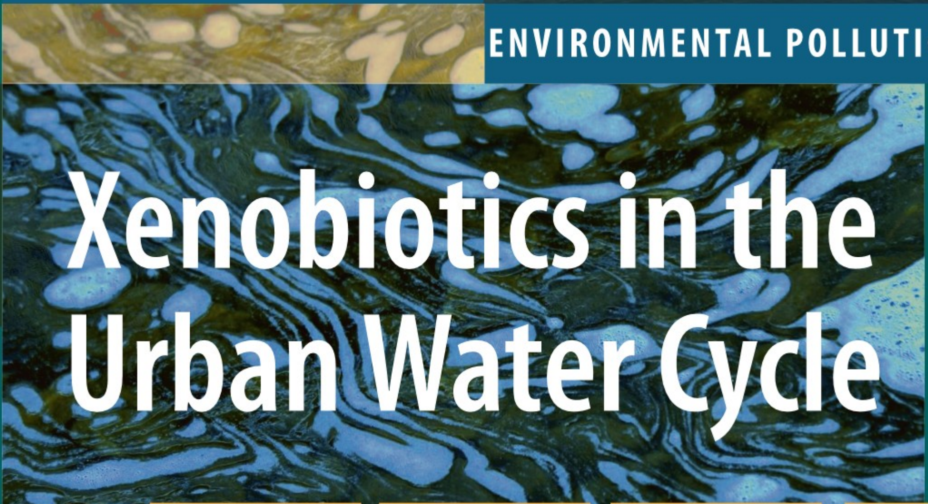
Despo Fatta-Kassinos
Kai Bester
Klaus Kümmerer
Editors

ENVIRONMENTAL POLLUTION 16



Xenobiotics in the Urban Water Cycle

Mass Flows, Environmental Processes, Mitigation and Treatment Strategies

Springer

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ENVIRONMENTAL POLLUTION

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Mass Flows, Environmental Processes, Mitigation and Treatment Strategies

Edited by

Despo Fatta-Kassinos
Department of Civil and Environmental Engineering,
University of Cyprus, Cyprus

Kai Bester
Department of Biotechnology, Chemistry and
Environmental Engineering, Aalborg University, Denmark

Klaus Kümmerer
Department of Environmental Health Sciences,
University Medical Center Freiburg, Germany

Springer

Editors
Despo Fatta-Kassinos
University of Cyprus
Department of Civil and Environmental Engineering
Kallipoleos 75
1678 Nicosia
Cyprus
dfatta@ucy.ac.cy

Kai Bester
Aalborg University
Department of Biotechnology, Chemistry and Environmental Engineering
Sohngaardsholmsvej 57
9000 Aalborg
Denmark
kb@bio.aau.dk

Klaus Kümmerer
University Medical Center Freiburg
Department of Environmental Health Sciences
Bresisacher Straße 115b
D 79106 Freiburg
Germany
klaus.kuemmerer@uniklinik-freiburg.de

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Foreword

The history of chemistry and pharmaceutical sciences is an impressive success story. The products of chemical and pharmaceutical industries are present everywhere in our everyday life. They help to pursue the modern way of living and they contribute to our high standard of living and safety, mobility, communication technologies, food, health, textiles and drinking water treatment, among many others. These products are labeled under the categories: pharmaceuticals, pesticides, detergents, fertilizers, dyes, paints, preservatives, food additives and personal care products, to name a few. Within these categories, groups of chemicals with similar structures can be found. However, often groups of chemicals with very different structures belong to the same category.

For a long time the production of chemicals and pharmaceuticals, their usage and application was connected with the heavy pollution of the environment and serious health effects. At the end of the last century, it was realised that the products of chemical and pharmaceutical industries are presenting a new type of environmental pollution that may also pose a health risk to the consumer. Most chemicals are used in so-called open applications in excessive amounts e.g. for personal care, hygiene, plant protection, health and in textiles. In many cases such as scents, detergents, textile chemicals, surface disinfectants, pesticides and others it is unavoidable that these chemicals are released into the environment according to their intended use. These chemicals are detectable in the environment at ng/L–μg/L concentration levels and are often called micro-pollutants (because their concentrations are very low) or emerging contaminants (since the concern about them is only recent) or xenobiotics (since most of them are synthetic, i.e. xenon to bios which means foreign to life). Some of the compounds that are of interest are of natural biological origin however, such as mycotoxins, aflatoxins, some hormones and others. But they do fall in the group of xenobiotics, since they are foreign to the organisms in which they are found, due to uptake and bioconcentration processes, after their release in the environment.

It has been learned that the xenobiotics often spread within the water cycle. The presence of these compounds in the water cycles is a widely acknowledged fact. However, knowledge on their fate and effects and on opportunities for their removal and input prevention is scarce. The presence of xenobiotics in the aquatic environment is seen as one of the big challenges for a sustainable water future, especially in arid countries where water reuse is of utmost importance. In countries with no water reuse, it is still desirable to have no contaminants in drinking water for health and ethical reasons.

Hazardous chemicals, like many of the xenobiotic organic compounds, are of rising concern in urban water management since water supply, urban drainage and wastewater treatment systems were originally designed solely to solve other problems (supply of potable water, flooding prevention and sanitation). Thus, there is a need to understand, in an integrated manner, the sources, flow paths, fate and effects of hazardous chemicals on both humans and ecosystems. This book does not aim at presenting all the related available information. Instead, it addresses some typical issues related to usage, occurrence, fate, effects and methods and measures for input reduction and the removal of such xenobiotic compounds.

This book was created within COST (European Cooperation in the field of Scientific and Technical Research) Action 636 (http://www.cost.esf.org/domains_actions/essem/Actions/Xenobiotics_in_the_Urban_Water_Cycle). The main objective of COST Action 636 Xenobiotics in the Urban Water Cycle was to assess the role of xenobiotics in the urban water cycle and to set up strategies for minimizing their impact on humans and ecosystems. The COST Action 636 provided the tools for the integration of knowledge and experience at the European level to create a critical mass required to assess the role of xenobiotics in the urban water cycle. The Action included a multi-disciplinary approach with discussions and exchange of knowledge among experts and stakeholders on the specific topics related to xenobiotics in the urban water cycle. The publication of the book would have not been possible without the support of the Chair of the COST Action 636, namely Dr. Anna Ledin, Professor at the Technical University of Denmark whom the Editors warmly thank.

The Editors would also like to acknowledge all those people who created the opportunity for discussions, exchange of ideas and sharing of results on xenobiotics in the urban water cycle, as well as the encouraging comments. They would also like to warmly thank their co-workers of their research groups for their support in the daily working routine, giving them the necessary time to edit a book in such a dynamic field.

The Editors would also like to express their gratitude to Ms. Betty van Herk and Mr. Paul Roos and their team at Springer Publisher who strongly supported the idea and helped to make this book a reality.

Last but not least, special thanks are extended to all the authors who devoted their precious time to contribute to this book.

June 2009

Nicosia, Cyprus — Despo Fatta-Kassinos
Aalborg, Denmark — Kai Bester
Freiburg, Germany — Klaus Kümmerer

Scope of the Book

The products of chemical and pharmaceutical industries are present everywhere in every day life. These products include medicines, disinfectants, contrast media, personal care products, dyes, laundry detergents, surfactants, pesticides, dyes, paints, preservatives food additives and personal care products, to name a few. Within these categories, groups of chemicals with similar structures can be found. However, groups of chemicals with very different structures often belong to the same category. The very wide array of chemicals on the market is expected to continue further to diversify and grow as knowledge and technology advance. Most of them are released into the environment according to their use, like for example, personal care products and pharmaceuticals. These types of chemicals enter the environment continuously via domestic and industrial sewage systems and via wet-weather run-off (e.g. from animal farms). Many of the chemicals of emerging interest, including pharmaceuticals, have not been fully examined yet for their negative environmental effects. This is surprising if one considers the fact that pharmaceuticals, for example, are designed to modulate immune and endocrine systems and cellular signal transduction and as such have obvious potential to interfere with organisms in the environment. Many of these chemicals are designed to have profound physiological effects, so it would not be surprising if they were found to affect fish, insects and other forms of life. Even relatively short-living chemicals can cause chronic exposures because they are continuously infused into the environment. It is important also to note that even though individual concentrations of such chemicals might be low, the combined concentrations from those sharing a common mechanism of action could be substantial. It is now appreciated that the transformation of the parent compounds may be incomplete in the environment and in treated effluents. These recalcitrant or persistent chemical entities may also add to the already huge number of potentially-toxic/suspicious/unsafe chemicals present in the environment. Even less is known about these transformed chemicals compared to their parent compounds, in particular in relation to their possible effects on environmental organisms and humans (easily reachable e.g. via drinking water). The various chapters of this book address these important issues along with other related issues and present specific examples.

The first section of the book is dedicated to the occurrence, sources and fluxes of various compounds in urban waters. Information is also included on quantitative mass flows of xenobiotics in waters and sewage treatment plants and examples on the identification and classification of sources and uses of such compounds in urban environments. The objective was to include information on compounds that were only recently investigated, like for example, scents, illicit drugs, toxins, and platinum group elements.

Illicit drugs constitute a new class of chemicals with potent psychoactive properties and unknown effects to the aquatic environment. A summary of the occurrence of such drugs in water resources is given, providing specific examples from various countries such as the U.S., Italy, Germany, U.K. and Spain. The increase of platinum group elements' contamination in different matrices is summarized, presenting data on their current environmental concentrations, their bioavailability and their effects on aquatic organisms. Furthermore, a short overview on the current usage and regulation of scents for Europe and the U.S. and the associated possible risks of their introduction into the environment is included.

The eutrophication of water resources, mainly attributed to antrophogenic activities such as sewage and agricultural runoffs, has led to a worldwide increase in the formation of cyanobacterial harmful algal blooms (Cyano-HABs). Cyano-HABs have the ability to produce and release toxic compounds, commonly known as cyanotoxins, which are a potent threat for human and animal health and have negative economical impacts. An overview on the sources and occurrence of species of cyanobacteria and their association with the production of cyanotoxins throughout the world is provided.

Marine sediments are characterized as the memory of the pollution constituting a sink for the more hydrophobic compounds posing an unacceptable risk to aquatic biota, in which these compounds can bioaccumulate, and to human health through the ingestion of contaminated fish and shellfish.

Information on the compounds most frequently occurring in marine sediments, namely PAHs, surfactants, halogenated compounds, organotin compounds and some pharmaceuticals, is provided. In the same line, sewage sludge contains a plethora of organic pollutants. Experiences related to the applicability of sewage sludge as a matrix for monitoring persistent lipophilic contaminants released from the anthroposphere are reported and discussed herein. Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine pesticides, phthalates, UV filters, biocides, synthetic fragrances, polybrominated flame retardants and surfactants were analyzed in stabilized sewage sludge from more than 20 sites (wastewater treatment plants, catchment area) in a monitoring network in Switzerland and are reported herein.

The second section of the book is dedicated to the fate, effects and risks associated with the presence of xenobiotics in urban waters including information on the:

- Co-metabolic removal of chlorinated organic compounds by providing examples on field, pilot and laboratory studies
- Photochemical transformation of pharmaceutical active ingredients when present in the aquatic environment and during the application of photo-induced treatment processes
- Analytical identification and quantification of the transformation products of selected pollutants

- Transport and fate of pollutants within cities by providing examples from Halle/Saale and Leipzig
- Novel concepts related to the environmental risk assessment of pharmaceuticals and hydroxyl benzoate preservatives

The third section presents various treatment processes and evaluates their potential to remove xenobiotic compounds. As an example, the removal potential of estrogens during wastewater treatment is assessed while the criteria that could contribute to the enhancement of the removal potential of treatment plants in respect to a number of xenobiotics are presented. The capacity of using membrane bioreactors as an efficient technology is presented by providing examples on the removal of various pollutants of industrial origin. Moreover, in a separate chapter, a synopsis on the current knowledge on membranes and xenobiotics is provided. Furthermore, the efficiency of the conventional and membranes bioreactors are compared in respect to their capacity to remove surfactants-derived alkylphenolic compounds, while the removals of xenobiotics from wastewater in sequencing batch reactors in conventional and two-phase configurations are presented.

The book gives also a short but necessary description of the key processes of advanced oxidation processes employed in water treatment and discusses process fundamentals, advantages and drawbacks. A concise review on the various advanced oxidation processes related to xenobiotic removal applications for water and wastewater, is given, including also examples on solar-driven catalytic processes. The review focuses on the science and engineering of water and wastewater treatment in relation to such applications. The book provides also a deeper insight into the reaction mechanisms involved and products formed during the advanced chemical and photochemical oxidation of important naphthalene sulphonates.

This section discusses also the phytoremediation processes, focusing on the advantages and potential drawbacks as well as information about recent developments in this field of research and applications, especially in the area of decontamination and cleaning of organic xenobiotics containing industrial and agricultural wastewaters.

