methane oxidation of residual emissions from old landfills

For all components except the last one consolidated methodologies are available from UNFCCC. For the methane oxidation a new methodology is expected to be registered at UNFCCC in the near future. Since there is a quick progress in developing CDM methodologies, more project ideas may be expected.

7.4. Landfill gas projects

LFG projects were the first CDM projects in waste management at all. One reason is that LFG projects promised to be highly reasonable with significant revenues from CER trading contributing to up to 80% of total project costs. Meanwhile LFG projects are state-of-the-art; all landfills in metropolitan areas are object to contracts and purchase agreements. However, all LFG projects under perform. From 13 early registered projects, 7 obtain less than 60% of the expected reductions, the other 6 less than 30%. It does not require extraordinary technical excellence or expensive western experts to compile a LFG CDM-project. The procedure may follow the consolidated UNFCCC methodology ACM0001. However, getting a project approval from UNFCCC does not necessarily mean CER revenues, because at first the gas needs to be extracted from the landfill. And this may become a tough task, particularly in tropical countries.

7.5. Composting and mechanical biological treatment (MBT)

Uncontrolled methane emissions that would occur at a waste disposal site are avoided by the biological stabilization of the waste. Stabilized biomass (SB) does not (or to a smaller extent only) turn into anaerobe condition when disposed to a landfill. Hence, the methane generation and emission will be significantly smaller. The CDM application for a MBT will be compiled using applied methodologies (AM0025), the PDD template, its guidelines to fill in, as well as calculation tools. All can be downloaded on the Website of the UNFCCC. The compiled Small Scale PDD consists of the following main topics:

- A description of the project with its effect for climate and sustainable development
- Determination of the reference scenario without the project (baseline)
- Calculation of the baseline emissions, project emissions and emission reduction which can be expected (ex-ante)
- Monitoring concept with calculation methods for the verification of the real greenhouse gas reductions based on measurements (ex-post)
- Demonstration of the project additionality
- Environmental impact analysis including local stakeholder’s comments

The methodology AMS III.F (Avoidance of methane production from decay of biomass through composting) provides the base of the baseline study and the monitoring concept for a MBT project. For calculations a useful tool is separately available, the "Tool to determine methane emissions avoided from dumping waste at a solid waste disposal site". In the greenhouse gas balance of the entire project, the emissions which result from the project activities are considered as a negative impact. Total CO_2 emissions of engines and electric machines are summarized and balanced with the baseline emissions, which are the avoided CH_4-emissions from the waste disposal. The calculation algorithms for both scenarios - baseline and project – are to a certain extent determined by the existing methodologies and tools. For the calculation of the virtual methane emissions due to waste disposal, a biological degradation of the deposited waste is simulated over several years by a layer model. With this model the highest methane emissions in a layer emerge during the first years and decrease in the subsequent years. Table 7.5.1 illustrates the preliminary calculation of the emissions for the MBT project Gaobeidian (China), a facility with a capacity of 40,000 t, for a period of 10 years.

Table 7.5.1. Emission calculations of the MBT Gaobeidian.

Year	Project emissions [t CO_2eq]	baseline emissions [t CO_2eq]	Emission reductions [t CO_2eq]
2008	497	2,339	1,842
2009	537	4,376	3,839
2010	577	6,156	5,579
2011	616	7,714	7,097
2012	655	9,081	8,426
2013	694	10,284	9,590
2014	732	11,345	10,613
2015	770	12,283	11,513
2016	807	13,114	12,306
2017	845	13,852	13,007
Total	6,729	90,541	83,812

The forecasted generation of emission certificates amounts to 83,812 t CO_2-equivalents for the project period 2008–2017. Presently, due to Kyoto regulation certificates are only tradable until 2012. In this period CERs of 26.783 t CO_2-equivalents may be generated. Based on current rates, CDM revenues 210,000 and 250,000 € may be expected. The calculations of benefits represent an estimation based on the emission reductions which are expected. Real revenues may differ clearly depending on the plant capacity, the waste composition and on the trading rate of the certificates. In the context of the monitoring process, all data that were used for the calculation of the emissions, if not constant, have to be determined or measured ex-post, in order to obtain the actual emissions during the lifetime of the project. Data comprise of, e.g., the power and fuel consumption, as well as the waste composition, which has to be monitored several times in the year.

7.6. Methane oxidation layer

A methane oxidation layer (MOL) is placed on top of an existing dumpsite in order to turn methane emissions passing through the layer into CO_2. From this point of view a MOL has the same effect as a LFG system (collection and flaring/ oxidation). However, the emission reduction cannot determine in the same matter like with LFG projects, because the amount of methane oxidized in the MOL cannot be monitored directly (like in a LFG project next to the flare). Just an indirect monitoring might be possible. Therefore, the central parameter describing the gas generation (and flux) as given in the baseline formula of the UNFCCC-tool may be monitored at two different locations, one with and one without MOL. The general concept for the MOL verification is not to rely on virtual emissions (from model calculation) but to monitor the baseline emissions in a testing area.

MOLs can be constructed using SB or compost or similar blended materials. Therefor, it is easy to combine a MOL and a MBT project. Total CDM revenues from MOL may be small, but maintenance and operation costs for a MOL are heading towards zero, what makes it generally reasonable.

8. Conclusion

At present, develop and emerging market countries increase their efforts to handle waste management and waste disposal issues. A number of measures are available and have been pointed out starting from source separated collection up to more climate friendly waste treatment and disposal methods. The various options have distinguished relevance and feasibility depending on the geographic and climate conditions in the countries. Currently, recovery of recyclables is the most reasonable activity due to booming markets for secondary resources. Recovery can be carried out by either establishing material recovery facilities (MRF) or source separated collection (SSC). However, it should be noted that markets for recyclables are volatile and may be subject to quick changes. The reuse techniques for the recyclables are object to future developments increasing material reuse aiming on significant savings of primary energy. This progress may increase the attraction of advanced recycling technologies. Regardless to what extent the recycling activities may be improved residual waste needs to be disposed. Dumping of untreated waste is still the most common disposal policy in emerging market countries. Various biological treatment technologies for residual waste are available such as aerobic MBT. In the past valuable but non monetary benefits could be materialized with MBT facilities, in particular landfill airspace savings and reduction of emissions on water and atmosphere. Since the establishment of the CDM, the reduction of methane emissions may be turned into so called Certified Emission Reductions (CERs) which are tradable and may be cashed in. With this additional funding investment barriers may be cracked at least for low cost technical solutions. Hence, it can be expected that CDM will push the waste treatment as measure prior to landfilling and will contribute significantly to a cleaner environment.

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PART V. RISK ASSESSMENT, MITIGATION MEASURES AND ENVIRONMENTAL AWARENESS

ESTABLISHMENT OF THE STRATEGIC ENVIRONMENTAL ASSESSMENT (SEA) SYSTEM IN THE REPUBLIC OF MOLDOVA

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Abstract. Sustainable development cannot be achieved without a sound environmental policy and management system. Strategic Environmental Assessment (SEA) is a systematic process that integrates environmental considerations into decision-making and can be used as an efficient environmental management tool. The objective of this paper is to describe a coherent approach for establishment of the SEA system in the Republic of Moldova. The 2005 EU-Moldova Action Plan envisages the adoption of additional legal acts for key environmental sectors, based on EU environmental acquits and, therefore, the creation of further national legislative framework is essential. Currently, the existing system of environmental assessment in the Republic of Moldova is accomplished by two activities: state ecological expertise and environmental impact assessment (EIA). The establishment of SEA can be done in one of two ways: (i) amending the Law on Ecological Expertise and Environmental Impact Assessment, or (ii) drafting a new Law on SEA. Moreover, there is no specific structure dealing with SEA, except the Focal Point for Espoo Convention. In order to comply with the provisions of the SEA Protocol and Directive, the Republic of Moldova has to designate a Competent Authority for Environmental Assessment that will deal with EIA and SEA. This can be done in one of three alternative ways: (i) to establish new institution subordinated to the Ministry of Environment and Natural Resources of the Republic of Moldova (MoENR), or (ii) to establish new department within the MoENR, or (iii) to reorganise functions and responsibilities of existing departments of the MoENR.

Keywords: sustainable development, Strategic Environmental, Assessment ecological expertise, environmental impact assessment.

1. Introduction

Sustainable development has become a major concern for policy makers and planners in both developed and developing countries. From the environmental point of view, this would not be achievable without a sound environmental policy and

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management system. UNEP [19] has proposed integrating Strategic Environmental Assessment (SEA) and an Environmental Impact Assessment (EIA) for sustainable environmental management.

Interest in SEA in Europe and elsewhere has grown out of both an acceptance of the fundamental principles at the heart of EIA and a recognition of its inherent limitations [21]. SEA is a systematic process that integrates environmental considerations into decision-making and aims to achieve sustainable development [3, 11]. SEA is becoming an accepted and widely used instrument for integrating environmental issues into the formulation of policies, plans and programs [1, 5] and can be seen as a process that informs planners, decision makers, and the affected public about the sustainability of strategic environmental decisions, facilitates the search for the best alternative and ensures a democratic decision-making process.

Directive 2001/42/EC [8] on ‘the assessment of the effects of certain plans and programmes on the environment’ required Member States to introduce the laws, regulations and administrative provisions. The justification for issuing a Directive on SEA is that the resulting systematic legal framework will enable EU Member States ‘‘to provide for a high level of protection of the environment and to contribute to the integration of environmental considerations into the preparation and adoption of plans and programmes with a view to promoting sustainable development’’ [4, Article 1]. The Directive aims to ‘achieve greater integration of the environment in sectoral policies, whilst exacting a minimum assessment of the plans and programmes that are likely to have an environmental impact before they are adopted’ [14, p. 5]. Such a Directive provides a comprehensive basis for the appraisal of plans and programmes through compliance with a minimum set of procedures, including the provision of an environmental report, consideration of alternatives, consultation and public participation, inclusion of recommendations, and monitoring and review mechanisms.

The Republic of Moldova is neighbouring EU and signed SEA Protocol in 2003. The purpose of introduction of SEA system is to achieve compliance of future activities of strategic planning in the Republic of Moldova. The objective of this paper is to describe a coherent approach for establishment of the SEA system. When it comes to SEA legislation, trans-boundary consultations are mandatory, as well as compatible legislation in force, particularly because this is also covered by a trans-boundary Convention ratified by Moldova (Espoo Convention). Also, there is very little common approach across sectors between environmental management and the management of other economic sectors. So far, while developing strategic documents, the environmental consideration is not included in the Republic of Moldova. Therefore, the creation of further legislative framework is required. The 2005 EU-Moldova Action Plan envisages the adoption of additional legal acts for key environmental sectors, based on EU environmental acquits.