Stormwater is one of the major pathways for the introduction of xenobiotics into the water cycle. The treatment of stormwater should of course constitute an integral part of precipitation water management. This could also contribute to meet current demands concerning water quality. In this respect, the requirements of the Water Framework Directive (2000/60/EU, WFD) continue to play a central role and provide a basis for discussion leading to further innovative solutions. In order to fulfill these requirements, major investments are necessary. An example taken from Germany is provided in this book.

The fourth section of the book is focused on the important issue of 'mitigation measures'. Various technical and socioeconomic instruments are presented based on real examples in Sweden.

The book ends with an outlook that provides the reader with information on the various lessons recently learnt by the research community that is active in the field of xenobiotics and the identification of some of the major current knowledge gaps.

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Part I
Occurrence Concentrations, Sources and Fluxes of Xenobiotics in Urban Waters

Chapter 1
Quantitative Mass Flows of Selected Xenobiotics in Urban Waters and Waste Water Treatment Plants

Kai Bester, Christa S. McArdell, Cajsa Wahlberg, and Thomas D. Bucheli

Abstract Typical concentrations and quantitative mass flows of anthropogenic compounds (such as personal care compounds, bactericides, flame retardants, plasticizers, detergents, complexing agents, as well as mycotoxins) in waste water are compared to typical per person loads in the influents and effluents of waste water treatment plants. They are evaluated to assess their significance for the contamination of the aquatic environment. Usually the number of persons serviced by a waste water treatment plant (WWTP) is well known, as the design parameters of the WWTP heavily rely on the per person usage of water and the per person emissions of nutrients as well as organic carbon. It is the intention to use these basic data together with concentrations from some waste water treatment plants to make assessments on emissions from WWTPs, for which only basic design parameters are available. These data can be used for predictions of waste water contamination concerning pollutant loads and concentrations for waste water treatment plants that have not undergone extensive monitoring. The relevance of the respective pollutants for surface waters as well as sludge is demonstrated.

The focus of this chapter is on those compounds that are emitted continuously during dry weather. – No storm water issues will covered in this book chapter.

K. Bester (✉)
Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Sohngaardsholmsvej 57, 9000, Aalborg, Denmark
e-mail: kb@bio.aau.dk

C.S. McArdell
Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH 8600, Dübendorf, Switzerland

C. Wahlberg
Waste Water Treatment Department, Development & Investment, Stockholm Water Co, SE-106 36, Stockholm, Sweden

T.D. Bucheli
Agroscope Reckenholz-Tänikon Research Station ART, Reckenholzstrasse 191, CH-8046, Zurich, Switzerland

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1.1 Introduction

This study was undertaken to help scientists and regulators to understand and predict concentrations and mass flows of organic pollutants (i.e. compounds that are regulated or have proven detrimental effects to some organisms, such as Nonylphenol, Brominated Bisphenylethers) other xenobiotics (i.e. man made compounds that are not necessarily toxic at environmental concentrations, such as fragrances) and some natural toxins (mycotoxins and isoflavones) from sources via waste water into the environment (Kolpin et al. 2002; Bester et al. 2008a, 2008b and 2008c). Lots of these compounds have come into focus of considerations of water managers as they are issues directly (as prioritised compounds in one of the annexes) or indirectly (as having possibly effects on the good ecological status) in the water framework directive (EU 2000).

This study focuses on those compounds that are introduced predominantly during dry weather normal flow conditions, thus compounds that are to our knowledge emitted mainly through storm water and rain events are ignored. This is due to the fact that at the current state it seems to be hard enough to compare dry weather data, while the understanding of the behaviour of organic micro-pollutants emissions in storm water is too poor to generalise or predict anything. The results included in this paper stem from very different studies but the authors have tried their best to compare and evaluate the most representative data. Usually this paper will represent data for urban European waste water treatment plants (WWTPs) larger than 30,000 person equivalent treatment capacity.

This contribution does not intend to observe in too much detail which process in the WWTP is relevant for which transformation or elimination but to give a general overview on the mass flows in waste water treatment with activated sludge processes (BOD removal, denitrification and phosphorus removal) which are standard in most European countries.

In this chapter the wording elimination rate will be used to indicate removal from water, without indicating for any mechanisms, as this wording has found some acceptance in the literature.

1.2 Results

1.2.1 Personal Care Compounds

1.2.1.1 Fragrances

Personal care compounds are used by all of us in daily life (Reiner and Kannan 2006). Fragrances such as HHCB (trade name, e.g. galaxolide®), AHTN (trade name, e.g. tonalide®), OTNE (trade name e.g. iso-E-Super®) and others are used in washing processes, especially softener, cosmetics, and in perfumery (Reiner and Kannan 2006). Obviously these applications can be expressed as a emission per average person

(Bester et al. 2008a, b; Bester 2004, 2005a). These fragrances are sooner or later washed into waste water, thus their loads could be assessed through sales data. However, in the past the sales data have not been made available by industries due to trade secrets. These musk fragrances are necessarily relatively lipophillic, as they are made to sorb on fabric (Schmid et al. 2007). Some of the polycyclic musks have been discussed because of their estrogenic properties (Seinen et al. 1999; Bitsch et al. 2001). They have also been discussed as markers for waste water discharge into surface waters. The concentration of these compounds in waste water ranges considerably depending on the fraction from industrial and municipal waste waters (Table 1.1). The elimination rates published in the different literature sources is diverse, depending on the respective waste water treatment technology used. In this paper reference is given to European urban waste water treatment. In these the elimination rate is usually due to sorption especially due to settling in the primary settler for HHCB and AHTN while for OTNE other mechanisms might be relevant as well (Artola-Garicano et al. 2003; Ternes et al. 2004; Bester 2004, 2005a; Bester et al. 2008a, b). These fragrances have been demonstrated to be present in urban fresh waters, in estuarine and marine waters (Andresen et al. 2007) as well as the respective biota (Nakata 2005; Schmid et al. 2007).

Other fragrances such as nitromusks, e.g., musk xylene, and musk ketone as well as their metabolites (musk amines) are now less relevant than in earlier days (up to 1990). Typical concentrations now (2000–2005) are 10–100 ng/L in the inflow of the WWTPs, while there were around 1000 ng/L in the 1980s. This indicates that a drastic substitution of nitro musks in most products occurred in this decade (Bester 2007). Newer fragrances such as the macrocyclic musks, for example, habanolide, cyclopentadecanolide, ethylenebrassylate were not (yet) found in waste water thus the concentrations are below the limit of quantification (1 ng/L). This finding is indicating the low usage, the low dosage or the easy degradability of these compounds (Gautschi et al. 2001).

Input into WWTPs: Considering the mass flows into waste water treatment plants and the number of inhabitants serviced, the per person input to waste water treatment plants can be calculated. The data presented here are means of five waste water treatment plants in the Rhine/Ruhr region with 30,000–1,000,000 person equivalents (PE).

Discharge into the receiving water: Considering the effluent concentrations as well as the water flow and the number of inhabitants (not the equivalents) the discharge per person into the surface waters can be calculated. For better guidance best guesses on concentrations and loads to expect are given by expert judgement. It should be mentioned that the ranges given in Table 1.1 for the Rhine/Ruhr WWTP samples refer to dry weather. The results for the diverse WWTPs were obtained from 24 h flow controlled composite sampling for several days. Thus the mass flow into the WWTPs is assessed to be 500 mg per person per year (HHCB) and 130 mg for AHTN, respectively (Table 1.1).

European usage assessment: Considering about 300 million inhabitants an estimated usage or emission into European waste water can be estimated to contain 175 t/a (HHCB), 46 t/a (AHTN) and 287 t/a (OTNE). This agrees to estimates on European sales which were published by OSPAR (2004) to be 1,400 t (HHCB), and

Table 1.1 Usage concentrations and emission data for various compounds in waste water and wastewater treatment. Per person input refers to input to WWTP; per person discharge refers to input from the WWTP into the receiving waters

	Log K_{ow}	Henry constant	pKa	Inflow concentration (ng/L)	Effluent concentration (ng/L)	Per person input (mg/a)	Per person discharge (into the river) (mg/a)	Literature/Source
Compound								
Personal care compounds								
HHCB (Galaxolide)	5.9	11.3	nr	1,900–4,700	660–1,300	400–660 bg:500	180	Simonich et al. 2000, 2002; Bester 2004, 2005a, unpublished data
AHTN(tonalide)	5.7	12.5	nr	160–1,100	80–250	90–150 bg: 130	40–50	Simonich et al. 2000, 2002; Bester 2004, 2005a, unpublished data
OTNE(iso-E-super)	5.7	31.8	nr	2,500–13,000	1,100–6,900	820+/−0.14	180	Simonich et al. 2000, Bester et al. 2008a, b
Musk xylene(MX)	4.3		nr	5–20	0.5–2	2	0.1	This book chapter (3 WWPT in the Rhine-Ruhr area), Simonich et al. 2000
Musk xylene 4-amine (metabolite of MX)	na	na	nr	0	10–20	0	0.5–3	This book chapter
Musk ketone	4.9		nr	20–60	13–35	1–6	2–5	This book chapter (3 WWPT in the Rhine-Ruhr area), Simonich et al. 2000
Habanolide	>6	40	nr	<10	<10	<2		This book chapter (3 WWPT in the Rhine-Ruhr area), NICAS 2002

Cyclopentadecanolide	6.2	na	nr	<10	<10	<2		This book chapter (3 WWPT in the Rhine-Ruhr area), OSPAR 2004
Etylenbrassylate	4.7	na	nr	<10	<10	<2		This book chapter
Triclosan	4.3	na	8.1	1,200–7,300	200–600	290–1,040 bg: 900	10–100 bg: 30	Lindström et al. 2002, Bester 2003, 2005b, Singer et al. 2002, Halden and Paull 2005
Triclosan-Methyl	5.0	na	nr	0	6–20	0	0.3–2.6 bg: 1	Balmer et al. 2004, Bester 2003, 2005a
Flame retardants:								
Organobromines			nr					
DecaBDE (PBDE)	5.8	na	nr			28		This book chapter
Decabromo-diphenylethane	na	na	nr			3.1		This book chapter
Organo-phosphates								
TCPP	2.6	na	nr	170–3,000	130–3,000	90–1,900	90–1,140	Bester 2007, unpublished data
TCEP	1.7	3.3*E-6	nr	110–250	130–250	30–710	45–670	Bester 2007, unpubl, Inchem (1998)
TDCP	3.8		nr	150–250	150–250	20–610	20–450	Bester 2007 unpubl.
Plasticizer								
TiBP	3.5	na	nr	60–200	120–1,000	21–1,300	14–1,300	This book chapter
TnBP	3.7	na	nr	80–200	50–60	21–1,000	6–860	This book chapter
TPP	4.7	na	nr	20–160	10–27	5–390	1–140	This book chapter
TBEP	3.7	na	nr	3,500–7,800	100–2,500	900	12–600	This book chapter

(continued)

Table 1.1 (continued)

	Log K_{ow}	Henry constant	pKa	Inflow concentration (ng/L)	Effluent concentration (ng/L)	Per person input (mg/a)	Per person discharge (into the river) (mg/a)	Literature/Source
DEHP	7.5	4.4	nr	3,400–14,000	100–700	1,400	20	This book chapter, EU 2008
Nonylphenols	4.4	11		14,000–18,000	300	500–1,800	40–100	This book chapter, ECB 2002
Mycotoxins								
Deoxynivalenol	−1.41[a]	na	11.9 ± 0.7[a]	32–56	18–42	3.5–13.5	43–70% of 3.5–13.5 mg/a	Inflow & effluent conc: Own unpubl. Per person input: Turner et al. 2008a, b; Meky et al. 2003;
Nivalenol	−0.75[a]	na	11.8 ± 0.7[a]	na	na	0.2–2.0[c]	na	SCOOP 2003
HT-2 toxin	2.27[a]	na	13.3 ± 0.7[a]	na	na	0.2–2.7[c]	na	SCOOP 2003, JECFA 2001
T-2 toxin	2.25[a]	na	13.2 ± 0.7[a]	na	na	0.2–1.3[c]	na	SCOOP 2003, JECFA 2001
Zearalenone	3.72[a]	na	7.4 ± 0.4[a]	3–18	nd – 36	<0.1–0.7[c]	na	Influent & effluent conc: Lagana et al. 2001, 2004, Spengler et al. 2001, Ternes et al. 2001, Pawlowski et al. 2004. Per person input: SCOOP 2003, JECFA 2000, Zinedine et al. 2007

Fumonisin B1	−0.6/−3.2[ab]	na	3.6 ± 0.2/9.2 ± 0.4[b]			<0.0001–4.380[c]	na	SCOOP 2003, JECFA 2001
Ochratoxin A	4.4/1.1[a]	na	4.4/7.3[d]	na	na	0.006–0.066	na	Gilbert et al. 2001, Castegnaro et al. 2006, Pena et al. 2006, Manique et al. 2008
Isoflavones								
Genistein	3.0[ad]	5.2E-17 atm*m3/mole[e]	7.2; 10.0; 13.1[f]	nd – 954	nd – 83	9–1,387	0–50% of 9–1,387 mg/a	See literature in Text
Daidzein	2.5[ad]	3.9E-16 atm*m3/mole[e]	7.2; 13.1[g]	nd – 1,685	nd – 81	15–1,570	0–39% of 15–1,570 mg/a	See literature in Text
Benzotriazoles								
Benzotriazole	1.23	na	1.6; 8.2	18,000	10,000	2,000	1,400	Voutsa et al. 2006 (data from discharge of primary clarifier)
Tolyltriazole	1.89	na	1.6; 8.5	2,100 (4-TT), 1,300 (5-TT)	2,200 (4-TT), 1,200 (5-TT)	na	na	Weiss and Reemtsma 2006

na: not available; nr: not relevant; bg: best guess; unpulb: unpublished data.