2. Analysis of the SEA EU directive and SEA protocol of the Espoo convention and best international practices

Consideration of a strategic level assessment system in the EU originated as early as the 1970s, and research to facilitate the drafting of a SEA Directive was undertaken for the European Commission in the early 1990s [20]. The Directive 2001/42/EC on the assessment of the effects of certain plans and programmes (P/Ps) on the environment was adopted in 2001 by the European Parliament and Council and entered into force 3 years later. The Directive requires three major SEA inputs to be taken into account in decision-making: (1) the environmental report; (2) the consultation responses of the public and 'authorities', and (3) the consultation responses of other Member States where appropriate [17]. The SEA Directive specifies which P/Ps should be subjected to SEA.

The proposed Directive represents a welcome commitment to the need for a higher level of environmental assessment. Though there are identified some positive and negative features of the SEA Directive. *Positive features* could include the following: (1) it covers a wide range of sectors; (2) it also makes a reasonable emphasis on the entire SEA process, rather than just on the preparation of a report; (3) it emphasizes alternatives; (4) it requires monitoring of the plan's actual effects, which will help to improve following SEA [17]. Nevertheless, there are some *negative features* of the SEA Directive: (1) it applies only to 'certain' plans and programmes, and thus does not refer to policies; (2) the Directive's rules for deciding which of the strategic actions require SEA, are very complex.

The Protocol on Strategic Environmental Assessment (SEA) to the Espoo Convention was adopted on 21 May 2003 in Kiev – Ukraine, which will enter into force after being ratified by 16 Parties. It applies the principles of the Espoo Convention to plans, programmes, policies and legislation. The aim of the SEA Protocol is ' *… to provide for high level of protection of the environment, including health: (1) by ensuring that environmental, including health, considerations are thoroughly taken into account in the development of P/P; (2) by establishing clear, transparent and effective procedures of SEA; (3) by providing for public participation in SEA; (4) by integrating environmental, including health, concerns into measures and instruments designed to further sustainable development*' (Art. 1). Once in force the Protocol will require its Parties to evaluate the environmental consequences of their official draft P/Ps. The Protocol also provides for extensive public participation in government decision-making in numerous development sectors.

Compared to the SEA Directive, the Protocol opens a space for the application of SEA for policies, though the application of SEA to these is not mandatory, and it also emphasizes the integration of the human health issues in the assessment. Certain provisions of SEA Protocol (not yet in force) do not exist in the SEA

Directive, such as: procedural phases; public information and consultation on scoping phase, etc. Under the Protocol ‘strategic environmental assessment’ means ‘the evaluation of the likely environmental, including health, effects which comprises the determination of the scope of an environmental report and its preparation, the carrying out of public participation and consultations, and the taking into account of the environmental report and the results of the public participation and consultations in a plan or programme’. Ultimately, the requirements of the SEA Protocol are mostly aligned with EU Directive (2001/42/EC). Its ratification and implementation may not provide significant additional benefits for EU member states, as well as accession and candidate countries. At the same time, the Protocol may have more relevance for the EECCA countries of the former Soviet Union, which currently do not participate in any international SEA regime.

3. SEA capacity development in countries in transition

Capacity development should facilitate systems by promoting networking and ability for critical learning [16]. An often-overlooked aspect of capacity and ability of a capacity development initiative to succeed is a resistance to change. Generally, it results in the lack of ownership or in a fear of loss. Therefore, organizations should have capacities that anticipate resistance, identify and measure its extent, and introduce mitigation measures [18]. Partidario [13, p. 658] defines three priorities for SEA capacity development: (1) improve SEA focus on decisions and SEA relations with decision-making; (2) improve communication skills and mechanisms in SEA; (3) make SEA attractive and increase win–win opportunities. SEA capacity development helps to facilitate in-country discussion on SEA, raise the awareness of developers, authorities and the public. To overcome the institutional resistance it is necessary to develop the capacity development strategy with key stakeholders. It should be mentioned that capacity development should evolve systematic strategies and should be based on a balance between international and domestic experience. At the final step the monitoring of effectiveness of capacity development should be conducted.

As mentioned by Sadler [15], ‘*an EA process can only be understood and evaluated in relation to the policy and institutional framework in which it operates’*. In this way, it is useful to describe the situation in countries in transition with their specific and constantly changing institutions. The *transition* has often been viewed as having three key dimensions: *geopolitical* (from structures dominated by the USSR to those involving independent nations integrated into various alliances), *constitutional* (from totalitarian to democratic political systems), and *economic* (from centrally planned to market economies) [9, 6, 12]. The process of transition has significantly influenced the evolution in EA systems. In response to changing of social conditions, most of the transitional countries undertook the reforms of their EA systems in the late 1980s - the early 1990s [2]. The EA development in the countries in transition includes three stages: (1) *initial reforms of EA systems* (from 'socialist environmental appraisals')*;* (2) *diversification of EA legislation;* (3) *adjustment of EA legislation and practice* [7]. The procedure for the EA development in the countries in transition is determined by two types of factors: (1) internal (the process of transition); (2) external (i.e. European Union's provisions). SEA implementation in the countries in transition is especially relevant. Firstly, many strategic documents with significant environmental impact are being made. Secondly, the changing institutions present opportunities for introducing new procedures of environmental decision-making. As mentioned by Cherp, many transitional countries have legal SEA requirements, sometimes even more 'progressive' than the Western countries have. However, these 'progressive' provisions are not always implemented in practice.

4. Analysis of the existent legal and institutional framework in the Republic of Moldova with regard to environmental assessment

4.1. Legal framework

Legal basis for SEA varies in countries and includes Laws on Environmental protection, Laws on State Environmental Review, Law on Environmental Permitting and Laws on Environmental impact assessment [10]. The national environmental laws in the Republic of Moldova do not foresee the mechanisms that a SEA procedure may be applied. Moreover, the SEA system, which would meet the requirements of the Protocol and SEA has not been elaborated and there is no direct mention about the SEA concept. Currently, the existing system of environmental assessment is accomplished by two activities: state ecological expertise[1] (SEE) and environmental impact assessment (EIA). SEE is mandatory for plans and project documentation of the objects and types of planned economic activities, which have or are likely to have environmental impact and which foresee the use of natural resources, irrespective of their purpose, location, type of property, and departmental subordination of these objects or activities. Ecological expertise is accomplished by several structural sub-departments and organizations, subordinated to the Ministry of Ecology and Natural Resources (further Ministry). The SEE could be carried out by one or another structural sub-department depending on complexity of the object and the level of its influence upon the environment. Public associations are also involved in the process of analysis. Thus, SEE can also be carried out by sector and non-governmental organizations. Results of these analyses are only recommendations until the Ministry approves them. SEE takes into consideration the conclusions of the state sanitary – epidemiological inspection and other

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[1] State Ecological Expertise = State Ecological Examination or Analysis, further SEE

state bodies that have the ability to effectuate supervision and control. New objectives and types of activities, which are likely to have essential environmental effects, are designed based on EIA documentation and are subject to SEE.

The list of objectives and types of activities, for which the EIA documentation is necessary, must be developed and legally approved before they are designed. EIA documentation is worked out at the first stage of planning and represents a compulsory component of plans and project documentation. The main procedures of the EIA are to effectuate the assessment, examination and coordination of the documents, SEE and decision-making. Law requires public participation in the EIA. State authorities, as well as NGOs, planning institutes, other specialized organizations and independent experts are also involved in the process of analysis. In 2003 addendums on SEE plans, programs and strategies were introduced in national legislation. Thus, the Law on Environmental Protection, especially Art. 23(1) stipulates that ‘Analysis is mandatory for new programmes and projects focused on economic and social development of the republic, separate zones, districts (rayons), municipalities, towns, communes (villages); reconstruction of municipalities, towns and communities (villages); water, gas, energy supply; development of sewerage network/system in settlements; housing and territorial development.’

The second part of Article 23 provides that ‘The Statement of programs and the projects stipulated by sub-items (a)–(j) parts (1), their financing and realization are allowed only with positive examination and under the condition of the observance of its recommendations’.

Article 6(2) of the Law ‘on ecological expertise and environmental impact assessment’ no. 851, dated 29.05.1996 with further changes and amendments says that ‘State environmental analysis is mandatory for: (c) new projects, programmes, plans, schemes, strategies and concepts’.

Article 16(2) of the Law also provides that upon the decision of central authority for natural resources and environmental protection, the EIA procedure is mandatory for strategic documents on the development of the national economy and other objects and activities depending on the expected level of environmental impact. This Law stipulates the ‘Public ecological analysis shall be carried out as well’. National legislation foresees public participation in the decision-making process and in the process of developing the laws, regulations and national programs, etc. regarding issues on environmental protection. The main legislative acts are:

- The Regulation on public participation in decision-making process regarding issues on environment protection, approved by Government Decision no. 72 from 25.01.2000.
  - ➢ Chapter II ‘Public proceeding in decision making process regarding the development of laws, programs and other normative statements’
  - ➢ Chapter IV, item 17 ‘Public participation in the process of development of national projects and programs related to social-economic development, that foresees use of natural resources that have a significant impact on the environment, mandatory’

  - ➢ Chapter V, item 20, ‘Public participation in the process of developing the laws, regulations and decision making for national projects, projects with trans-boundary effects and other laws and regulations.’
- The Regulation on public consultation in the process of development and approval of territorial development and housing documentation approved by Government Decision no. 951 dated 14.10.1997.
- The *Law ‘on ecological expertise and environmental impact assessment’* no. 851, dated 29.05.1996 (Chapter III ‘Public environmental expertise’ Art. 9 – 12, Section VI. Participation in EIA of NGOs and temporary public associations for solving problems.)

In practice, carrying out SEA plans, programs and strategies according to the requirements of the Protocol was not accomplished. Assessment of these strategic documents (strategies, programmes, plans, laws, and others) was made by examination and conclusions of the Ministry of Ecology and Natural Resources and other ministries and departments that analyse and issue notes on these documents.

The procedure for coordination of draft laws and regulations is established by the following document:

- Government Decision no. 1104 from 28.11.1997 ‘On the procedure for legal assessment and state registration of regulations of the departments’
- Government Decision no. 128 dated 05.92.1998 ‘On approval of the rules for developing of regulations’
- Law no. 317-XV dated 18.07.2003 ‘On Government and other central and local public authorities’ normative acts’

This Law states that: ‘The interested bodies and departments, to which the project of the statutory act is presented for coordination, directs to the proponent of the project, the conclusion with motivated remarks and offers …’ (Item 40). Article 41 (2) says: ‘By the decision of the body which has prepared the project of the statutory act, as well as the body responsible for its edition, the project is ready for financial, economic, ecological and other kind of examination. Foreign experts and international organizations, the organizations and the citizens who did not participate directly in preparation of the project, can act as experts’. ‘From the legislative and normative documents set forth above, it is possible to draw a conclusion that current legislation already incorporates the basis of SEA realization and the Republic of Moldova has the potential for its creation and development.’

However, for practical realization of SEA it is necessary to make essential additions to: (i) the existing legislation concerning mechanisms and procedures for carrying out the SEA consultations with necessary bodies; (ii) mechanisms of public involvement in the development of SEA for national plans and programs; (iii) Consultations, notification, monitoring; and (iv) methodological guidance in transboundary situations. It can be done in one of two ways: (1) amending the Law on Ecological Expertise and EIA; or (2) drafting a new law on SEA.

As the current EA system neither meets the requirements of the SEA Directives nor interprets the requirements in the light of former ecological expertise, the required amendments will change the spirit of the existing laws quite significantly. In this case drafting a new Law would require less effort than amending the existing one. Actually there is no specific structure dealing with SEA, except the Focal Point for Espoo Convention. In order to comply with the provisions of the SEA Protocol and Directive, a Competent Authority for Environmental Assessment (dealing with EIA and SEA) has to be designated. It can be done in one of three alternative ways: (i) establishment of a new institution subordinated to the Ministry, or (ii) establishment of new department within the Ministry, or (iii) Reorganisation of functions and responsibilities of existing departments of the Ministry.

4.1.1. Establishment of a new institution subordinated to the ministry

The institution will be responsible for organisation of EIA, including trans-boundary EIA, and SEA system in the Republic of Moldova. The institution has to be subordinated to the Ministry of Ecology and Natural Resources and take over current responsibilities of the Department of Prevention of Environmental Pollution and Department of Environmental Policy and European Integration in this area. The Ministry should be the first body to appeal a decision taken by the newly established institution. The Department of Policy Analysis, Monitoring and Evaluation should remain responsible for bilateral cooperation and information exchange on trans-boundary process and results. The MoENR should define which structure would have responsibility for drafting SEA legislation. Pros are (i) an independent institution responsible for EIA and SEA; (ii) efficient and straightforward institutional System. Clear definition of responsibilities; (iii) designed system clear for all involved and interested parties, while cons (i) more administrative resources needed.

4.1.2. Establishment of new department within the ministry

The responsibilities and role of a new Environmental Assessment Department would be as described for a new institution in the above section. The only unclear issue at this stage is what would be an institution to appeal a decision made by the Ministry of Ecology and Natural Resources. The advantages will be that there will be a separate structure responsible for EIA and SEA with clear definitions and responsibilities that will require less administrative resources and disadvantages that the system will not be fully politically independent.

4.1.3. Reorganization of the existing departments at MoENR

The Department of Prevention of Environmental Pollution is in charge of carrying EIA and Department of Policy Analysis, Monitoring and Evaluation is in charge of ensuring the procedures in trans-boundary context. Thus, these units of the Ministry could share the responsibility for EIA and SEA. In this case, the main role should be given to the Department of Prevention of Environmental Pollution, which apart from being responsible for setting emission limit values for air, water and soil as well as air, water and soil quality standards, would be responsible for EIA and SEA process in the Republic of Moldova.

The Department of Policy Analysis, Monitoring and Evaluation would remain responsible for bilateral cooperation and information exchange on trans-boundary EIA process and results. Again, it remains unclear what would be an institution to appeal a decision taken by the Ministry of Ecology and Natural Resources. The advantage is that there will be less administrative efforts to set up an EIA and SEA system and disadvantages will be that the system won't be fully politically independent and it will be more complicated for developers.

4.2. Gap analysis of the national legal system with regard to EU SEA directive and SEA protocol

In order to figure out the gaps for the EA system it should be made a gap analysis for EIA, as between EIA and SEA exists a strong linkage. In Moldova, the whole EA system is based mainly on EIA, which differs from the EIA approach in EU. Thus, it is important to start with the analysis of EIA. There are neither gaps nor contradictions between the draft law presented and the SEA Directive 2001/42/EC. Moreover, the draft law makes detailed provisions for the implementation of the SEA procedure, based on the previously mentioned guidance documents and best practice in the Member States, as well as additional provisions in order to ensure compliance with the SEA Protocol when this will become into force and/or will be ratified by the Republic of Moldova.

It should be noted as well that certain provisions of SEA Protocol (not yet in force) that are not existing in the SEA Directive (such as: procedural phases; public information and consultation on scoping phase, etc.) were also introduced in the proposed draft law. This decision was justified by the planned deadline for the approval of the SEA draft law (in 3 years from now), according to the SEA Strategy of the Ministry of Ecology and Natural Resources. The draft SEA Law is fully compliant with the provisions of SEA Directive 2001/42/EC.

5. Conclusions

Implementation of the SEA procedure requires certain experience and knowledge of involved parties, mainly department or institution responsible for EIA and SEA (Competent Authority). At the initial stage, it will be crucial to build institutional capacity by developing a manual to provide further support in enhancing understanding of the SEA mechanism and application of particular steps of SEA procedure and organisation of training for staff responsible for SEA process.

As nongovernmental organisations and general public also play a substantial role in the SEA process, thus better information to public and capacity building of the NGOs with nation-wide presence would ensure a better and more constructive dialogue during the SEA process. Other stakeholders as sectoral ministries, scientific institutions, administrative bodies and municipalities, which all have to provide relevant environmental information and to be consulted during the SEA process, and to be informed on changing legal requirements.

Finally, the ultimate goal of the SEA is the provision of reliable information on environmental effects of the P/Ps to the decision makers. Consequently, decision makers have to be able to understand and to make use of such information. It is important to explain to the municipal authorities and relevant governmental departments, how implementation of the EU requirements in the field of SEA and SEA Protocol would affect their decision-making practices.

Obviously, there is a critical need for training of the staff of the competent environmental authorities for introduction of the SEA in the Republic of Moldova.

Fortunately, the 3 years transitional period of time before the adoption of legislative and normative framework will allow the preparation of such trainings. However, certain provisions of the draft SEA law are expected to be implemented very soon after its approval, and the environmental authorities need to be trained on these provisions as well. The MoENR plans to adopt this law in 2 years time, after the adoption of the framework law on environmental protection, according to the requirement of this new law.

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BIOSENSORS IN THE SYSTEM OF EXPRESS CONTROL OF CHEMICALS, REGULARLY USED AS TERRORIST MEANS, TO PREVENT NON-DESIRABLE CONSEQUENCES

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Abstract. Instrumental analytical devices were developed for the control of environmental toxicity of objects and determination of group of toxins present in contaminated materials, and revealing of the individual toxic substances are shortly characterized. Among the latter the main attention is paid to pesticides and some detergents, especially nonylethoxylates, and mycotoxins.

Keywords: biosensors, electrolyte-insulator-semiconductor structures, pesticides, detergents, mycotoxins.

1. Introduction

Scientific-technical progress gives a lot of new possibilities to sharply improve the life of people. Unfortunately, at the same time it brings a number of difficulties for human beings, which could be overcome with specific measures for the adaptation of living organisms to new conditions. First, it means the application of very wide spectra of chemical substances. For example, pesticides are the essential part of the modern agro-technologies. Due to their use one has the possibility to keep 50% of the crop capacity. However, as a consequence of high pesticide toxicities a complex system is needed to eliminate their negative effects, and first of all, a constant control of these substances in different classes of environmental objects is needed. The traditional approaches for pesticide detection, which are based on spectrophotometric, chromatographic and mass-spectrometric methods require the use of complex and expensive devices, they are labor-intensive and time consuming. Also, for certain purposes their sensitivity and specificity are insufficient. All these drawbacks may be overcome with application of enzymatic or immune-chemical methods.

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Today, methods were developed for the immune analysis for more than 50 pesticides. Although the transfer to the immunochemical analysis provided a better level of rapidity, the further reduction of analysis duration is needed. A further progress in pesticide control methods is connected with the development of technology based on the principles of biosensors [8, 9, 18, 19, 35–44, 47, 52, 53, 55, 56, 57].

Another aspect of the production of chemical substances is their application as detergents in different fields of human activity and especially in domestic use. Usually they do not have direct toxic effects but after their biodegradation some of these substances may form so-called "endocrine disrupters". Nonylphenol ethoxylates (nPhEthO) are one of group of such substances [45]. The last third group of chemicals belongs to the biological weapons and may be used by bio-terrorists [11, 47]. In all cases it is necessary to have the instrumental analytical equipment for the express, sensitive and simple monitoring of the contamination of environmental objects with certain toxins. Among the possible agents for bio-terrorist action three groups can be identified: chemicals and biochemicals, pathogenic microorganisms and viruses, as well as radioactive materials. Nevertheless, due to a very big danger, which pathogenic microorganisms and viruses present not for the victims only, but for the community of terrorists too, and due to the very limited availability of radioactive materials, it is most probably that chemicals and biochemicals will be the most attractive target for bio-terrorists.

Certainly, to prevent the non-desirable effects and to perform this monitoring effectively, a family of biosensors was developed. First of all, it is intended to use for the determination of general toxicity of analyzed objects, then to reveal, which group of toxins is present in the contaminated material, and finally, to discover the individual chemical substances. This article is devoted to the analysis of biosensors created by the authors. The results of analysis (especially mycotoxins) depend on the conditions of sample preparation, so the consideration of this aspect will be done at the beginning of this article.

2. General information about biological weapons (BW)

BW now attract the attention of the people, in particular because of their possible use by bio-terrorists. They were first used in very ancient times, beginning with the treatment of arrowheads by poisons of plants or animal origin. The history knows different cases of toxins and some pathogenic microorganisms used in military confrontations. Here, attention will be paid to the use of mycotoxins. They were used from 1975 to 1983 in some countries of South Asia in the form of "yellow rains" [23]. As a consequence, an increased level of some trichotecenes and polyethylene glycol in soil was detected. It is well known that T2 toxin may be dissolved and simultaneously evaporated together with organic solvents [50].

It is worth to mention that in contrast to pure chemical weapons, which use requires big reserves, some types of BW are self-reproducing, for example, one bacterium dividing once during 20 min may form up to 10^9 colonies in 10 h. That is why the availability of small initial biomaterial may accumulate a very large volume of dangerous materials by means of biotechnology. Due to this fact, all countries organized special centers (e.g., Center for Disease Control in USA), which accomplish the hard control of storing and using of biological substances, which may be used by bio-terrorists. Among the mycotoxins, the most attractive ones may be T2 toxin and aflatoxin. During cultivation *Fusarium tricinctum* may form about 9 g of T2 toxin per 1 kg of solid or liquid substrate with a final output of a crystalline product of about 2–3 g/kg [3, 5, 24]. This toxin is unique. Its toxicity is 400 times higher than of yperite [2, 21].