[a] Data from Apfelthaler et al. 2008 (Data were taken from SciFinder scholar database whereby all values were calculated with ACD/Labs Software V8.14, Advanced Chemistry Development Inc., Toronto, Canada).

[b] At pH 3 and 7, respectively.

[c] From dietary intake, assuming 100% excretion (Valenta 1998).

[d] Rothwell et al. 2005.

[e] Estimated, using the method by Meylan and Howard 1991.

[f] Zielonka et al. 2003.

[g] Analogous to genistein.

385 t (AHTN) with strongly falling trends in 1997. In most assessments no significant mass fraction of HHCB or AHTN is volatised.

1.2.1.2 Household-Bactericides

Similar application patterns appear to be relevant for synthetical bactericides that are used in consumer products such as triclosan (Singer et al. 2002). This compound is used to increase shelf life in cosmetics. It is also used to prevent unwashed sports clothes and shoes from developing odours (Adolfsson-Erici et al. 2002). Additionally it is also used for some anti-microbial protection in food processing and in tooth paste. Most of the triclosan is washed of the respective materials sooner or later and is thus present in waste water (Singer et al. 2002; Bester 2003, 2005b). The elimination rates in the waste water treatment plants (WWTPs) are usually rather high (>90%), high elimination efficiencies occur in the primary settlers as well as in the main treatment tanks, probably due to biodegradation processes. – No degradation pathway has been published yet. However it can still be detected in the effluents, in sludge and in surface waters (Balmer et al. 2004; Bester 2005b). Triclosan can be detrimental for algae at environmental concentrations (10–30 ng/L) (Wilson et al. 2003). This bactericide can be transformed into its methylated form, triclosan-methyl (Lindström et al. 2002; Bester 2005b) in waste water treatment and eventually in the environment. This metabolite is bio-accumulating to a high extent, and causes currently the dominating peak when analysing lipophilic pollutants in fish from urban waters (Balmer et al. 2004). Considering the partition behaviour, it should be kept in mind that triclosan is a phenolic compound and its actual structure is very much pH dependent (Lindström et al. 2002).

Usually the concentrations of triclosan in waste water are in the range of 1,000–10,000 ng/L, while the concentrations in the effluents are rather in the range of 100–600 ng/L (Table 1.1). This variation is largely reflecting the mixing of municipal waste water (source) with the industrial waste water (no triclosan) as well as the water infiltrated into the sewer (no triclosan). Triclosan-methyl can be found with concentrations of about 10 ng/L in the effluents of the WWTPs (Bester 2003, 2005b). Considering dilution of waste water into surface water by 1:10 a concentration around 10 ng/L in surface waters for triclosan and about 1 ng/L for triclosan-methyl can be estimated. This agrees well to the actual findings (Bester 2005b; Xie et al. 2008).

The data on triclosan presented in this paragraph stem from the same WWTPs as those for the other personal care compounds. The estimated total mass flow of triclosan in Europe considering the WWTP inflow data would be 245 t/a, which would be correlated to a European sale of about 350 t/a (Singer et al. 2002).

1.2.2 Organobromine and Organophosphate Flame Retardants

Considering waste water, two groups of flame retardants are currently relevant: On one hand the lipophillic organobromine compounds such as the prioritised polybrominated biphenyl ethers (PBDE), brominated bisphenol A, hexabromocyclododecane etc. and on the other hand the hydrophillic chlorinated organophosphates such as tris(2-chloro-1-methylethyl) phosphate (TCPP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro, 1-chloromethyl-ethyl) phosphate (TDCP). These two groups have distinctly different emission behaviour but also their physico-chemical data are quite different. While the organobromines are more emitted from textiles (during laundry and production), the organophosphates are most probably emitted from construction materials than from textiles. While the organobromines are extremely lipophilic with log K_{ow} often higher than six, the organophosphates usually are rather hydrophilic with log K_{ow} often significantly lower than four (Table 1.1). This results in a situation were organobromines are usually very much attached to sediments and particulate matter and can thus be easily trapped in the sludge in waste water treatment, while organophosphates are usually found in the effluents of WWTPs (Meyer and Bester 2004; Marklund et al. 2005). However, compounds that are more closely connected with commercial activities (construction, commercial laundry etc.) will give less predictable mass flows than compounds that originate from the "statistical" household (Meyer and Bester 2004; Bester 2007).

1.2.2.1 Organobromine Flame Retardants

Brominated flame-retardants (BFRs) are used to prevent materials such as plastics and textiles from catching fire. The most common BFRs are polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD or HBCDD) and tetrabromobisphenol A (TBBPA). PBDEs can in turn be divided into the three technical mixtures, PentaBDE, OctaBDE and the fully brominated DecaBDE. The world production 2001 of these BFRs was about 200,000 t, the largest part being TBBPA (Thuresson 2006).

While PBDEs and HBCD are used mainly as additives to plastics and textiles, TBBPA is chemically incorporated into the polymer molecules and are therefore not as easily emitted from the materials as the additives (de Witt, 2002). It has been shown that TBBPA is not more abundant than the other BFRs in sludge although it is used in much larger amounts. In a Swedish study of sludge from 50 WWTPs the mean concentrations of DecaBDE, PentaBDE (as the sum of the most abundant congeners BDE47 and BDE99), HBCD and TBBPA were 0.12, 0.11, 0.045 and 0.040 mg/kg d.w. respectively (Nylund et al. 2002).

The organobromines discussed here are not readily biodegradable, they are very lipophilic (logK_{ow} is 5.9–10 for tetraBDE to decaBDE, 5.8 for HBCD and 4.5 for TBBPA) and they are distributed mainly into the sludge phase during waste water treatment (Table 1.1). PBDE are included in annex X of the Water Framework Directive (EC 2001) and pentaBDE is a priority hazardous substance. The EU risk assessment of HBCD (ECB 2007) recommends that HBCD is considered a persistent, bioaccumulative and toxic (PBT) substance although there is not an official classification yet. The EU risk assessment of TBBPA suggests the classification "Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment".

Another emerging BFR, marketed as a replacement for DecaBDE, is decabromodiphenyl ethane (deBDethane). DeBDethane has a chemical structure similar to decaBDE and would accordingly have similar properties concerning bioaccumulation and persistence. Recently a survey was conducted of decaBDE and deBDethane in sludge from 42 WWTPs in 12 different countries around the world (Ricklund et al. 2008a, b). In most cases the sludge had been unaerobically digested. DecaBDE was found in all samples in concentrations from 0.003 mg/kg dry matter (d.m.) to a maximum of 19 mg/kg d.m. in a US sample. Two English samples also showed high levels (12 mg/kg d.m.). DeBDethane was present in all samples but two, in levels from 0.001 to 0.22 mg/kg d.m. The highest deBDethane/decaBDE ratios were found in Germany and neighbouring countries, while the lowest ratios were found in the U.S. and the U.K. This reflects the use patterns of the substances, according to Ricklund et al., with known high imports of deBDethane into Germany and the largest market demands for decaBDE in the US and the UK.

A mass balance of DecaBDE and deBDethane in the Stockholm WWTP Henriksdal showed an influent load of 78 μg/person and day of DecaBDE and 8.5 μg/person and day of deBDethane. In Table 1.1 the annual mass flows are given. Less than 1% of this was present in the effluent water, mainly due to the high removal of solids in Henriksdal WWTP (>99.5%) which resulted in the bulk organobromines partitioned into the digested sludge. The concentrations were 0.80 and 0.081 mg/kg d.m. of DecaBDE and deBDethane respectively (Ricklund et al. 2008b).

1.2.2.2 Organophosphate Flame Retardants

About 30,000 t/a of these chlorinated organophosphates are being produced in the European Union. Ninety four percent of these are supposed to be used in rigid polyurethane foam plates for thermal insulation, 5% of the production is used in construction foams to fix windows etc. Minor fractions might be used in textiles. While the chloroethyl (TCEP), the dichloropropyl (TDCP) and the dibromopropyl (TBPP) derivatives have been used in the past, currently the usage in these applications is focussing on the monochloropropyl derivative (TCPP).

The data presented here stem from five WWTPs in the Rhine/Ruhr region. The concentrations range from a few 100 to above 10,000 ng/L, depending on the respective activities in that catchment area. As these compounds are usually not eliminated in waste water treatment, the effluent concentrations are identical to the inflow concentrations (Meyer and Bester 2004; Marklund et al. 2005; Bester 2007).

Theses compounds are most probably emitted from commercial activities, such as constructing and re-constructing as well as demolition of buildings, thus inflow concentrations often decrease Friday to Monday (Meyer and Bester 2004). The usual annual mass flow in the influent of the WWTP would currently be between 90 and 1,900 mg per person for TCPP, while it is less for the other chlorinated organophosphates (Table 1.1). The mass flows in the effluents are similar.

However, considering the concentrations in waste water, Bester (2007) estimated the emission of TCPP to be 0.09–0.64 g/a inhabitant. Assuming similar emission in the European Union with 350 million inhabitants), this leads to emissions of 30–220 t/a for Europe, which is of course only a minor mass flow in comparison to the production of 30,000 t/a. Also in this respect these materials are different to the personal care compounds. Additionally it should be considered that a considerable mass fraction of these compounds enter the WWTPs as foam particles (Bester 2007), thus it is very hard to assess a full mass balance and to identify the most relevant routes of input into waste- and surface waters for these flame retardants.

1.2.3 Plasticizers

1.2.3.1 Organophosphates

Non-chlorinated organophosphates such as tri-*n*-butylphosphate (TnBP), tri-*iso*-butylphosphate (TiBP), triphenylphosphate (TPP), tris(ethoxybutyl) phosphate (TBEP) and others are used as plasticizers in polymeric materials, as concrete additive, as hydraulic fluids, as floor polishers etc. (Bester 2007). From these diverse applications it can easily be derived that the concentrations of the single compounds in waste water can vary quite massively depending on the respective watershed. However we try to give some guidance, especially as some of these compounds are regulated with discrete target values in the EU surface water directive (EEC 1976).

1.2.3.2 Phthalates

Phthalates such as bis (2-ethyl-hexyl) phthalate (DEHP) are present especially as plasticizer in PVC products (EC 2008). Phthalates are essential as plasticizers for PVC, as pure PVC is a glass like compound and not suited for a lot of applications (EC 2008). Additionally phthalates are added to other polymers and paints. As phthalates are effective on the estrogen receptor (Blom et al. 1998) and the production volume is several 200,000–600,000 t annually (EU 2008), this group of compounds received special attention and thus especially DEHP is prioritised under the Water Framework Directive (EU 2000). DEHP is a lipophilic compound with a log K_{ow} of 7.5 (EC 2008; Table 1.1). However, though the concentrations in the crude waste water are usually pretty high (13,000 ng/L) DEHP sorbs very well to the sludge particles, thus DEHP is hardly found in relevant concentrations in the WWTPs effluent. DEHP is an issue of debate considering the sludge and for sludge disposal, as concentrations in sludge are again very high (some 10,000 ng/g dry matter). It should be considered for future monitoring that DEHP is currently phased out and being substituted by other lipophillic phthalates such as bis nonylphthalate (EC 2008). While the inflow concentration are higher than most other pollutants reported in this paper (3,000–14,000 ng/L) it effluent concentrations are relatively small (100–700 ng/L) especially when considering problems with limit of detection and the blanks in lots of the analysis. This is indicating high elimination (as sorption to sludge) during the waste water treatment process. Thus the mass inflow of DEHP can be considered to be about 1,400 mg per person each year. A European consideration would give emissions of about 500 t DEHP into the waste water in Europe, which is only a small mass fraction of the DEHP produced.