Existing methods of trichotecene (T2 toxin) analysis may be divided in two main groups: biological and physical-chemical tests. In biological tests different biological objects are used – from living vertebrates to cell cultures. Unfortunately biotests have a lot of disadvantages since they demand a long time and special labor techniques for analysis. Moreover, they are usable for the concrete type of control only. Physical-chemical methods are based on the use of thin-layer chromatography (the sensitivity is 2–2.5 mg/mL), gas-liquid chromatography (10 ng/mL), radioimmunoassays (2–5 ng/mL), immunochemical analysis (2–50 ng/mL), mass-spectrometry with gas liquid chromatography (1 ng/mL) and mass-spectrometry with high performance liquid chromatography (0.01 ng/mL) [1]. Notwithstanding the high sensitivity of the developed methods, it is necessary to find such approaches, which allow performing analysis during a very short time or in the on-line regime. In the real perspective, the creation of these methods may be based on the involving of biosensor principles.

2.1. Peculiarities of the samplING at the screening of mycotoxins in environmental objects

More than 150 trichotecenes were identified, among them T2, dexynivalenol, vomitoxin, and anhuidin are the most toxic ones [29]. Except of *Phusarium,* the trichotecenes are produced by such mixomicetes as *Trichoderma, Stachybotrys* òà *Cepalosporium* [48]. *F. sporotrichioides*³ *F. poae* are primary producers of T2 [25]. For the most animals the semi lethal dose of T2 is 5 mg/kg body weight (bw) [26] although the biochemical indexes of brain may be changed already at the dose of 0.1 mg/kg bw [6]. According to the legislations of some countries and commissions of FAO/WHO the permissible concentration of T2 was established on the level of 0.1 mg/kg bw [51]. Taking into account the above mentioned toxicity values and permissible concentrations of mycotoxins, it is necessary to extract and analyze these substances from environmental objects as sensitive and efficient as possible, in order to prevent their loss during the sample preparation. For the identification of the type of the respective mycotoxin it is enough to correctly choose the contaminated places but for the estimation of the contamination level the samples should be mixed up to a homogeneous state.

2.1.1. General principles of sample preparation

Some mycotoxins are soluble in water, polar-, or non-polar solvents. As a rule, solutions of mycotoxins are concentrated by vacuum evaporator. For the extracts containing the different metabolites of T2 mycotoxin the concentration should be performed at the low pressure [54]. Then the sample is transferred on a column with XAD-2 amberlyte followed by elution with methanol. At last, the sample is transferred into the Florisil column and elution is accomplished by a mixture of chloroform and methanol at different ratio, depending on the set of T2 metabolites. The similar procedures are carried out with other mycotoxins but sometimes additional procedures are included, namely, extraction with 50% water saturated methanol, or 1:4 of their ratio, or introducing of acetone in the mixture of water-methanol (in the ratio of 1:2.5). The extract may be dried, dissolved again and treated with chloroform [13]. For the extraction of mycotoxins from corn it is proposed to use 40% of a water-methanol mixture with the ratio of solvent to sample equal to 2:1 [49]. For this purpose, other authors used mixture of acetonitrile with water (5:1) [17]. It is recommended to apply the extraction of some trichotecene mycotoxins from rice by 70–100% with methanol which is later removed by ethyl acetate [4]. The last solvent is used for the extraction of aflatoxin, ochratoxin, searelenone, T2, and total set of trichtecenes [16]. Then, the obtained extracts are treated using some additional procedures in order to purify the sample for analysis.

3. Biosensors for the control of total toxicity of environmental objects

For this purpose, the authors developed optical biosensors based on the application of *Daphnia magna* St. (*Cladocera*) and bioluminescent bacteria from Azov and Black seas as sensitive organisms.

It was demonstrated that 1–5 *Daphnia* individuals only are sufficient for the experiments [14]. The chemiluminescence (ChL) of the medium was registered in the presence of luminol and H_2O_2. Stationary, semi-portable and portable devices supplied with optrods, high sensitive photomultiplier, or photo resistors were created for the determination of the intensity of ChL. Potassium dichromate was used as standard, and its toxicity was checked by the generally accepted method (according to index of *Daphnia* immobilization) and biosensor based on the determination of level of ChL *Daphnia* living medium. It was stated that the generally accepted method allows to reveal 0.1 mg/L of potassium dichromate as minimum level. At the same time the sensitivity of the proposed biosensor was almost two orders higher [20]. It is worth to be mentioned that the overall analysis time was very different in both cases (about 24 h for the generally accepted and 30 min for biosensor methods, respectively). The detection range of the T2 toxin by the generally accepted method was about 0.01–0.1 mg/L. At the same time, in case of biosensor method this range reached from 0.001 to 1 mg/L. As for patulin, there was a possibility of its quantitative determination by the biosensor method within 0.001–1 mg/L [12, 28].

Photobacterium phosphoreum K3 (IMB B-7071), *Vibrio fischeri* F1 (IMB B-7070) and *Vibrio fischeri* Sh1 were used. The value of EC_{50} (the concentration, which caused 50% decrease of BL intensity) oscillated in the range of 7–19 mg/L in dependence of bacteria incubation time in T2 mycotoxin solution. The sensitivity of *V. fischeri* F1 to micotoxin T1 is much higher than the sensitivity of *P. phosphoreum* Sq3 [15]. An increase of patulin concentration from 0.63 to 40 mg/L caused the decrease of the BL intensity during 12–60 min. The EC_{50} value for patulin was 0.63–1.25 mg/L [15]. But the appropriate conditions of patulin may be revealed at the concentration less than 0.15 mg/L. Moreover, with the prolongation of incubation time (up to 90 min) the toxic effect of patulin increased and EC_{50} value was 0.15–0.63mg/L. At the decrease of medium's pH to the lower physiological limit (5–5.5) the sensitivity increased up to one order. The EC_{50} value was similar to semi lethal dose established for animal and correlated with other indexes of toxicity (cytotoxicity, irritation of mucouses, etc.) [10]. It should be mentioned that the intestinal barrier in animals is destroyed at patulin concentration is about 1 mg/L [22]. nPhEthO and some surfactants are inhibitors of bioluminescence, too [46].

3.1. Biosensors for the control of individual toxins

For this purpose the surface plasmo resonance (SPR), total reflection ellipsometry (TRIE) and calorimetric based biosensors was applied.

The principles of SPR biosensor action and main algorithm of analysis with its help were described in [33]. The sensitivity of 2,4-D analysis by direct way is about 5–10 µg/L, which is not high. Such low level of sensitivity at the direct way of analysis is observed in case of the determination of other low weight substances, for example: T2 toxin, nPhEthO. Much more sensitive was the analysis performed by the "competitive" or "saturated" way. Biosensor based on the TIRE allows to reveal mycotoxin T2 up to 0.15 ng/mL [27, 37]. Both optical immuno biosensors can provide the analytical sensitivity which is needed for practice. Total analysis time is about 5–10 min if the transducer surface is preliminary prepared. It is to be noted that the immuno biosensor based on the SPR is simpler then TIRE biosensor. In addition, the first one may be provided as portable device. Calorimetric immuno biosensor was designed in two different forms: as micro calorimeter and thermistor based device. It was demonstrated that the "direct" detection of nPhEthO by calorimetric biosensor might be at the sensitivity about 1 μg/mL [7]. The overall time of analysis is about 20–30 min. Unfortunately, it is much less than in case of application of SPR or TIRE biosensor but it is worth to mention the simplicity of the measurement. Maybe, thermal biosensor could be used for the screening of toxic elements in environmental objects with further verification of results with by optical immuno biosensors.

3.2. Multiparametrical and multifunctional biosensors

The measurement of one parameter with complicated and multifactoral character of biochemical processes could not in principal allow to provide the creation of biosensor which will fully meet the practical needs including selectivity, sensitivity, stability in general and versus contaminated substances, repetition of results, needed time of functioning and others. To achieve this scope, a microelectronic enzymatic biosensor was created which makes it possible to register a number of parameters, namely: the determination of glucose, sucrose, and lactose for the control of technological process at the sucrose production or the estimation of glucose, insulin (I) and anti-insulin antibodies (anti-I Ab) level at the control of the diabetes and autoimmune processes. Such integral biosensor contains simultaneously two separate channels: amperometric and thermometric. It was demonstrated that thermometry allows to control the concentrations in the limits 0.002–25; 0.005–100; 0.1–10 mM and sensitivity about 2.35; 0.45 and 0.85 rel. units/mM for glucose, sucrose, and lactate correspondingly. On the other hand, amperometry was characterized by the values of controlled concentrations within 0.5–50; 0.1–80; 0.1–200 mM and sensitivity at the level of 4.3; 3.3; 3.3 nA/mM for the above mentioned substances correspondingly. In general, it should be noted that these values correspond to the practical requirements in respect of sensitivity. It is very important to underline that total analysis time is very short. The sensitivity of determination of I and anti-I Ab in serum blood of patients with diabetes is highest at the application of immune enzymatic amperometric biosensors than the others. Unfortunately, it is not possible to measure the concentration of I with needed sensitivity by thermometric channel. Maybe, it is necessary to optimize the type and concentration of buffer systems.

To determine the group specific toxic substances, for example, organophosphorus, and organochlorinated compounds, cyanides and others, multi-biosensor based on electrolyte-insulator-semiconductor (EIS) structures were developed [35, 47]. The sensitivity of the EIS structures based biosensor to simazine, when the HRP-conjugates were used, was 5 μg/L approximately. The linear plot of the response lied in the concentration range of 5 to 150 μg/L. This sensitivity of the EIS structures based sensor towards both herbicides was lower than requested in practice. It may be connected with difficulties to register sensor output due to the formation of air bulbs, which appear as a result of high activity of the HRP. The use of high concentrations of ascorbic acid may be another reason for the lower sensitivity of this sensor. At the changing of HRP to glucose oxidase the sensitivity of the analysis obtained was approximately five times higher. The linear plots for simazine and 2,4-D were in the range of 1.0–150 and 0.25–150 μg/L, respectively.

The overall analysis time by this biosensor is about 40 min. It gives the possibility to carry out analyses of 8–10 samples simultaneously. For the verification of the result other types of biosensors may be used, for example, based on the ISFETs, which sensitivity at the determination of the above mentioned herbicides is at the level of 0.05–0.1 μg/L (37–39, 44). The sensitivity of the EIS structures based immune biosensor can be still increased. One of the ways to do it can be the development of special suitable membranes for providing of a very high density of the immobilised specific antibodies. Maybe, synthetic biologically compatible polymers can serve as a perspective material for such membranes [31, 32]. If the membranes were prepared in advance the duration of the analysis may be shortened up to 10 min.