1.2.4 Nonylphenol and Nonylphenol Ethoxylates

Nonylphenol ethoxylates (NPE) constitute the major part of the group alkylphenol ethoxylates (APE) and are widely used as detergents, emulsifiers and dispersive agents. Also nonylphenol (NP) is used for some applications, such as resins, plastics and stabilisers (ECB 2002). The most commonly used NP and NPE are mixtures of a large number of isomers that differ in the degree of branching of the nonyl group situated in the para position, and, for NPE, in the length of the ethoxy-chain which can vary from a few homologues up to 60–80.

In the WWTPs, nonylphenol ethoxylates are degraded to nonylphenol and nonylphenoxy carboxylic acids (Ahel et al. 1994). When calculating the mass flows of NP in WWTPs it is thus crucial to use NP equivalents (NP_{eq}) since they occur in the form of ethoxylates in influents, in the form of free NP and in the carboxylic acid form in effluents and, finally, mainly as NP in digested sludge.

NP is toxic to aquatic organisms and not readily degradable. It has also been shown that NP exhibits estrogenic activity (ECB 2002). NP is included in the list of currently 33 substances in annex X of the Water Framework Directive (EC 2001) where it is identified as a priority hazardous substance. Environmental quality standards have recently been established for NP in surface waters: 0.3 μg/L as an annual average (EQS-AA) and 2.0 as a maximum allowable concentration (EQS-MAC) (EC 2008). In a study of some Swiss rivers NP was found in ranges from below detection limit (0.13 μg/L) to up to 0.3 μg/L (ECB 2002). In a recent Swedish investigation of surface waters NP was found in concentrations above the EQS-AA in 12% of 92 sampling points (Sweco Viak 2007).

The total use of NP and NPEO within the EU was 78,500 metric tons in 1997 according to the ECB Risk assessment report (ECB 2002). Since 2005, there is a restriction within EU on the use of NP and NPE above 0.1% in formulations intended for domestic, industrial or institutional cleaning, textiles and leather processing, metal working, etc., except in processes where there is no release into waste water (EC 2003).

In Sweden there have been a number of voluntary agreements between the industry and the Swedish Chemicals Inspectorate to phase-out the use of NP and NPE since the early nineties. In contrary to this, NPE is still found in influents and NP is present in sludge from Swedish WWTPs. In 2002, the average concentration was 17.2 mg/kg d.m. in sludge and the levels have been fairly stable since 1998 (Thuresson and Haapaniemi 2005), see also Fig. 25.1, Chapter 25 of this book.

Månsson et al. (2008) describes in a substance flow analysis (SFA) the flows of alkylphenolethoxylates (APE) through Stockholm, Sweden, with nonylphenol being one of the studied compounds. During 2004 a total of 4–13 t of AP/APE entered the system, which was defined as the City of Stockholm with 766,000 inhabitants. Half of this amount was explained by the NPE content in textiles, mainly imported from outside the EU. Other sources were, for example, paints, lacquers and cleaning agents. The, by far, largest single source (2–7 t) from the system was estimated to be emissions from imported textiles, entering the waste water during the washing procedure.

The average number of ethoxy units of the NPE found in textiles was eight which is the typical chain length of NPE in detergents (Rosenblom 2005). The molecular mass relation NP:NPE with eight units, is 2:5 and thus the total NP_{eq} contribution to the Stockholm WWTPs from textiles was 0.8–2.8 t in 2004.

The total amount of NP in digested sludge in the Stockholm WWTPs in 2004 was 426 kg based on analysis of monthly composite samples. The fate of the NP/NPE entering the plants was estimated to be 30% of NP_{eq} to the sludge, 40% degraded and 30% in the effluent waters. This is based on the study by Ahel et al. (1994) who showed a 20% distribution to sludge and approximately 40% degradation in two Swiss WWTPs, as well as an American investigation of three plants where the sludge contained around 20% of the nonylphenols present in the inflow in two cases and 64% in the third (Loyo-Rosales et al. 2007). In studies in Stockholm, a higher degree of NP distributed into the sludge was found. This was presumably due to the use of chemical precipitation of phosphate before primary sedimentation in the WWTPs. Thus the inflow of NP_{eq} to the Stockholm WWTPs was estimated to 1.4 t and consequently the contribution from textiles was 60–200%. The annual per persons discharge of nonylphenols into the waste water was 1.8 g. Similar considerations in the Rhine/Ruhr lead to the assumption that in this region 0.5 g per person were emitted (Table 1.1) (unpublished data).

Later analysis (2007) of influent water to the two Stockholm WWTPs resulted in NP levels of 1.05 and 1.22 µg/L and in NPEO (average of eight ethoxy units) levels of 13 and 17 µg/L respectively. Recalculation of NPEO levels into NP_{eq} and adding the NP gives a total of 6.3 and 8.0 µg/L NP_{eq} in influents. This corresponds to a total of 963 kg for the two plants, which can be compared to the previously mentioned, somewhat larger estimated amount for 2004. The NPE concentration in the effluents from both plants was 0.3 µg/L while NP was <0.2 µg/L. The nonylphenoxy carboxylic acids, which according to Ahel et al. (1994) accounted for almost 50% of the NP_{eq} in effluents from the Swiss WWTPs, were not analysed in this study.

1.2.5 Benzotriazoles

The complexing agents benzotriazole (BT) and tolyltriazole (TT, a mixture of the two 4- and 5-methyl isomers with the methyl substituent attached to the benzene ring) are widely used as anticorrosive additives, for example, in cooling and hydraulic fluids, in anti-freezing products, in aircraft de-icer and anti-icing fluid (ADAF), and in dishwasher detergents for silver protection. These compounds are characterized by high water solubility, low vapour pressure and low octanol water distribution coefficients (log K_{ow}: 1.23 and 1.89, respectively). Cancilla et al. (2003a) found that a mixture of BT and TT was the primary cause of toxicity to *Vibrio fischeri* (Microtox) in one ADAF formulation they tested. BT is classified as toxic to aquatic organisms; it can cause long-term adversary effects in the aquatic environment. The first reports on the environmental occurrence and on risk assessments of BT and TT were in connection to their application as corrosion inhibitors in ADAFs (Cancilla et al. 1998, 2003b; Corsi et al. 2003). BT and TT anti-corrosives were detected in the subsurface waters underneath airports at concentrations of 126 mg/L for BT and 17 mg/L for 4-TT as well as 198 mg/L for total TT. Concentrations of TT in receiving streams were less than 0.08 mg/L (Cancilla et al. 2003a). Giger et al. (2006) found that 55% (71 kg) of the total amount of BT set free at the airport (130 kg) directly entered the River during or shortly after de-icing activities took place and that the pattern of the weekly loads agreed well with the pattern of usage of ADAF.

However, the overall contribution of the airport to the yearly BT mass flows of the investigated river watershed was only 18% (Giger et al. 2006). The main input of BT into the aquatic environment occurs due to its application as dishwasher detergent additives, being discharged in municipal wastewaters. Mean annual amounts of BT used in dishwasher detergents are 2 g/person (Table 1.1, data for Switzerland from Ort et al. 2005; McArdell et al. 2009). BT and TT were found in the μg/L range in the samples of primary and secondary effluents from 24 municipal WWTPs in Switzerland (Voutsa et al. 2006). The BT concentrations were always by a factor of 10–100 higher than the corresponding TT values. The median values for BT concentrations in primary and secondary effluents were 18 and 10 μg/L, respectively. The elimination of BT in WWTP is relatively low with an average of 30%. Weiss and Reemtsma (2006) found similar concentrations in Germany. The benzotriazoles were determined in untreated municipal wastewater with mean dissolved concentrations of 12 μg/L (BT), 2.1 μg/L (4-TT), and 1.3 μg/L (5-TT). Removal in conventional WWTPs ranged from 37% for BT to insignificant removal for both TT. Compared to the other contaminants reported in this paper, benzotriazole is occurring in the highest concentrations in surface water and the mass discharge into the environment is considerable. BT has been suggested by some authors as a marker for waste water discharge in surface waters (McArdell et al. 2009).

1.2.6 Mycotoxins

Mycotoxins are a large and diverse group of fungal toxins which infect various crops both in the fields and during storage. The major classes of mycotoxins are aflatoxins, trichothecenes, fumonisins, zearalenone (ZON), ochratoxins and ergot alkaloids. These are produced by several species of the genera *Aspergillus*, *Fusarium*, *Penicillium*, and *Claviceps* (CAST 2003). Many mycotoxins are of concern for human and animal diseases. Consequently, their occurrence is widely investigated in food and feed. In contrast, much less is known about their environmental fate and behaviour of these toxins (Bucheli et al. 2005; Hartmann et al. 2007, 2008a, b). Since humans are continuously exposed to mycotoxins via food intake, and because a certain fraction of these compounds is usually excreted (in native, metabolized or conjugated form), we suggest that mycotoxins potentially classify as micropollutants in urban and natural waters (Bucheli et al. 2008). Moreover, these facts legitimate their inclusion in this review.

Unfortunately, very little data has been published on the occurrence of mycotoxins in urban waters and sewer systems. The highly estrogenic ZON (as well as its metablites α-zearalenol, α-zearalanol, and β-zearalanol) was occasionally present in German and Italian WWTP in- and effluents at the low ng/L concentration level (Lagana et al. 2001, 2004; Spengler 2001; Ternes et al. 2001; Pawlowski et al. 2004). We quantified deoxynivalenol (a trichothecene) in the inflow (discharge of primary settling tank) and the effluent of three WWTPs in the river Glatt catchment. While the concentrations in the inflow were between 32 and 65 ng/L they ranged between 18 and 42 ng/L in the effluent (Table 1.1). Corresponding elimination rates ranged from 30% to 57% (own unpublished data).

Alternatively, expected concentrations in urban waters can be calculated from data of mycotoxins in human excrements. In the case of deoxynivalenol (DON), the quantified mean annual excretion via urine ranges from 3.5 to 13.5 mg/(capita*a) (Table 1.1, Data from UK: Turner et al. 2008a, b, and China: Meky et al. 2003). Interestingly, the predicted and measured concentrations of DON in the influents match well when using such excretion rates together with numbers of inhabitants and hydrological information in the catchments of the river Glatt WWTPs.

In a worst case scenario, concentrations in urban waters may be estimated from annual dietary intake data assuming a 100% excretion rate (usually, literature data on human excretion rates are rather scarce, highly variable, and dependent on the experimental conditions, but generally, excretion can be quite considerable). The annual intake of DON is estimated to vary between 1.9 and 31 mg/(capita*a) (SCOOP 2003; JECFA 2001). It is instructive to compare this range with the above stated 3.5–13.5 mg/(capita*a) for human excretion: both estimates are in the same range, with the intake data being slightly higher than those for excretion. This excellent match lends credit to the independent methodologies used to gather the data. Moreover, for a first exposure assessment of urban waters it seems justified to use intake as surrogates for excretion data.

Ochratoxin A was the only other mycotoxin for which we were able to find human excretion data. Mean annual amounts excreted via urine range from 6 to 66 μg/capita (Table 1.1, data from UK: Gilbert et al. 2001; Bulgaria: Castegnaro et al. 2006; Portugal: Pena et al. 2006; Manique et al. 2008, and Spain: Manique et al. 2008), and the frequency of excretion (number of observations per number of test persons) from 45% to 100%.

Further dietary intake data are available for ochratoxin A. Thuvander et al. (2001) indicated for 30 μg/(capita*a), while JECFA 2001 published somewhat higher number, that is, 135 μg/(capita*a). This is also exhibiting a good match with excretion estimates (see above). For nivalenol SCOOP (2003) published 0.2–2.0 mg/(capita*a). For HT-2 toxin SCOOP 2003 and JECFA 2001 found 0.2–2.7 mg/(capita*a). The T-2 toxin was emitted with similar amounts (0.2–1.3 mg/(capita*a), according to SCOOP 2003 and JECFA 2001). ZON was detected with 0.02–0.7 mg/(capita*a) (SCOOP 2003; JECFA 2000; Zinedine et al. 2007), while fumonisin B1 (FB1) was described by SCOOP (2003) with <0.1–15 μg/(capita*a), and by JECFA (2001) with 440–4,380 μg/(capita*a).

The data is less clear for FB1. Mean urinary FB1 concentrations ranged from 13 to 54 μg/(capita*a) in Mexican population, depending on the maize consumption (Gong et al. 2008). However, FB1 is stated to be mainly excreted via feces (Shephard et al. 2007), but data is scarce. In South Africa, 33% of 40 rural fecal samples contained 0.5–39 mg/kg (Chelule et al. 2001). Unfortunately, the authors did not specify whether their data represents wet or dry weight. No other data are available for other mycotoxins.