Since a number of enzymes, which have serine residuum in the active centre (first of all a different forms of choline esterases – ChE), are very sensitive to organophosphorus pesticides (PhOrPe), and urease with the thiol groups can react with heavy metal ions (HMI), there is possibility to simultaneously determine these classes of toxins [30, 34]. The controlled concentration of HMI is within the range from 10^{-4} to 10^{-7} M, depending on the type of the metal used. The range of the linear detection covered two to three orders. The effects of both pesticides are very similar. The limit of their detection was 10^{-7} M. The range of the linear response was from 10^{-5} to 10^{-7} M. GOD was used as reference enzyme which has a minimal reaction in respect of both types of groups of toxins.

4. Conclusions

The above information testifies that scientific-technical progress promotes people to improve their life but simultaneously it brings a lot of problems with the increasing of toxic substances in the environment. To overcome this disadvantage, it is necessary to accomplish the constant, very simple, faster and very sensitive monitoring of environmental objects. It is possible to do it with modern analytical instruments based on the biosensor principles. Today, the created prototypes of such devices fully meet the practical requirements.

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COMPARATIVE STUDY OF KNOWLEDGE IN ENVIRONMENTAL PROBLEMS IN THE CONTEXT OF VARIOUS POPULATION GROUPS IN TWO EU MEMBER STATES

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Abstract. In this paper the results of the comparative study carried out in two countries members of the EU are presented. These countries, respectively Austria and Romania have adhered to the European Union in 1995, respectively in 2007. Four sets of questions have been elaborated, each set containing 20 questions, which were answered by different categories of education. The questions followed the main environmental problems and aspects regarding the administration organizations specialized or qualified for administration of environment problems. The distribution of the sets of questions was carried out with the direct involvement of the youth organizations and of volunteers from the neighborhood organizations. The analyses of the results were first considered separately for each group of subjects and then perceptual analyses were carried out on the correct answers. The comparison of the data obtained using the subjects of the two countries has emphasized a similar interest and a comparable level of knowledge.

Keywords: Environmental administration, environmental awareness, biodiversity, ecosystems.

1. Introduction

In the actual context of EU development, a new problem of the new member states is the reconstruction and development of the infrastructure at multiple levels: educational, scientific and cultural. In the context of this study, it means the management of international projects in the biodiversity and ecosystems field, the construction of water capture and purification systems, the capture of different polluting agents and the protection of biodiversity systems.

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In the case of developed countries, joined the EU from the very beginning, the efforts in pollution monitoring and control are huge, sometimes with impressive results. Despite of the efforts of the new members of EU – Romania and Bulgaria – in this field, the results are not as expected.

An important role regarding the implementation as well as the development of the new concepts in the environmental problems is attributed to educational system. It is addressed to all population categories and comprises the classic forms of teaching at different levels. But it should be created a separate system of education for entire population as a whole.

The aims of this pilot study were to evaluate the knowledge in the environmental problems [1–4] of different population categories divided by age and levels of professional degree from two EU members' states with different EU entries moments: Austria and Romania. The study compares the attitude regarding the environmental problems of young population [5–7], starting to prepare a professional career, and also to realize the complex nature of existential problems [8], with adult or aged population. The levels of knowledge in this field are compared between pupils, students coming from different fields, students oriented towards environmental problems, and mature people (adults and aged subjects).

2. Materials and methods

The population study (247 subjects, 175 from Romania and 72 from Austria) was divided in different categories by different levels of educational degree (Table 2.1):

Table 2.1. Number of cases (N) from each category of subjects tested.

Categories tested	N (no. cases)	N-RO (no. cases – Romania)	N-AUS (no. cases – Austria)
School children	55	30	25
High school and students	76	56	20
Adults or seniors	60	33	27
Students in environmental field	46	46	–

The tests comprised 20 questions with 2–7 response variants, different as difficulty degree and as correct or incorrect number of responses. These tests follow different aspects of environment problems:

- **Group A** of questions refer to the environmental pollution and its components: environment pollution, natural and artificial pollution sources, natural resources administration and recycling (main requirement of environment protection) and lasting development concept (main component of EU politics) [9]

- **Group B** of questions refer to institutions and organizations specialized or qualified for administration of environmental problems, ecological monitoring
- **Group C** of questions refer to air pollution, organic and inorganic polluting agents, aerosols from smog, exhaust gases [10]
- **Group D** of questions comprise questions referring to water pollution and health, water protection and water ecosystem protection, water quality monitoring
- **Group E** of questions refer to soil pollution sources (fertilizers, pesticides, other anthropogenic sources of soil degradation) [11]
- **Group F** refer to radioactive pollution, noise and electromagnetic pollution
- **Group G** refer to administration of residues and waste
- **Group H** refer to renewable resources and energy, ecological materials [12] (Tables 2.2 and 2.3)

Table 2.2. Number of questions from each category.

Subjects	A	B	C	D	E	F	G	H
School children	3	1	5	3	3	5	–	–
High school and students	5	4	5	1	2	–	1	2
Students in the environmental field	5	5	5	1	2	–	–	2
Adults or seniors	6	2	2	1	1	–	2	6

From 80 questions in total, the contribution of each type of question was: Group A = 23.75%; Group B = 15.00%; Group C = 21.25% ; Group D = 7.50%; Group E = 10.00%; Group F = 6.25%; Group G = 3.75%; Group H = 12.50%. Each question had 2–7 variants as follows:

Table 2.3. Number of questions from each category.

Subjects	A	B	C	D	E	F	G	H
School Children	12	6	17	15	12	21	–	–
High school students or students	16	17	23	4	7	–	3	9
Students in environmental field	22	19	24	3	9	–	–	10
Adults or seniors	23	7	7	3	3	–	8	21

From 311 variants in total of all 80 questions, the contribution of each type of question was: Group A =22.50%; Group B=15.75%; Group C = 22.82%; Group D = 8.03%; Group E = 9.96%; Group F=6.75%; Group G=3.53%; Group H =9.64%.

The contribution of each type of question in all 80 questions and all 311 was approximately the same. The tests distribution and evaluation were done by volunteers: teachers, students, researchers from Timişoara, Arad and Graz.

Statistical software package SPSS V16.0 was used for all analyses. Two sided probability was chosen at $p < 0.05$. Independent student t-tests and ANOVA were used for comparisons between groups.

3. Results and discussion

Two questions had the maximum percent of correct responses (100%). One of the 100% correct response was registered in school subjects from Austria and they respond to question regarding the exhaust gases composition. This reflects the knowledge as direct result of school programs (Fig. 3.1):

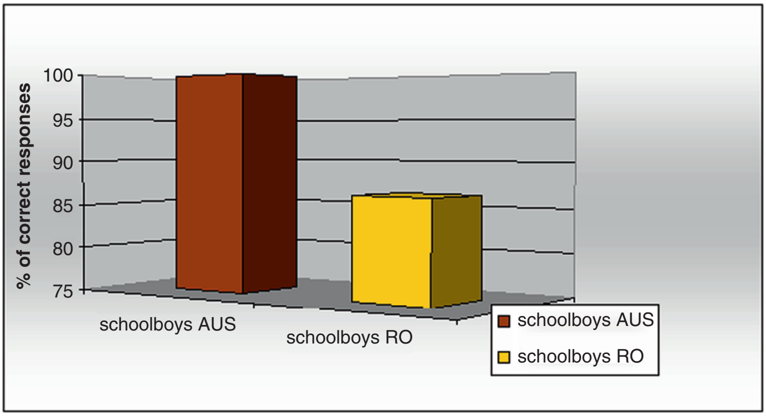

Fig. 3.1. Analysis of correct responses to type C questions (revise: School Children!!).

The second maximum percent for correct responses was obtained by the Romanian adult subjects regarding one of the ecological projects of 17 millions Euros funding started in 2008 in Timişoara to ecological administration of Bega River.

The minimum percent of correct responses, fewer than 20% (12.32%–18.30%) was registered at three types of questions as follows:

- Regarding the composition of humus, Romanian students have given only 12.35% correct responses and they also have chosen 10.14% wrong responses.
- School Children from Austria have had only 18% correct responses regarding artificial pollution compared with 46.6% correct responses of Romanian School Children.
- Adults or senior subjects from Austria gave only 17.7% correct responses to the question with two variants regarding the ecological town concept about the city hall responsibilities. Romanian adults gave 92.4% correct responses (Fig. 3.2).

Evaluation of incorrect responses has revealed that more than 11% (11.9–14.3%) was obtained at 12 questions representing 15% from all 80 questions, respectively 3.85% from all 311 variants analyzed. Their distribution based on category of age and types of questions is (Table 3.1):

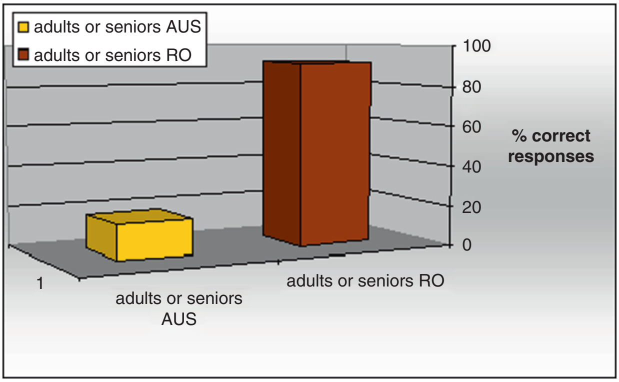

Fig. 3.2. The comparative analysis of adults or senior responses.

Table 3.1. Number of incorrect responses at questions from each category.

Subjects	A	B	C	D	E	F	G	H
School children	–	12.2	–	–	22.2	–	–	–
High school and students	13.6	12.1	13.8	–	19.1	–	12.5	12.5
Students in the environmental field	14.3	–	–	–	–	–	–	–
Adults or seniors	–	–	–	12.1	–	–	12.7	–

A comparative analysis of incorrect responses reflects that Romanian high school students and students gave the highest number of incorrect responses (Fig. 3.3):

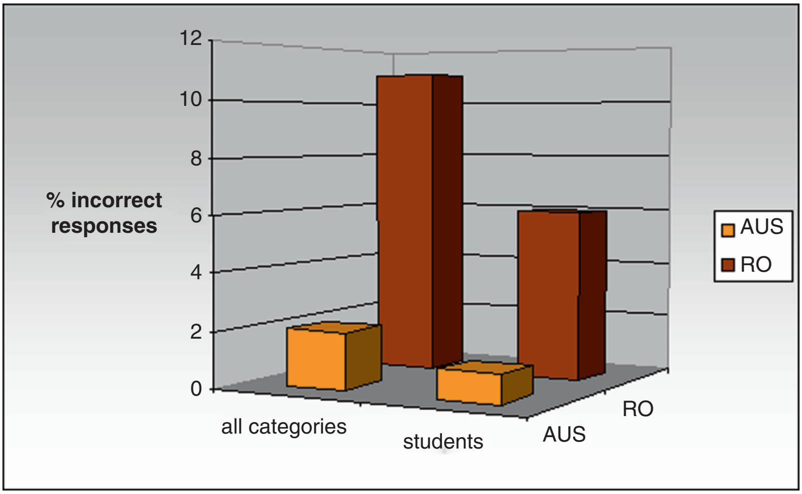

Fig. 3.3. The comparative analysis of incorrect responses between categories of subjects.

The number of questions registered without incorrect answers in the two countries is shown in the Table 3.2:

Table 3.2. Number of questions from each category (Romanian/Austrian) registered without incorrect answers.

Subjects	A	B	C	D	E	F	G	H
School children	2/2	0/0	0/1	0/2	1/1	1/1	–	–
High school students and students	1/1	1/0	2/2	1/1	0/0	–	0/0	–
Students in environmental field	11/–	7/–	0/–	0/–	7/–	–	–	21/–
Adults or seniors	3/4	2/2	1/2	0/0	0/0	–	1/2	2/4

– Represents no subjects or no questions, respectively.

Table 3.2 reveales that adult subjects from AUS are more confident in their responses. Opposite, the Romanian students are less confident in their responses.

The global comparisons of responses for all 247 tested subjects based on question type revealed that there were significant statistical differences between correct answers percentage regarding the type A, B and C questions. Statistical analyses using SPSS v16.01 have shown significant statistical difference ($p \leq 0.05$) between subjects from Austria and those from Romania in the following situations:

1. Responses to type A questions regarding environment pollution with five variants were significantly different ($p < 0.002$) when the correct responses of the AUS students and RO are compared (Fig. 3.4). As expected, there is a statistical difference ($p = 0.006$) between the percentage of correct answers of the high school students or students from Romania (70.88%) and the answers of the School Children (46%); the comparisons between the correct answers of the students from Austria (57.8%) and of the School Children (43.64%) gave evidence for the same trend. The percent of correct answers of the adults group from Romania (64.01%) is significantly higher ($p = 0.001$) compared with the adults group from Austria (43.64%). Contrary as expected, the percentage of correct answers of the Romanian students (70.88%) are higher ($p = 0.031$) compared with the percentage of correct answers in Romanian students in ecological field (49.01% correct answers).
2. Responses to type B questions regarding the institution, specialized organizations qualified for administration of environmental problems were significantly different ($p = 0.028$) between different categories of subjects (Fig. 3.5): Between the high school students and students from RO (61.2% correct answers) versus AUS (45.06% correct answers) was a significant difference ($p = 0.001$); between adults or seniors from RO (63.25% correct answers) versus AUS (37.18%) there was a significant difference ($p = 0.001$); the answers of the School Children from AUS (52.7% correct) were significantly better compared with adults from Austria (37.18% correct).
3. Comparative analysis of answers to type C questions regarding the air pollution revealed a significant statistical difference ($p < 0.001$) between the analyzed categories. The highest number of correct responses was registered at the

School Children category from both countries (Fig. 3.6). There was a significant statistical difference ($p = 0.013$) between the number of correct responses of Romanian students (58.7%) and students from Austria (41.39%). Also, there was a significant statistical difference between the correct answers of adults from both countries (59.85% RO vs. 44.41% AUS); the answers of School Children from AUS were significantly better compared with students from Austria ($p = 0.028$) and adults from Austria ($p < 0.001$).

4. Responses to type D questions regarding the water pollution with 15 variants were statistically different ($p < 0.001$) when the correct responses from School Children AUS and RO were compared and, also between the adults or seniors from AUS and RO (Fig. 3.7). The correct responses registered in the high school students and students from both countries were similar to each other.

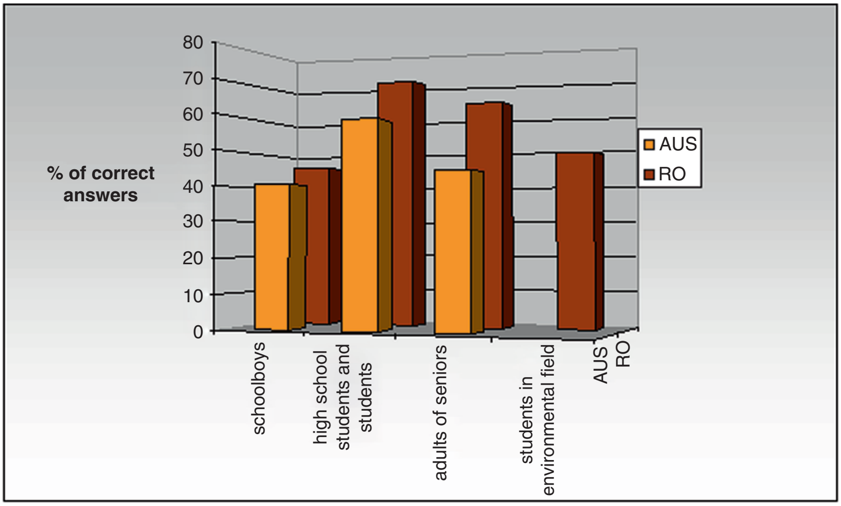

Fig. 3.4. The comparative analysis of the correct answers to type A questions.

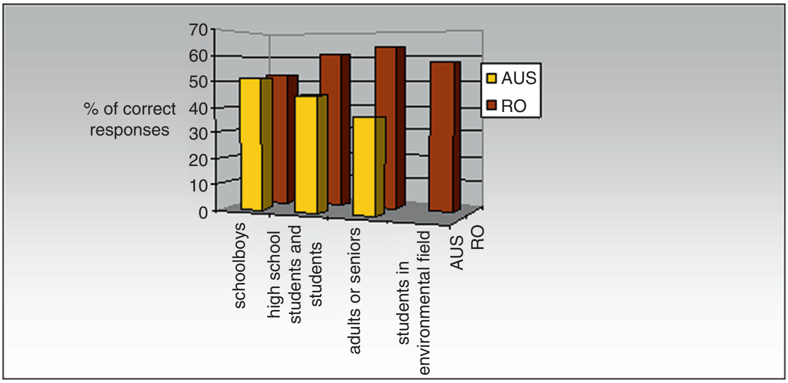

Fig. 3.5. The comparative analysis of correct answers to type B questions.

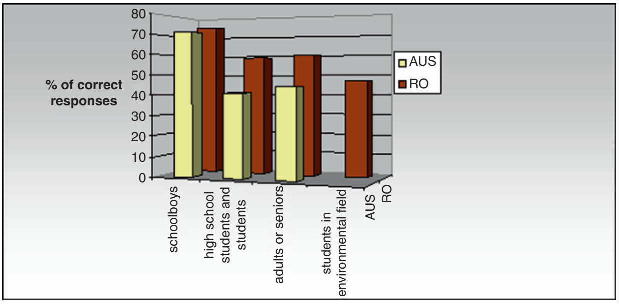

Fig. 3.6. The comparative analysis of correct answers to type C questions regarding the air pollution.

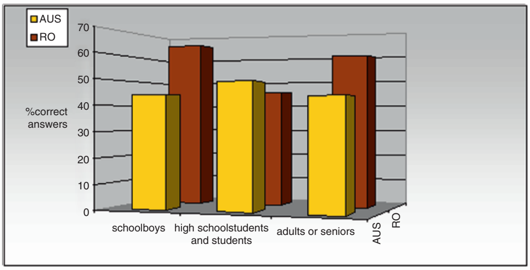

Fig. 3.7. The comparative analysis of answers to type D questions regarding the water pollution when the correct responses of the students from AUS and RO are compared.

4. Conclusions

The results of this pilot study gave evidence that today environmental problems have a large audience and are perceptible for all categories analyzed as sense of duty. It seems that the adults are more involved in these problems and they had a higher number of all correct responses (12.5% RO vs. 19.4% AUS).

The knowledge of environmental problems of School Children from Austria, seen as a whole is more solid and accurate compared with Romania. On the other hand, Romanian students have a large knowledge of these problems compared with students from Austria.

The results of this first study are encouraging and the new experience accumulated suggests new aspects which should be improved. The subjects attitude, kindness and rapidity to respond, and also the volunteers involving have proved that today, environmental problems and their solutions are not only attributed to specialists but also to entire population in a country.

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A GREEN CHEMISTRY LAB COURSE

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Abstract. The traditional course content of chemistry classes must change to achieve better awareness of the important issues of sustainability in chemistry within the next generation of professional chemists. To provide the necessary material for the organic chemistry teaching lab course, which is part of almost all study programs in chemistry, material was developed and collected (http://www.oc-praktikum.de) that allows students and teachers to assess reactions beyond the experimental set up, reaction mechanism and chemical yield. Additional parameters like atom economy of chemical transformations, energy efficiency, and questions of waste, renewable feed stocks, toxicity and ecotoxicity, as well as the safety measures for the chemicals used are discussed.

Keywords: basic organic teaching laboratory, Internet-based learning, green chemistry, sustainable chemistry.

1. Introduction

The right education of future professionals in the field of chemistry is the key achieving a more sustainable development [1, 2]. Taking on this challenge for the area of basic practical organic chemistry in higher education, a collaborative project of six German universities has created a collection of lab experiments that is accompanied by background information on sustainable development, classical and new laboratory techniques and the evaluation of chemical substances and reactions. The material is freely accessible on the internet in English (http://www.oc-praktikum.de) among other languages. The NOP acronym is derived from the German title "*Nachhaltigkeit im Organisch Chemischen Praktikum*" (sustainability in the organic chemistry lab course) [3, 4].

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Organic teaching labs are a typical element in university education in chemistry, biochemistry, biology, pharmacy, physics, medicine and even some areas of environmental and civil engineering. However, most curricula are still based on traditional lab classes in chemistry. They focus on teaching basic experimental techniques for synthesis and analysis, and how to handle hazardous chemicals. The efficiency of a chemical transformation is usually measured by the chemical yield of the product obtained. Students do not learn how to get a more complete picture of a reaction, by using indicators of its sustainability, and they are not provided with tools to increase its overall efficiency and sustainability. However, aspects of overall efficiency and sustainability of a reaction must be added to the content of teaching lab courses in organic chemistry to prepare future generations of chemists. Toxicological and ecotoxicological knowledge and data have to be integrated in a way that it becomes a natural part of the discussion of an experiment. Within this considerably wider scope (Fig. 1.1) students learn how to plan, set up and analyze organic reactions taking their effect on the environment and human beings into account. Sustainability starts with the conceptual planning of a chemical transformation.