1.2.7 Isoflavones

Isoflavones belong to the diverse class of the flavonoides. Several of their representatives are weakly estrogenic (Breinholt and Larsen 1998; Zand et al. 2000; Choi et al. 2008), and occur naturally in a wide range of plants, such as soy or clover (e.g. Fletcher 2003). Although the occurrence of flavonoides in food, and their metabolism and effects on human health have been widely investigated, little is known about their fate in urban waters. Here, we focus on the two compounds for which we believe that sufficient data allow a discussion in the context of this chapter, that is, genistein and daidzein.

The presence of genistein and daidzein in WWTP in- and effluent was investigated by several authors. Studies in Australia (Kang et al. 2006), Germany (Spengler et al. 2001; Ternes et al. 2001; Pawlowski et al. 2004), Italy (Lagana et al. 2004; Bacaloni et al. 2005), Spain (Farré et al. 2007), and Switzerland (own unpublished data) reported influent concentrations of genistein and daidzein from below the limit of detection (LOD) up to 954 ng/L, and from below the LOD up to 1,685 ng/L, respectively. Respective effluent concentrations were in the range of below LOD – 83 ng/L for genistein, and below LOD – 81 ng/L for daidzein (Table 1.1). These numbers translate into general removal rates of 50–100% for genistein, and 61–100% for daidzein. Lee et al. (2008) determined similar concentrations and removal rates in a pilot sewage treatment plant.

Excretion rates of humans (mainly via urine, e.g. Rowland et al. 2003) vary widely, depending on the diet, age and sex of the test persons. Mean numbers of roughly a dozen studies conducted in Australia, Germany, Japan, the UK, and the US range from 9 to 1,387 mg/(capita*a), and from 15 to 1,570 mg/(capita*a) for genistein and daidzein, respectively (Dalais et al. 1998; Grace et al. 2004; Hutchins et al. 1995; Lampe et al. 1999; Liu et al. 2005; Moors et al. 2007; Ritchie et al.

2004; Valentin-Blasini et al. 2003, 2005; Wolff et al. 2007; Yamamoto et al. 2001), with a frequency of observation of close to 100%. The median number of these studies is at 24 mg/(capita*a) and 36 mg/(capita*a) for genistein and daidzein, respectively.

These excretion rates can be compared with data on dietary intake. Data on isoflavone intake varies considerably and is much elevated if the traditional diet is based on soy products. Although there are numerous studies published, many of them report data on total isoflavone intake only. A non-exhaustive literature search for genistein and daidzein consumption in several European countries, Canada and the US yielded ranges from 26 to 2,336 mg/(capita*a) and 14–1,338 mg/(capita*a), with median numbers of 134 and 115 mg/(capita*a), respectively (Cotterchio et al. 2008; Clarke and Lloyd 2004; de Kleijn et al. 2001; Kirk et al. 1999; van der Schouw et al. 2005; van Erp-Baart et al. 2003). Excretion of isoflavones occurs predominantly via urine, but at highly variable rates: 5–30% for genistein, and 6–62% for daidzein (Rowland et al. 2003; Lampe 2003; Manach et al. 2005). Considering all uncertainties inherent to these estimates, the match between ingested and excreted amounts is still surprising.

1.3 Conclusions

In this study we give an overview on the emission of compounds in concentrations as well as in mass flows. They can be used for comparison on whether other WWTPs may have a rather high or low load. Additionally these data may be used to predict the loads in WWTPs, and their receiving waters without the absolute need to start huge monitoring programmes. Interestingly, diverse as they are in nature, application and consumed amounts, most of the compounds compiled here exhibit annual per person loads in range of about 1–1,000 mg. These can be used as a predictive tool for the exposure of environmental compartments. Whether or not effects are to be expected in these compartments is a matter of toxicity as well as of exposure.

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Chapter 2
Identifying and Classifying the Sources and Uses of Xenobiotics in Urban Environments

Erica Donner, Eva Eriksson, Hans-Christian Holten-Lützhøft, Lian Scholes, Mike Revitt, and Anna Ledin

Abstract The sources and uses of xenobiotics in urban environments are very diverse, making structured approaches to source and use classification a fundamental requirement for effective pollution management. This chapter provides a general introduction to the topic of substance source and use identification, highlighting the key differences between different types of sources (e.g. processes vs. commodities; natural vs. anthropogenic etc.) and different types of uses (e.g. active vs. passive; dispersive vs. non-dispersive, etc.). Examples of relevant classification systems and their applications are also given, and the diversity of potential xenobiotic sources and uses is clearly demonstrated through the description of a series of ‘archetypes’ (i.e. model examples). The chapter concludes with an overview of useful source tracking approaches (e.g. database mining, marketing surveys, forensic approaches etc.).

2.1 Introduction

What do a burning forest, a plastics factory and a baby’s playsuit have in common?

E. Donner (✉)
Centre for Environmental Risk Assessment and Remediation (CERAR) University of South Australia Building X, Mawson Lakes Campus Mawson Lakes, 5095 Australia
Ph: +61 (08) 8302 3624
e-mail: erica.donner@unisa.edu.au

L. Scholes and M. Revitt
Urban Pollution Research Centre, Middlesex University, Hendon Campus, The Burroughs, London NW4 4BT, United Kingdom
e-mail: e.donner@mdx.ac.uk
Phone: +44 208 411 5308
Fax: +44 208 411 6774

E. Eriksson, H.C. Holten-Lützhøft, and A. Ledin
Department of Environmental Engineering, Technical University of Denmark, Miljovej B113, 2800 Kgs, Lyngby, Denmark

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The answer is that despite their clearly disparate nature, the items listed above share the following characteristic; they are all potential 'sources' of xenobiotics.[1] This can also be said of toothpaste (Capdevielle et al. 2008), laundry detergents (Gordon et al. 2008), volcanoes (Capaccioni et al. 1993; Pyle and Mather 2003), dolls (Biedermann-Brem et al. 2008), mobile phones (Nnorom and Osibanjo 2009; Monteiro et al. 2007), car washes (Boussu et al. 2007), shoes (Kolomaznik et al. 2008), railway sleepers (Mateus et al. 2008; Thierfelder and Sandstrom 2008), wastewater treatment plants (Sabik et al. 2004), and numerous other commodities and facilities. Although the extent and nature of the xenobiotics released from these different sources will certainly differ, each one is nevertheless a potential cause of environmental pollution, and hence a potential challenge for environmental management. For the fact is that modern societies are highly dependent on commodities and processes that involve the use/release of artificially synthesised compounds and/or natural elements such as metals that would not normally be present on the earth's surface in such an abundance and which in many cases are harmful to organisms (including humans) and ecosystems (i.e. they are hazardous substances). Thus, we are surrounded by a very extensive range of useful processes, facilities and commodities which have the unfortunate feature of also acting as pollutant[2] storage and/or supply vessels. The challenge then is to exploit both the beneficial 'uses' of xenobiotics and the beneficial features and services of xenobiotic 'sources', whilst also undertaking to limit the emissions of harmful pollutants into the natural environment. Policy makers continually seek to meet these challenges, with new regulations such as the European REACH regulation (EC 2006a) not only reflecting the need to protect human health and the environment from adverse chemical effects, but also acknowledging the need to protect the competitiveness of the European chemicals industry.

The inherent properties (e.g. solubility, volatility, biodegradability etc.) of xenobiotics are just as varied as their potential sources and uses, and the behaviour of different xenobiotic substances upon release to the environment varies accordingly (see Holt 2000 for background information on the fate of chemical substances in the environment). The ecotoxicity and environmental persistence of a substance have a large bearing on its environmental hazard, and it is clear that a 'safe' emission level for one compound may be orders of magnitude higher or lower than that specified for another. To further complicate matters, some sources/uses of xenobiotics may release a single harmful substance, whilst others release a mixture. The form of pollutant(s) released can also vary (e.g. different ionic species, isotopes, degradation products, metabolites etc.). Overall, the identity and form of the xenobiotic substance(s) released and the relative mix of substances in the emission stream is dependent on the specific source and/or use of the substance. The spatial distribution and scale of that source/use within the area of interest (e.g. a city, country etc.) and the type of regulatory and/or voluntary controls imposed upon it will

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[1] The term xenobiotic is used here to refer to substances which are foreign to biological systems. This includes substances which may be found in an organism but not produced by it, and which are potentially detrimental to life. This definition includes artificially synthesised compounds as well as naturally occurring elements and compounds which, due to anthropogenic activities, are present at unnaturally high concentrations in the environment.

[2] An environmental pollutant is a contaminant with the propensity to adversely alter the physical, chemical or biological properties of the environment.

play a major role in determining its importance in relation to the overall emission of hazardous substances into the environment and to the overall risk posed by the particular substance(s) emitted. The relative hazards and risks associated with different xenobiotics and their release to the environment is not the focus of this chapter, but it is important to recognise that risk assessment activities are heavily dependent on adequate knowledge of substance sources and uses. This knowledge also forms an important basis for pollution monitoring, exposure assessment, and source control strategies for emission prevention and/or reduction.

When faced with such an extraordinary diversity of xenobiotic sources and uses to manage, it is useful to think about them in a more structured manner. For example, in designing a source control programme for a hazardous substance it is beneficial to know the full extent and array of sources from which that substance may be released. We need to know which sources are the most important in terms of the quantity of substance released, which sources will be relatively easy to control using on-site treatment technologies, which sources are mobile, which sources are continually emitting and so on. This knowledge is vital for building up a picture of the patterns and pathways of substance flow throughout the environment and for supporting the calculation of mass balances and the evaluation of different pollution control strategies, as well as enabling typically limited monitoring resources to be optimally allocated.

It is also helpful to know the breadth of use of the target substance. Is it only used as a specialised insecticide for a single type of garden plant, or is it used as a solvent in dozens of different formulations of paints, car maintenance products and carpet cleaning materials? Is there any potential to substitute the use of this substance in a particular application with that of another, and if so, would this substitution reduce the environmental risk? Alternatively, is the use of this substance the basis of a key industrial process, upon which tens of thousands of people rely for their livelihood? Clearly the range of questions we must ask in relation to managing xenobiotic sources and uses is extremely extensive with many different layers of complexity. That is precisely why it is so imperative to be able to categorise the sources and uses of substances in a structured manner, one that is suitable for organising and generating the information needed to answer these questions.

This chapter provides a general introduction to the topic of xenobiotic source and use identification and classification. The extensive range of potential sources and uses of xenobiotics in urban environments is illustrated and key differences between different types of sources and uses are highlighted. Examples of relevant classification systems and their applications are also given. Finally, an overview of the range of methods for tracking and identifying sources is presented.

2.2 Definitions of Key Terms

2.2.1 Sources and Uses

Although the sources and uses of xenobiotics are often closely related, the terms are by no means synonymous. For example, a wastewater treatment plant (WWTP) is almost always considered a major point source of pollutants, even though the vast majority of pollutants emitted in the effluent are not actually used within the WWTP itself but are introduced into the sewage system from numerous different diffuse sources located within the wastewater catchment area.

Throughout this chapter the term 'source' is taken to mean a potential xenobiotic emission source. As such, the term covers a myriad of different commodities, facilities, and processes (activities) which have the potential to release xenobiotics into the wider environment, and which may therefore have implications for the urban water cycle. For the purposes of monitoring and management, these sources are often divided into subcategories such as point and diffuse sources, mobile and transient sources, natural and anthropogenic sources and so on. The relevance of these and other key categories will be considered further in Section 2.4.

Henceforth, the term 'use' is taken to refer to the specific use/application of a substance in a process or commodity. Whether a substance is suitable for use in a particle process or commodity depends both on its chemical structure and on its characteristic emergent properties. For instance, chemical structure will play a major role in determining a substance's ecotoxicity and therefore its biocidal potential, whilst key properties such as boiling and freezing points will determine whether a substance may potentially be used as a coolant or anti-freezing agent.

The use of a particular substance in an industrial process might lead to the release of that substance in the waste streams associated with that industry, and the relevant industrial facilities should hence be identified as possible sources of that substance. However, as indicated earlier the situation is not always so straightforward and there are many examples of unintentional (and possibly unregulated) sources of pollutants that do not result from the specific use of a substance but from its indirect use or accidental release.

It is therefore important to recognise that:

1. Not all sources of a particular substance are associated with the deliberate use of that substance and
2. Not all uses of a potential pollutant will necessarily result in its release

As evidence for the first of these statements, consider the combustion of wood for household heating. This is a common source of air pollution, emitting a range of pollutants including polyaromatic hydrocarbons (PAHs), volatile organic compounds (e.g. aldehydes), and metals (see, for example, Bonvalot et al. 2000; Hedberg et al. 2002) and yet it is very clear that the process of burning wood has nothing to do with the deliberate use of these substances. A forest fire or volcano would be another suitable example supporting this statement, these being natural sources of xenobiotics such as aromatic hydrocarbons, alkenes and metals (Capaccioni et al. 1993; Pyle and Mather 2003; Watt et al. 2007). There is also the case of the formation of degradation products, where the substance itself is not deliberately used but forms later due to chemical- and/or bio-degradation processes (e.g. formation of 4-nonylphenol isomers due to degradation of nonylphenol ethoxylates during wastewater treatment (Sabik et al. 2004; Di Gioia et al. 2008). Finally, consider the case of contaminated sediment (previously acting as a pollutant sink) that has been resuspended by a storm event and has subsequently become a source of pollutants to the downstream environment (Old et al. 2004).

To clarify the second statement above, consider the use of a substance as an intermediate in a closed industrial process (e.g. during pharmaceutical production), where the intermediate is produced on-site and is not isolated as part of the process but is contained within consecutive reaction vessels. Occasionally the reaction vessels are cleaned and the first flush of wastewater incinerated. Under this scenario the intermediate should not be emitted to the environment despite its deliberate use in this process. Of course, there is still the possibility of an accidental spill occurring, resulting in an emission, but overall, the substance should be contained on-site and not be released from the facility. This highlights another key point, which is that high substance usage does not necessarily translate to high emissions, particularly where uses are not of a dispersive nature and/or where very efficient emission control systems are in effect. By the same reasoning it must also be recognised that in some cases a relatively minor substance use may actually represent a very significant emission pathway.

2.2.2 Emissions and Releases

The terms ‘release’ and ‘emission’ are often used interchangeably in discussions about pollution and this is generally not problematic. Historically, ‘emission’ has been the term more commonly used to describe the discharge of a pollutant into the environment, typically being found in phrases such as emission permit, emissions monitoring, emission control strategies etc. However, in recent years there has been a gradual move towards greater use of the term ‘release’. For instance, until quite recently the Europe-wide pollution reporting and monitoring system established by the European Commission (EC) was called the European Pollutant Emissions Register (EPER), but in 2007 this was succeeded by a new system known as the European Pollutant Release and Transfer Register (E-PRTR). The term ‘release’ was not defined in the EPER decision document (EC 2000), whereas an emission was defined as a “direct release of a pollutant to air or water as well as the indirect release by transfer to an off-site waste water treatment plant”. In contrast, the E-PRTR decision document (EC 2006b) does not define the term ‘emission’ but defines ‘releases’ as “any introduction of pollutants into the environment as a result of any human activity, whether deliberate or accidental, routine or non-routine, including spilling, emitting, discharging, injecting, disposing or dumping, or through sewer systems without final waste-water treatment”

For some purposes it may be useful to make a distinction between the two terms in order that ‘emission’ can be used to refer to relatively large scale point source emissions from industrial installations which have traditionally been the focus of pollution research, whilst ‘release’ can be used to refer to the gradual ongoing release of a substance from an article or surface (e.g. clothing, building materials, painted surface etc.) during its life cycle (including the service life and waste disposal phases).

In such cases the emission sources are likely to be subjected to emission limits and/or monitoring and reporting requirements, whereas the releases relate to more diffuse pollution sources, which can be described by release factors but which are less likely to be monitored or controlled. For the purposes of this chapter no distinction is made between emissions and releases, with the terms being used interchangeably.

2.3 Uses of Xenobiotics

2.3.1 Classifying the Uses of Xenobiotics

Due to their extensive range of physico-chemical properties, xenobiotics can be used for an extremely diverse range of potential applications. Indeed a great deal of time and money is spent in developing new substances specifically designed to have the appropriate characteristics for a particular use. Some substances are perfectly suited to a rather narrow range of specialist uses (e.g. 95 % of 1,2-dichloroethane is used to produce vinyl chloride which is further converted to polyvinyl chloride; BMU 2002), whereas other substances may be suitable for a wide variety of applications (e.g. the use of polybrominated diphenylethers (PBDEs) as flame retardants in polystyrene, textile coatings, wire and cable insulation, electronics etc.; Danish EPA 1999; US EPA 2006). The range of appropriate functional uses for a substance (e.g. as an antioxidant, softener, heat transfer agent, solvent etc.) is largely determined by the substance's chemical structure and inherent properties, but even if a substance appears to be ideally suited for a particular use on the basis of its physico-chemical properties and chemical reactivity, it may be omitted from use due to other factors such as toxicity, regulatory controls, excessive cost, hazardous degradation products, voluntary agreements etc.

Generally, the 'use' of a substance can be classed as being either active or passive. For example, the active use of a substance could refer to the use of a pesticide in which the substance (e.g. endosulfan) is the active ingredient in the pesticide formulation. Continuing with this example, a passive substance use could be demonstrated by a compound used as a carrier substance or dispersing agent (e.g. nonylphenol ethoxylate) in the same formulation. These substances are being used as additives rather than as active substances, but they are nevertheless released to the environment upon application of the pesticide. It is very common for substances to be incorporated into a commercial product in this manner, where they do have a functional role but where their own properties become secondary to that of the finished article (e.g. a plasticiser used in a rubber duck, or a biocide used in a paint formulation). Indeed the EU REACH legislation (EC 2006a) defines an article as "an object which during production is given a special shape, surface or design which determines its function to a greater degree than does its chemical composition". It should also be noted that some substances could be present in an article merely as a by-product, impurity, or degradation product. In this case the substance has no functional use in that article, but may still be leached from the matrix during use or throughout the waste disposal and degradation pathway.

Substance use can be classified on a number of levels. The most appropriate classification to use will of course depend on the actual purpose of the data collection and analysis. For instance, is the purpose to collect information about the range of potential functional uses of a group of substances, or to gather data about the quantity of substances used for manufacturing purposes on an industry by industry basis? In the European Commission Technical Guidance Document on Risk Assessment (TGD) (EC 2003) three different types of categories are applied for the description of substance use. These TGD use categories are used as the basis for assessing the extent of environmental and human health risks associated with substance use and emissions in the EU. The first category type (TGD main categories; see Table 2.1) provides a framework for classifying the extent of substance dispersion associated with a particular use (and hence potential worker and/or environmental exposure), whereas the second category grouping is used to identify the major types of industry where the substance is in use (TGD industrial categories; see Table 2.1). Finally, the functional uses of a substance can also be utilised as the

Table 2.1 Main categories and industrial categories used for characterising substance use according to the European Technical Guidance Document on risk assessment (TGD) (EC 2003)

Main categories	
1	Use in closed systems
Ia	Non isolated intermediates (substances restricted to the reaction vessels)
Ib	Isolated intermediates stored on-site
Ic	Isolated intermediates with controlled transport
II	Use resulting in inclusion into or onto a matrix
III	Non-dispersive use
IV	Wide dispersive use
Industrial categories	
1	Agricultural industry (e.g. pesticides)
2	Chemical industry: basic chemicals (e.g. solvents)
3	Chemical industry: chemicals used in synthesis (e.g. intermediates)
4	Electrical/ electronic engineering industry (e.g. semiconductors)
5	Personal/ domestic (e.g. cosmetics; cleaning agents; insecticides for domestic use)
6	Public domain (e.g. products used in public areas such as offices; cleaning agents; insecticides)
7	Leather processing industry (e.g. dyestuffs)
8	Metal extraction, refining and processing industry (e.g. heat transferring agents)
9	Mineral oil and fuel industry (e.g. motor oil; fuel additives; gasoline)
10	Photographic industry (e.g. antifogging agents; sensitisers)
11	Polymers industry (e.g. stabilisers; softeners; antistatic agents)
12	Pulp, paper and board industry (e.g. dyestuffs; toners)
13	Textile processing industry (e.g. dyestuffs; flame retardants)
14	Paints, lacquers and varnishes industry (e.g. solvents; viscosity adjusters; pigments)
15	Engineering industry: civil and mechanical (e.g. construction materials; hydraulic fluid)

Table 2.2 Substance 'use categories' specified in the European Technical Guidance Document on risk assessment (TGD) (EC 2003)

Use categories			
1	Absorbents and adsorbents	29	Heat transferring agents
2	Adhesives, binding agents	30	Hydraulic fluids and additives
3	Aerosol propellants	31	Impregnation agents
4	Anti-condensation agents	32	Insulating agents
5	Anti-freezing agents	33	Intermediates
6	Anti-set-off and anti-adhesive agents	34	Laboratory chemicals
7	Anti-static agents	35	Lubricants and additives
8	Bleaching agents	36	Odour agents
9	Cleaning/washing agents and additives	37	Oxidising agents
10	Colouring agents	38	Pesticides
11	Complexing agents	39	Pesticides, non-agricultural (biocides)
12	Conductive agents	40	pH-regulating agents
13	Construction materials additives	41	Pharmaceuticals
14	Corrosion inhibitors	42	Photochemicals
15	Cosmetics	43	Process regulators
16	Dust binding agents	44	Reducing agents
17	Electroplating agents	45	Reprographic agents
18	Explosives	46	Semiconductors
19	Fertilisers	47	Softeners
20	Fillers	48	Solvents
21	Fixing agents	49	Stabilisers
22	Flame retardants and fire preventing agents	50	Surface-active agents
23	Flotation agents	51	Tanning agents
24	Flux agents for casting	52	Viscosity adjusters
25	Foaming agents	53	Vulcanising agents
26	Food/feedstuff additives	54	Welding and soldering agents
27	Fuels	55	Others
28	Fuel additives		

basis for classification (TGD use categories; see Table 2.2). This last approach is particularly useful when considering the possible options available for substitution of a substance (for emission control purposes), as suitable alternative substances will most likely be classified under the same use category.

2.3.2 Archetypes of Xenobiotic Substance Use

In order to further illustrate the diversity of xenobiotic uses in urban environments and the key ways in which these uses differ, a use typology with model examples (i.e. 'archetypes') is presented in Table 2.3. The archetype examples are drawn from a range of different industrial and functional use categories, and

Table 2.3 Archetypes (i.e. model examples) of xenobiotic uses

Archetype 1a – Use resulting in inclusion into or onto a matrix: Active use

- Use of brominated flame retardants in consumer products such as electronic equipment and upholstered furniture (Kemmlein et al. 2003).

Archetype 1b – Use resulting in inclusion into or onto a matrix: Additive use

- Organic lead compounds added PVC as stabilisers to enhance heat resistance and durability during both manufacture and use (Thornton et al. 2001).

Archetype 2a – Non-dispersive use: Active use

- Use of 1,2-dichloroethane as an intermediate in the production of vinyl chloride which is subsequently used to produce polyvinylchloride (PVC) (BMU 2002).

Archetype 2b – Non-dispersive use: Additive use

- Use of fixed bed nickel catalysts for the industrial hydrogenation of oils and fatty acids (Morawski 2003)

Archetype 3a – Dispersive use: Active use

- Use of tributyltin (TBT) as the active ingredient in anti-fouling paint formulations for application to ships. These formulations are designed to gradually release the TBT over time to prevent the growth of algae, barnacles and other organisms (Santillo et al. 2001)

Archetype 3b – Dispersive use: Additive use

- Inclusion of inert additives in a pesticide formulation used for spraying. The additives are not intended to affect the target pest species but are used for preservation, UV-protection, stabilisation etc. They are released together with the active ingredients during spraying. (Cox and Surgan 2006)

Archetype 4 – No specific use

- Emissions of cadmium due to presence as an impurity in phosphate fertiliser applied to gardens (Grant and Sheppard 2008; Nziguheba and Smolders 2008).

clearly demonstrate that the type of use will have a major bearing on the nature of the resulting emission (e.g. whether the emission will be diffuse or otherwise). It is important to recall, however, that the scale of use does not necessarily bear relation to the scale of emission (i.e. high substance usage does not necessarily equate to high emissions). The typology of uses is not intended as an exhaustive use classification system but as an illustrative tool for enhancing understanding of the potential range of xenobiotic uses and the potential implications for substance release to the environment.

2.4 Sources of Xenobiotics

2.4.1 Classifying the Sources of Xenobiotics

Given the extraordinary diversity of potential emission sources, a structured approach to source classification is a fundamental requirement for effective pollution management. Most of the existing large-scale emissions inventories were originally designed to facilitate the monitoring of major point sources of key pollutants (e.g. persistent organic pollutants, greenhouse gases, etc.) and hence focussed predominantly on classifying industrial emission sources. For example, the first Europe-wide emissions register, the EPER, was designed to classify and store emissions data for large and medium-sized industrial facilities operating within the industrial sectors covered by the Integrated Pollution Prevention and Control Directive (IPPC Directive) (EC 1996). The emissions data were classified according to the pollutant identity, the IPCC industrial activity category, and the geographical location of the relevant industrial facility. With the focus firmly on point sources of industrial pollution, diffuse emissions such as those from the transport sector, natural sources, household sources and most agricultural sources were not covered. However, following the EU ratification of the UN-ECE Protocol on Pollutant Release and Transfer Registers (PRTRs) and the adoption of EC Regulation No. 166/2006 (EC 2006b) concerning the establishment of a European PRTR, the EPER was succeeded in 2007 by the more comprehensive E-PRTR. This development and the associated changes in reporting requirements corresponded with a general increase in efforts to monitor and account for diffuse emission sources (e.g. road traffic, domestic heating etc.). Other large-scale emissions inventories have also been moving in this direction. For instance, the US EPA Source Classification Codes (SCC) system (US EPA 2008) has also evolved to include appropriate categories for classifying non-industrial emissions, using Area and Mobile Source (AMS) codes to identify residential sources, mobile sources and a range of other non-industrial sources.