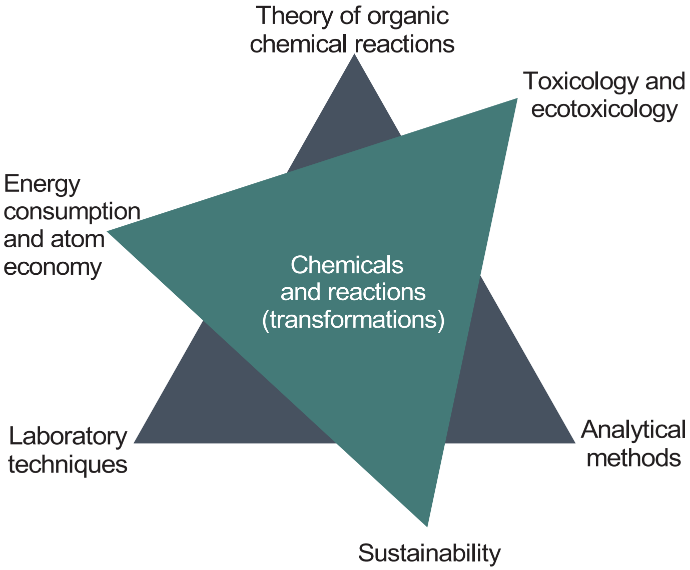


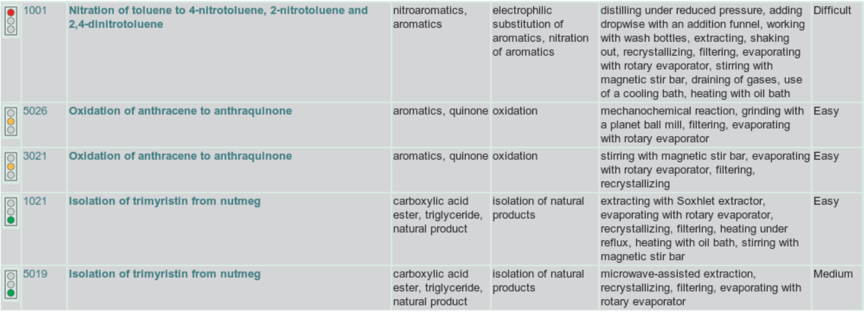
Fig. 1.1. The classical elements of organic chemistry education (black triangle) are extended by topics assessing sustainability of chemical reactions and compounds (green triangle).

We introduce in this chapter the NOP internet database, which provides a wealth of material, covering experimental procedures, toxicity data, alternative reaction procedures, some data about energy efficiency and more to assess a chemical reaction in a wider sense. The provided information can be individually adapted to classes at various levels of University education.

Education in chemistry has a very long history. For a long time the most important goal of a chemist was to make a compound in suitable amounts and high purity from available starting materials. This biased the chemical education, which had a strong focus on practical lab techniques and methods for compound purification. The question of how much energy is needed for a reaction and how much waste is produced was raised for industrial processes only. Although the goal for synthetic organic chemist is still the same, to make a compound in good yield and high purity, additional parameters must be considered in the development of new processes today. The last 20 years in which much more attention was paid on the effect of chemical production and chemical compounds on human health and the environment have taught us one clear lesson: It is much better, easier and less expensive to develop processes and compounds that are sustainable from scratch than to optimize an existing poorly developed chemical process or to remove dangerous chemicals from the environment in order to reduce potential hazards and pollution. For these purposes, chemists, biochemists, engineers, scientists working in drug development or constructing new materials must think in terms of long-term sustainability when transforming their ideas into products and processes. This calls for a different chemical education which teaches more than reaction mechanisms and experimental techniques. Students must learn to judge the suitability of a chemical transformation or the use of a chemical compound within a matrix of many parameters. It is not only the yield of the reaction that counts. Which starting materials are needed? Can they be made from renewable resources? Do we get toxic by-products and how can they be avoided? How much waste is generated by the process and is it energy efficient? Are we terminating the reaction at the earliest possible time? Asking these questions at the beginning of chemical research and technology development will lead to a more efficient and sustainable use of chemistry. Asking these questions in the teaching lab course will clearly change the way students conceive a chemical reaction and prepare them much better for their professional career.

2. Laboratory experiments of NOP

In contrast to alternative chemistry lab course experiments developed by Hutchinson and other groups [5] it was not tried to exclusively select “green” experiments, i.e., with an especially low hazard potential of the involved substances. The approach of the NOP project is rather based on the idea that we will always need chemists that are trained in handling hazardous substances in a responsible manner. However, in order to foster the conscience of the overall greenness of an experiment in organic chemistry, a classification of the experiments in three groups was developed, which are intuitively visualized by green, yellow and red traffic lights (Fig. 2.1).



🔴	1001	**Nitration of toluene to 4-nitrotoluene, 2-nitrotoluene and 2,4-dinitrotoluene**	nitroaromatics, aromatics	electrophilic substitution of aromatics, nitration of aromatics	distilling under reduced pressure, adding dropwise with an addition funnel, working with wash bottles, extracting, shaking out, recrystallizing, filtering, evaporating with rotary evaporator, stirring with magnetic stir bar, draining of gases, use of a cooling bath, heating with oil bath	Difficult
🟡	5026	**Oxidation of anthracene to anthraquinone**	aromatics, quinone	oxidation	mechanochemical reaction, grinding with a planet ball mill, filtering, evaporating with rotary evaporator	Easy
🟡	3021	**Oxidation of anthracene to anthraquinone**	aromatics, quinone	oxidation	stirring with magnetic stir bar, evaporating with rotary evaporator, filtering, recrystallizing	Easy
🟢	1021	**Isolation of trimyristin from nutmeg**	carboxylic acid ester, triglyceride, natural product	isolation of natural products	extracting with Soxhlet extractor, evaporating with rotary evaporator, recrystallizing, filtering, heating under reflux, heating with oil bath, stirring with magnetic stir bar	Easy
🟢	5019	**Isolation of trimyristin from nutmeg**	carboxylic acid ester, triglyceride, natural product	isolation of natural products	microwave-assisted extraction, recrystallizing, filtering, evaporating with rotary evaporator	Medium

Fig. 2.1. Evaluated experiments of the NOP database.

Some experiments have been developed using two alternative techniques, i.e., conventional heating under reflux and conducting in a microwave apparatus [6] (*not* a household microwave system!). This allows a comparisons of different experimental techniques.

The red traffic lights are not intended to express that such reactions should not be carried out in the laboratory. They merely visualize that a high level of care is needed when conducting those experiments, and that there is an especially large potential for optimization of the reaction in terms of sustainability. The green light is given for experiments that are especially favourable regarding their substance and energy efficiency, as well as their treatment/avoidance of hazardous substances. The yellow light is attributed to experiments that do bear risks for men and/or environment, and that should be carried out with considerable caution.

From the 75 experiments currently available in the NOP database, only 13 have undergone a complete evaluation at present (October 2008). For the remainder of the experiments, a traffic light with a question mark is shown. These experiments meet the criteria for inclusion concerning quality and reproducibility, and a standardized set of background information is given as well. This set includes an assessment of data availability for every substance, its risk and safety phrases according to the EU directive 67/548/EEC and its amendments on the classification and labelling of dangerous substances, as well as an assignment of effect factors according to the German Hazardous Substance Regulation (TRGS 440). An operating scheme visualizing the experimental procedure is given for each experiment (Fig. 2.2) and substantial information is provided on how the final product can be checked for its identity, purity and side products. The concise experimental instructions for each experiment are available as a PDF file in a standardized way.

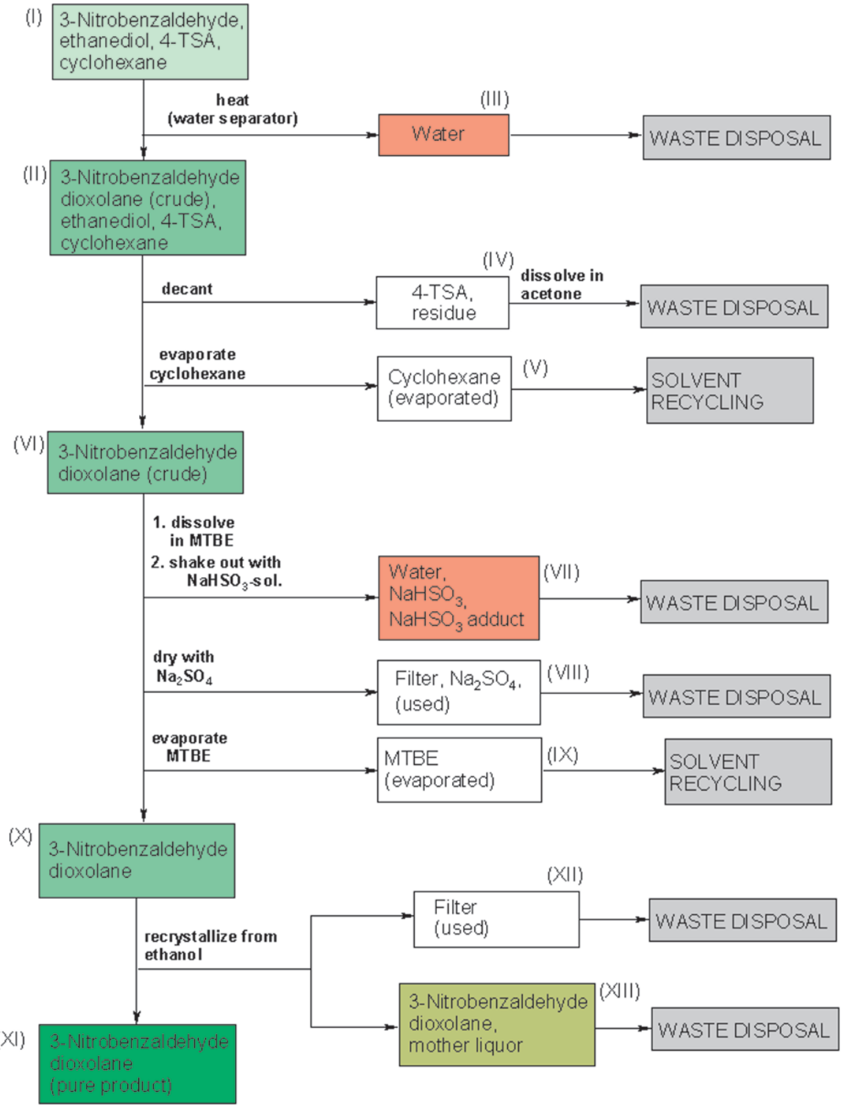
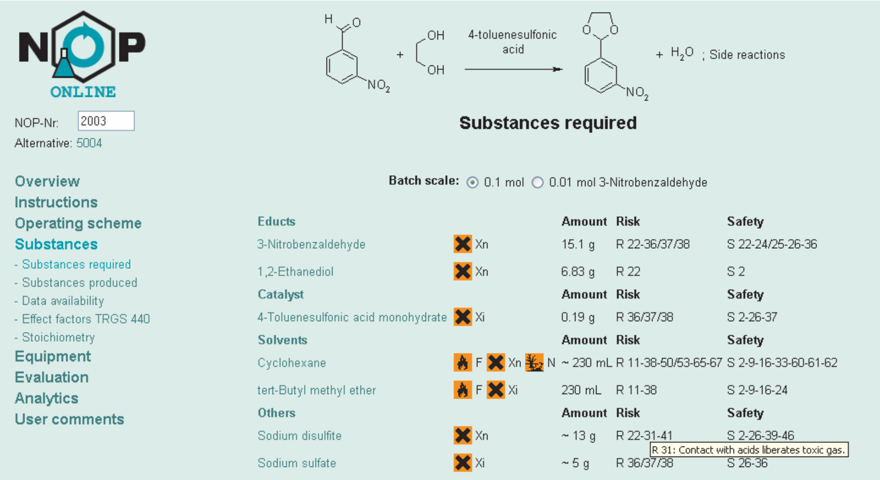


Fig. 2.2. Example of a flow chart (“Operating Scheme”) for an experiment in the NOP database.

The “Globally Harmonized System of Classification and Labelling of Chemicals” (GHS) is currently being established providing a unified way of communicating hazard potentials. While this is still under way, the substance specific hazard information in the NOP is largely based on the system of the European Union, consisting of a system of 10 hazard symbols and a large number of various risk (R) and safety (S) phrases. For each experiment, the website provides a substance overview, listing amount, name, hazard symbols, R and S phrases for any substance and auxiliary material used in the reaction (Fig. 2.3).



NOP-Nr: 2003
Alternative: 5004

Substances required

Batch scale: ● 0.1 mol ○ 0.01 mol 3-Nitrobenzaldehyde

Educts		**Amount**	**Risk**	**Safety**
3-Nitrobenzaldehyde	Xn	15.1 g	R 22-36/37/38	S 22-24/25-26-36
1,2-Ethanediol	Xn	6.83 g	R 22	S 2
Catalyst		**Amount**	**Risk**	**Safety**
4-Toluenesulfonic acid monohydrate	Xi	0.19 g	R 36/37/38	S 2-26-37
Solvents		**Amount**	**Risk**	**Safety**
Cyclohexane	F Xn N	~ 230 mL	R 11-38-50/53-65-67	S 2-9-16-33-60-61-62
tert-Butyl methyl ether	F Xi	230 mL	R 11-38	S 2-9-16-24
Others		**Amount**	**Risk**	**Safety**
Sodium disulfite	Xn	~ 13 g	R 22-31-41	S 2-26-39-46
Sodium sulfate	Xi	~ 5 g	R 36/37/38	S 26-36

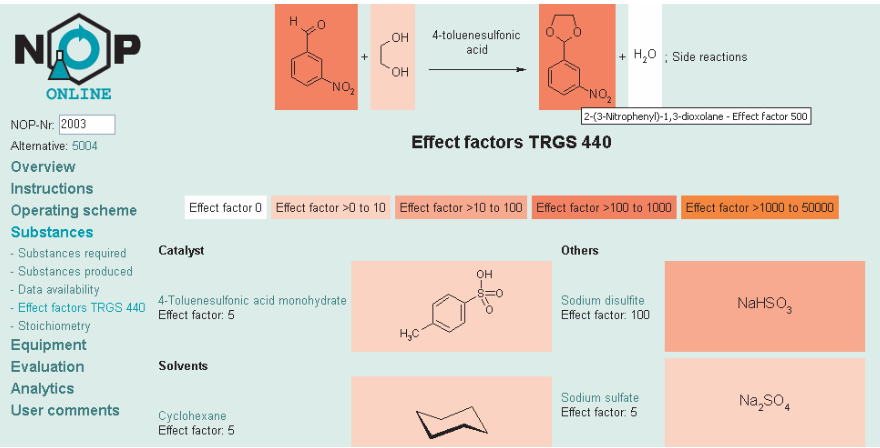
R 31: Contact with acids liberates toxic gas.

Fig. 2.3. Overview of required substances together with quantities, risks and safety information.

Based on the risk and safety phrases, the German Technical Directive for Hazardous Substances TRGS 440 defines effect factors ranging from zero to 50,000, which is an indicator for the level of workplace risk caused by a particular substance. Effect factors have been determined for all substances in the NOP substance database. These effect factors are visualized for each experiment, using a colour scale from white (effect factor 0) to dark orange (effect factor 50,000). An example is given in Fig. 2.4.

For the experiments that have already been fully evaluated, a comprehensive search on physical–chemical properties, toxicological and ecotoxicological data has been conducted and the most important results are available on the NOP website, together with a source attribution for all data.

An important aspect is the provision of a comprehensive set of data for the characterization of the experiments and all chemicals used by means of instrumental analyses (GC, HPLC, MS, coupled systems) of raw and purified substances as well as spectral information (FT-IR, NMR (^{1}H/^{13}C) etc.) that enables the teachers and students to use for advanced instrumental analytical and spectroscopic courses without having these instruments and/or substances at their own institutes.



NOP-Nr: 2003
Alternative: 5004

2-(3-Nitrophenyl)-1,3-dioxolane - Effect factor 500

Effect factors TRGS 440

Catalyst
4-Toluenesulfonic acid monohydrate
Effect factor: 5

Solvents
Cyclohexane
Effect factor: 5

Others
Sodium disulfite
Effect factor: 100

Sodium sulfate
Effect factor: 5

Fig. 2.4. Effect factors of an experiment from the NOP database.

3. NOP material in teaching

The NOP website is not a ready-to-use class. The material has to be adapted to the specific needs of a teaching unit by the instructor. The 75 experimental instructions may find use in the basic organic teaching lab of degree courses in chemistry, biology, biochemistry, but also for students of medicine or engineering. The instructor can select and extract the experiments that are suitable for the course using the NOP database. However, the material does also provide the basis for a specialized class in environmental chemistry or ecotoxicology, one may teach safety regulations using the material or discuss the examples in a class covering spectroscopic identification of organic compounds or HLPC and GC techniques. Team tasks are another option: Starting from one of the given procedures the challenge is to increase its efficiency by finding the minimal reaction time for saving energy, the optimal reaction temperature or the best work up conditions. Reactions are run in parallel by the team members using different conditions and monitoring the conversion. The individual lab training remains, but only all the results together will give a full picture of the reaction and answer the question. The team task can be designed from very simple, e.g., varying temperature or reaction time, to complex, e.g., energy consumption or choice of solvent.

4. National versions of NOP

The NOP platform allows including versions in different languages. So far, the NOP is available in German, English and Italian. Translations into Russian, Indonesian, Arabic, Turkish and Greek have been completed and will be available on-line soon. The translation into Portuguese is in progress. The national versions are coordinated by a national editor, who is responsible for the content, the translations and the continuous improvement of the database. The benefits of NOP as teaching material is particularly accepted by universities of emerging countries since this material is freely accessible via the internet and the translation into their own languages allows the use of this material also for students who are not familiar with the English language. The NOP project team welcomes national editors from any country, who would like to translate and adapt the NOP material for their national higher education system.

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CONCLUSIONS

The NATO Advanced Research Workshop *"The Role of Ecological Chemistry in Pollution Research and Sustainable Development"* was held during October 8–12, 2008 in Chisinau, Republic of Moldova. Fifty participants from 13 countries attended the Workshop. From them there were scientists from Armenia, Austria, Czech Republic, Egypt, Germany, Italy, Jordan, Moldova, Romania, Russia, The Netherlands, Turkey and Ukraine, representing international and national research institutions, universities and other research centers as well as ministries, dealing with the various aspects of environmental problems. Thirty-four presentations and communications have been presented and discussed at the Plenary Meeting, Platforms and Poster Sessions.

The Academy of Sciences of Moldova and Braunschweig University of Technology, Germany organized the Conference jointly, with the valuable help of the Moldovan Research and Development Association (MRDA) and Department of Industrial and Ecological Chemistry of Moldova State University.

This workshop was a continuation of the series of successful International Conferences on Ecological Chemistry held in Chisinau in 1985, 1995, 2002 and 2005, which served as a base for further strengthening of the research potential and the development of scientific research in this field.

The Workshop Program involved the following sessions:

- Organic Pollutants and POPs in the Environment – Occurrence, Fate and Prevention Measures
- Water Pollution and Wastewater Treatment
- Soil Pollution and Prevention
- Waste Management
- Risk Assessment, Mitigation Measures and Environmental Awareness

Recently, environmental experts have broadly recognized an increasing number of processes that cause environmental pollution at a level that is harmful to plants, animals and human life. The ecosystems subjected to enormous anthropogenic loads are degrading, thus threatening the health and lives of people. Therefore, today the ecological chemistry is called to provide a positive impact on the environmental conditions and, accordingly, to a sustainable development.

The papers presented at this workshop demonstrate clearly the essential impacts of human activity and other related factors on all the environmental compartments, including water, soil, and air. We believe that the research in ecological chemistry in our countries has to be supported by both the scientific community and business, which becomes more and more oriented towards the environmentally-friendly production technologies leading to a sustainable development in future.

Therefore, the Workshop participants proposed the following actions:

- To appeal to all stakeholders in the society, including scientific, educational and business communities, manufacturers and decision-makers, to recognize the priority importance of the problems which are subjects of research of ecological chemistry and sustainability
- To initiate a closer cooperation of scientists and manufacturers from Western and Eastern countries, from North and South, and Mediterranean Dialogue Countries to establish the dialogue between the countries on pollution research and sustainable use of resources
- To set up topical networks on the urgent fields of environmental sciences, e.g., soil sciences and humics, water and waste management, POPs and environmentally-friendly flame retardants, (bio)sensors for environmental monitoring and control, and environmental education and awareness (Annex I)
- To develop promising technologies to overcome the negative impacts of climate change on soil deterioration causing desertification and decline of the abundance and biodiversity in related ecosystems
- To organize biennial follow-up Conferences on Ecological Chemistry in different countries in order to report on the achievements obtained in the meantime

Present Resolution was approved at the Closing Session of the NATO ARW on The Role of Ecological Chemistry in Pollution Research and Sustainable Development.

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ANNEX I

NETWORKS CREATED

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