The SCC approach uses an extensive hierarchical classification system to identify the specific economic activity and process resulting in an emission. As the system is hierarchical and includes four different levels of description, it is possible to use the codes to describe emissions sources to different levels of detail as required. It also facilitates the reporting and analysis of aggregated emissions data, so that emissions can be compared on the basis of particular industry groupings (e.g. chemical manufacturing vs. primary metal production). A selection of SCC/AMS codes and matching descriptions are presented in Table 2.4 to illustrate the type of information that is encoded with each additional level of detail.

The highly structured source classification systems described above were developed specifically to support the collection, storage, and interrogation of large amounts of emissions data. An advantage of adopting such a highly standardised, systematic approach to source classification for emissions reporting is that the use of harmonised classification structures (e.g. the EU Standard Nomenclature for Economic Activities [NACE]) can also facilitate the extraction of relevant data from other reporting systems which also use these standard classifications (Mikkelsen et al. 2008). For example, NACE codes could be used to extract information from EUROSTAT (EC 2008) showing the average annual environmental protection expenditure for a particular industry group, or the number of people employed in that sector. Combined assessment of this type of information together with emissions data can be very informative, providing an indication of the potential socio-economic impacts of changing regulations (e.g. banning a substance or restricting some forms of industry). Clearly, it is important to take such factors into account when planning emission reduction strategies.

Table 2.4 Examples of the United States Environmental Protection Agency's Source Classification Codes (SCC) and Area and Mobile Source (AMS) codes and descriptions of the information encoded by them (US EPA 2008)

SCC/AMS	Level 1	Level 2	Level 3	Level 4
30100905	Industrial Processes	Chemical Manufacturing	Cleaning Chemicals	Alkaline Saponification
30100508	Industrial Processes	Chemical Manufacturing	Carbon Black Production	Bagging/Loading
30200966	Industrial Processes	Food and Agriculture	Beer Production	Ethanol Removal from Waste Beer
30203201	Industrial Processes	Food and Agriculture	Bakeries	Bread Baking: Sponge Dough Process
30303009	Industrial Processes	Primary Metal Production	Zinc Production	Raw Material Handling and Transfer
50100402	Waste Disposal	Solid Waste Disposal – Government	Landfill Dump	Fugitive Emission
2104008010	Stationary Source Fuel Combustion	Residential	Wood	Woodstoves: General
220100123T	Mobile Sources	Highway Vehicles – Gasoline	Light Duty Gasoline Vehicles (LDGV)	Urban Interstate: Tire Wear
2265004021	Mobile Sources	Off-highway Vehicle Gasoline, 4-Stroke	Lawn and Garden Equipment	Chain Saws < 6 HP (Commercial)
2282020010	Mobile Sources	Pleasure Craft	Diesel	Outboard

From a more general perspective, it is also useful to consider the ways in which sources can be divided on the basis of major characteristics such as their spatial distribution, release patterns etc. Some of these groupings should already be apparent, being widely used to differentiate between different types of sources (e.g. point vs. diffuse sources; natural vs. anthropogenic) whereas other characteristics have less commonly been used to delineate differences between sources (e.g. intentional vs. unintentional use/release). Depending on the particular application, some types of sources may be more relevant than others, and recognition of the ways in which they differ can be very useful in targeting source data collection (e.g. for regional pollutant emissions reporting, local source control planning, public education campaigns, emission permitting activities, etc.). Whilst the categories described below are not necessarily all appropriate for creating a structured source classification system, they are suitably illustrative of the manner in which source and release characteristics can differ. Major source categories include:

- Processes vs. commodities

Processes (e.g. production of vinyl chloride; generation of electricity by coal combustion; application of herbicide for roadside maintenance etc.) can directly produce emissions due to the use/formation and release of a pollutant. Processes can range from industrial processes to transport activities, household activities, natural processes and so on. The process may also lead to the production of a commodity (e.g. pesticide formulation). As indicated already throughout this chapter, a wide range of different commodities (i.e. articles, formulations, and products) may release substances at one or more stages throughout their lifecycle (i.e. during production, transport, storage, use and/or waste disposal).

- Point sources vs. nonpoint sources (i.e. diffuse pollution)

Point source pollution comes from a single specific site and is generally used to refer to relatively large sources such as a factory smokestack or industrial wastewater outlet. The European Environment Agency (EEA) defines a point source as “a stationary location or fixed facility from which pollutants are discharged; any single identifiable source of pollution” (EEA 2008). By contrast, diffuse pollution does not come from a single identifiable site but from many different points across a ‘source area’. Consider the emissions from car exhaust in an urban area for example, where there are many cars travelling at any one time within that area. Diffuse pollution sources often emit to air, or to the urban surface, from where they may be mobilised by stormwater and hence transferred to receiving waters. According to the E-PRTR Regulation (EC 2006b) “diffuse sources are the many smaller or scattered sources from which pollutants may be released to land, air or water, whose combined impact on those media may be significant and for which it is impractical to collect reports from each individual source”.

- Continuous sources vs. intermittent sources

This category is based on the pollutant release pattern from a particular source type. Traffic in a city centre or effluent release from a municipal sewage treatment plant are examples of relatively continuous sources, whereas a forest fire (whether deliberately lit or accidental) is only an occasional source. In reality the pattern of release can be extremely complex, as even continuous sources are likely to have pulses of lesser and greater release rates rather than a constant release rate (Holt 2000). In fact, release patterns may actually show a characteristic daily, weekly, monthly or annual pattern, but whilst these detailed patterns are extremely important in the calculation of emissions using 'release factors', they are less important for the purposes of source classification. For a detailed overview of pollutant release patterns see de Keyser et al. 2008.

- Intentional vs. unintentional

This distinction is not intended to indicate that any release of pollution to the environment should be intentional, but rather that the use/release of a substance in a process/article is deliberate (e.g. biocide application) rather than accidental (e.g. due to spilling, or unintentional leaching), without purpose (e.g. by-products released from incomplete combustion), or even unrecognised (e.g. formation of a hazardous degradation product). In this case, the substance use is applied as an indicator of the type of source.

- Restricted vs. unrestricted (regulated vs. unregulated)

Some sources are more suited to regulatory control than others. For example, large industrial sources may require emission permits and/or have emission limits imposed, whereas household sources are much harder to control in this manner. Nevertheless, it is important to recognise that the cumulative effect of many small unregulated sources together may actually be greater than that of larger more restricted sources (especially if the regulated sources are required to carry out pre-treatment or follow best available techniques [BAT]) (see EIPPCB 2006).

- Mobile vs. stationary sources

A mobile source is used to refer to a moving source of pollution such as an aeroplane, car, or ship, whereas a stationary source is easily demonstrated by an industrial facility. Although these categories may seem to overlap somewhat with point and diffuse sources they are not always the same. For example, many small stationary sources (e.g. households) in the same source area would be considered as a diffuse source, even though they are stationary.

- Natural vs. anthropogenic

Anthropogenic emission sources are clearly exemplified by any type of industrial activity releasing pollutants, whereas a natural source could be a forest fire, a volcano, or even an area of soil with naturally high metal concentrations.

- Receiving compartment (e.g. soil, water, air)

A single source can release pollutants to one or more different environmental compartments (see Fig. 2.1). The compartments most commonly used in emissions inventories are air and water. However, a range of more specific compartments may also be used to facilitate modeling applications for investigating substance fate.

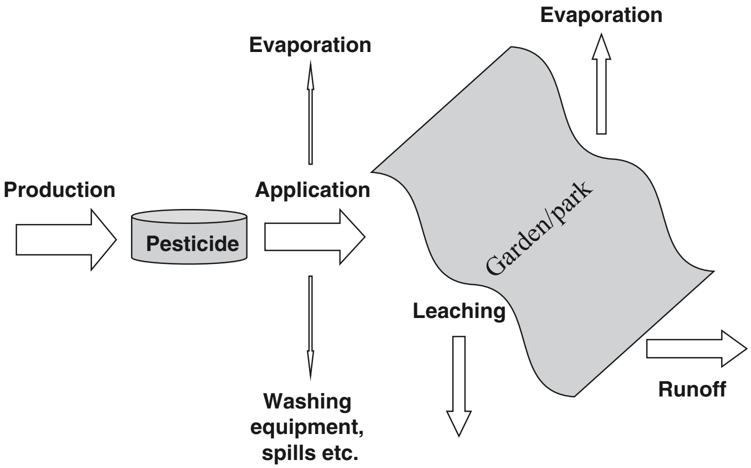

Fig. 2.1 Source visualisation – non-agricultural pesticide application

For example, major environmental compartments could be represented as air, surface water, groundwater, permeable surface, and impermeable surface. The distinction between permeable surfaces (e.g. bare soil, grass, porous paving) and impermeable surfaces (e.g. roofing, tarmac, concrete paving) can be an important consideration in terms of the volume of surface runoff generated and the relevant pollutant transfer pathways and processes.

- Indoor vs. outdoor source

The indoor vs. outdoor categories can be used simply to divide sources into those releasing substances within a confined space (i.e. indoors) and those releasing substances directly into the outdoor environment. This category is of particular importance for studies investigating substance dispersal and/or human exposure risks. Both indoor and outdoor sources may release to a variety of environmental compartments (i.e. water, air, etc.).

- Stage in life cycle at time of release

The life cycle of a substance can be divided into a number of different stages, with releases into the environment potentially taking place at any stage of the life-cycle. The major stages are production; transport and storage; formulation; use (industrial/professional/private use of an article/process containing the substance); service life (for articles used over extended periods of time such as electric cabling, shoes, carpet); and waste disposal (including waste treatment and recovery) (EC 2003).

- Size of ‘release factor’

The size of the release factor refers to the quantitative release of the substance from the source and can be described using units such as μg triclosan/g toothpaste; mg PCB/m^2 roof area; mg nonylphenol/m^3 effluent, etc. The overall effect in terms of the mass released will of course depend on the extent of use of the commodity/process for which the release factor is specified. It should also be noted that the release factor may not be constant during the service life of a commodity.

- Fast vs. slow release

The time scale refers to the speed with which the substance is released from the source. Examples are the fast dispersal of anti-freeze substances due to the application of de-icers, as opposed to the slow release of plasticisers from shoes due to wear and tear throughout the service life. The release time scale can be established by considering the time from start up of the process/article use, until the time when the substance can be detected in the ambient environment.

- Direct vs. indirect release

The direct release of a substance to the environment can be represented by the direct release of air or water pollutants from an industrial process, whereas an indirect release would first be subjected to some form of treatment or diversion (e.g. released via a gas scrubber or WWTP).

- Type of release process

For any given source a number of different release processes may be relevant (Fig. 2.1), including evaporation, physical abrasion, weathering, leaching, and migration (diffusion). The physico-chemical properties of the substance (e.g. volatility, water solubility), the way in which the substance is used (i.e. applied to a surface, bound into an article etc.), and the location of the source (i.e. local climate), largely determine which release processes will be applicable and their relative release rates.

2.4.2 Archetypes of Xenobiotic Sources

In this section a typology of xenobiotic sources is presented (Fig. 2.2). As with the typology of uses presented in Table 2.3, this is not proposed as a complete and comprehensive classification system, but as a framework within which model examples of different source types can be presented. Access to a source typology such as this during project planning can support researchers and environmental managers in considering the wide array of potential sources for any target substance(s) and help them decide on the most relevant source types to focus on in order to achieve their project objectives. A further key benefit of this approach is that sources showing similar kinds of release characteristics may be amenable to the same kinds of monitoring and source control approaches (e.g. voluntary agreements, end of pipe treatment etc.), and this could be an advantage when planning and testing emission control strategies. Consulting the source typology may also help to ensure that all types of sources are investigated and accounted for in studies dependent on such information (e.g. mass balances). However, an important point

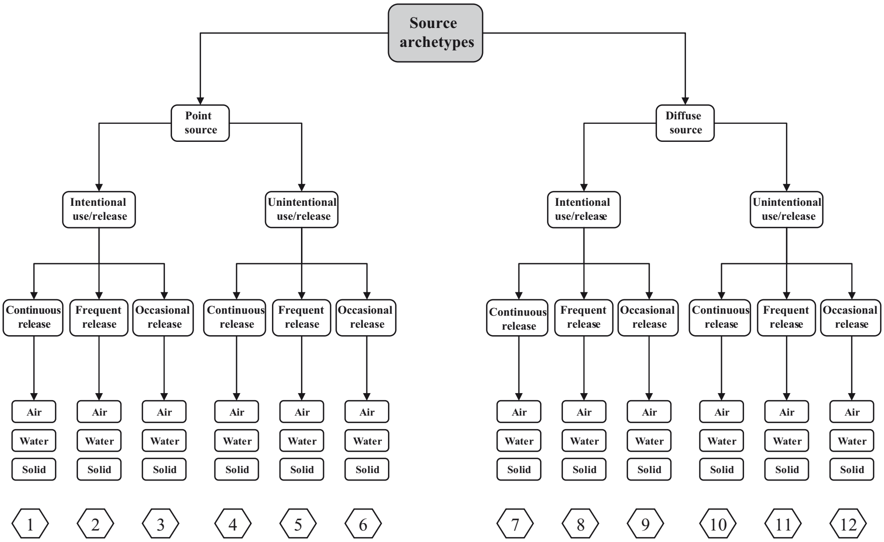

Fig. 2.2 Key showing the derivation of 12 different source archetype categories. Model examples have been chosen to demonstrate the characteristics of each of these archetypes (see Table 2.5)

to note is that the differences between categories are seldom as distinct as indicated in the typology (e.g. constant vs. frequent vs. occasional release) with most categories actually representing a continuum with extremes at either end rather than clear cut groups. Nonetheless, for the purposes of demonstration it is possible to provide model examples for each of the 12 archetypes derived using the developed typology, and these are presented in Table 2.5.

The four categories used to delineate the source typology are:

1. Diffuse vs. point sources – The challenges for control of diffuse and point source pollution are quite different, with non point source pollution particularly difficult to control because of the large areas, multiple landowners and numerous sources involved. Recall also that there is some overlap of mobile and stationary sources with these categories, and that a single point source such as a municipal WWTP may actually be releasing pollutants (e.g. triclosan) which have originally been sourced from multiple diffuse sources discharging into the wastewater transport network.
2. Intentional vs. unintentional use/release – Note that the choice of this category also takes account of anthropogenic vs. natural sources as natural sources cannot be considered intentional.
3. Continuous vs. frequent vs. occasional use/release – This does not specify the release pattern as such but does have broad implications for source control options.
4. Receiving compartment (air, water, urban surface) – Note that a single source may actually emit to multiple environmental compartments in different loads, patterns and quantities (see Fig. 2.1).

Table 2.5 Archetypes (i.e. model examples) of xenobiotic sources

Archetype 1: Point source; Intentional use/release; Continuous release
- Process: Release to air – Release of dichloromethane (DCM) due to the use of DCM-based paint strippers at an industrial facility.

Archetype 2: Point source; Intentional use/release; Frequent release
- Process; Release to water – Release of contaminated cooling water from nuclear power plants.

Archetype 3: Point source; Intentional use/release; Occasional release
- Process: Release to water – Release of cleaning agents during reaction vessel cleaning at an industrial plant

Archetype 4: Point source; Unintentional use/release; Continuous release
- Process; Release to water – Formation and release of chloroform due to reaction of chlorine and organic matter during disinfection of water by chlorination.

Archetype 5: Point source; Unintentional use/release; Frequent release
- Process; Release to air – Formation and release of dioxins during industrial waste incineration.

Archetype 6: Point source; Unintentional use/release; Occasional release
- Process; Release to urban surface and air – Accidental spill of chemicals due to a traffic accident involving a transport lorry

Archetype 7: Diffuse source; Intentional use/release; Continuous release
- Article; Release to urban surface, air and water – Slow, continual release of biocides from roofing materials (added to prevent growth of algae, moss, lichen and fungi in moist environments).

Archetype 8: Diffuse source; Intentional use/release; Frequent release
- Article; Release to water and air – Release of fragrances due to the use of perfumes and other scented personal care products.

Archetype 9: Diffuse source; Intentional use/release; Occasional release
- Article; Release to water and air: Emission of solvents and de-icers due to use on cars and planes.

Archetype 10: Diffuse source; Unintentional use/release; Continuous release
- Article; Release to urban surface – Release of platicisers and softeners to the urban surface due to car tyre wear and abrasion.

Archetype 11: Diffuse source; Unintentional use/release; Frequent release
- Article; Release to water – Leaching of biocide (e.g. tributyltin) from clothing during washing

Archetype 12: Diffuse source; Unintentional use/release; Occasional release
- Article; Release to urban surface and air – Release of solvents and metal based pigments during paint application.

For the source archetypes presented in Table 2.5 a combination of both indoor and outdoor examples has been selected, as well as examples from both article and process based sources. This is merely for the purposes of brevity as separate examples from each of these groups (indoor, outdoor, article, process) could potentially be identified for each of the different archetype classes. For the same reasoning, examples have been drawn from any of the potential receiving compartments, rather than providing a separate example for each. It should also be noted that a single source may actually emit different substances in different patterns and quantities during different stages of its life cycle, and may also emit to several different environmental compartments at once. Hence, it is possible for some sources to fit into more than one of the different archetype categories (see Fig. 2.1, for example).

2.5 Source Tracking and Identification

With such a wide array of potential xenobiotic sources, comprehensive source tracking can prove to be quite a challenge. In this final section, a brief review of useful source tracking approaches is provided.

2.5.1 The Literature

The initial stage in any source tracking exercise typically involves a review of relevant literature. Both grey and peer-reviewed literature may provide useful information. For example, it is quite common for special interest groups (e.g. trade organisations, environmental groups etc.) to compile and publish relevant information on selected substances (e.g. pesticides). However, the lack of peer review can lead to the publication of subjective assessments and interpretations of data and this should always be borne in mind when consulting data from non peer-reviewed sources. A further useful literature source can be found in reports prepared by government departments such as emissions monitoring reports and risk assessments, although again it should be noted that these sources have often not undergone rigorous peer review.

2.5.2 Database Mining

A wide range of databases contain useful information regarding substance use. Some of these are open source databases whereas others operate on a ‘pay per view’ basis (e.g. research library databases). Relevant data may also be held in restricted use databases which typically contain confidential commercial information and do not allow general public access. For example, quantitative release data can be hard to source due to commercial sensitivities and an associated lack of studies being reported in the scientific literature. It is likely that governmental testing facilities and the production industry themselves do have such data for a wide range of substances in many different types of articles, but these studies are often associated with patent restrictions and confidentially agreements which make them difficult to obtain. Nevertheless, by establishing contacts with relevant industry officials it may be possible to view the data held within such databases in an aggregated form (for example, where substance use cannot be traced to any specific product line or industrial facility, but can be viewed for a particular industrial sector. This requires the co-operation of trusted contacts within the industrial sector).

Examples of useful databases that could be consulted for source tracking purposes include national emissions databases (e.g. the UK National Atmospheric Emissions Inventory) (NAEI 2008), the Merck Index (Merck 2006); the EU EPER

(EPER 2008), the E-PRTR (E-PRTR 2008), the US Hazardous Substances Data Bank (US HSDB 2008) and the US Household Products Database (US HPD 2008). These are just a few of the many relevant data sources.

2.5.3 Chemical Screening and Monitoring

Chemical screening and monitoring is a very useful approach to source tracking and widely employed by both public authorities and industry. The costs associated with monitoring are very system dependent and can vary substantially depending on the target substance(s) to be measured. In some cases, cost related concerns may exclude this option from the range of tools available to researchers and environmental managers.

Screening and monitoring approaches which may be particularly beneficial include analysing WWTP influents and effluents, comparing weekend and working day wastewaters and/or air concentrations; monitoring wastewater and stormwater from individual buildings or catchment areas; analysing source separated wastewaters such as greywater; and conducting substance release testing on selected commodities.

2.5.4 Questionnaires/Marketing Surveys

Questionnaires and consumer surveys are usually done by marketing companies but some surveys are also carried out by independent researchers (these being frequently complemented by in situ market surveys or interviews). The second type of survey can be commonly found in the literature, whereas marketing surveys are typically commercially sensitive and therefore more difficult to access. Questionnaires may be given to the general public, to householders, businesses etc. to help determine the types and quantities of products that they use. The structure and wording of questionnaires is extremely important, as this can significantly affect the results obtained. Previous experience has shown that people can easily forget or omit to give complete information.

2.5.5 Official Statistical Records

Official statistical records such as international trade statistics can be extremely good sources of information indicating the extent of production and trade of specific substances and commodities. This information is also generally available for public use. Examples of useful classification systems and relevant statistics include the World Customs Organisation's Combined Nomenclature (CN) (a systematic list of commodities which forms the basis for international trade negotiations and can be used to determine international and EU trade statistics for specific commodities and chemical products) (EC 1987); the Common Nomenclature for Economic Activities (NACE) (EC 2002); the Nomenclature for Sources of Emissions (NOSE) (Eurostat 1998); PRODCOM (EC 2007) for the collection and dissemination of statistics on the production of manufactured goods; and emissions reporting systems such as the E-PRTR (EC 2006b).

2.5.6 Green Procurement Information Programmes

Increasingly a range of both government and non-government organisations are documenting information about the environmental credentials of different product types and making this information available to professionals and the public to assist with green procurement and more informed purchasing and use practices. For example, the Danish EPA has a programme for the identification and assessment of substances in consumer products (Surveys on chemicals in consumer products) and the reports from their analyses are publicly available on the internet (Danish EPA 2008). Similarly, the US EPA maintains a publicly accessible 'Household Products database' (US HPD 2008) whilst in Sweden, the Swedish Society for Nature Conservation regularly conducts literature/monitoring surveys of substances in consumer products and, based on the results, issues an eco-label for "Good Environmental Choice" (SSNC 2008).

2.5.7 Forensic Source Tracking

Environmental forensics is a specific form of source tracking involving the systematic evaluation of physical, chemical and historical information to develop defensible conclusions regarding the source (and/or timing) of pollutant emissions to the environment (Morrison 2000a, b). Often the purpose of this work is to bring companies or individuals who have caused serious environmental damage to justice. Interestingly this field has seen the application of a range of very useful source tracking techniques, such as the use of diagnostic ratios (e.g. isotope ratios, isomer ratios, elemental ratios) and chemical fingerprinting approaches to identify the most likely sources of pollutants. Examples include the use of Pb isotope ratios to determine the major source of human exposure to Pb (Kamenov 2008; Levesque et al. 2003); the analysis of isomer ratios and assemblages to determine whether local PAH contamination is predominantly due to petrogenic or pyrogenic sources (Boehm and Farrington 1984); the use of lead/arsenic ratios to determine the relative contributions of Pb smelter operations and herbicide applications to soil arsenic contamination (Folkes et al. 2001); and the use of biomarker fingerprinting approaches for forensic oil spill investigations (Hostettler et al. 2007; Christensen et al. 2004). Environmental forensics is a growing field of research which is likely to further stimulate the development of optimised source tracking approaches.

2.6 Conclusions

The sources and uses of xenobiotics in urban environments are very diverse, making structured approaches to source and use classification a fundamental requirement for effective pollution management. There are many potential approaches for classifying xenobiotic sources and uses, with the most appropriate method being largely dependent on the actual purpose of data collection and analysis (e.g. mass balance calculation, emissions reporting, etc.). Pollutant source identification and monitoring approaches draw upon a variety of useful data mining and source tracking methods, and the source tracking 'toolbox' is likely to continue to grow in future years.

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Chapter 3
Illicit Drugs in the Urban Water Cycle

Maria Huerta-Fontela, Maria Teresa Galceran, and Francesc Ventura

Abstract In recent years, the presence of human-use compounds in the aquatic environment has been recognized as an important issue in environmental chemistry. Among them, illicit drugs have been described as a new unexpected group of water contaminants with potent psychoactive properties and unknown effects to the aquatic environment.

The presence of these drugs in water resources is of rising concern and several studies are being conducted all over the world estimating discharged levels of drugs of abuse. In this chapter, a summary of the last works studying and reporting the occurrence of illicit drugs in water resources is performed. Up to now, drugs of abuse have been already detected in wastewaters and surface waters in the USA, Italy, Germany, the UK and Spain. These drugs reach wastewater treatment plants either unaltered or in their main metabolite form. Depending on the removal efficiencies, they can persist through wastewater treatment and be detected in receiving waters, which in some cases are used for drinking water production. The presence of these compounds in raw waters and their elimination through the drinking water treatment must be considered as an issue with regard to the quality of water supplies.

3.1 Illicit Drugs in Water Resources

The presence of human-use compounds in aquatic environments has been recognized as an important issue in environmental chemistry. Water analysis has demonstrated to be able to provide exhaustive and reliable information regarding human habits and activities. For instance, the presence of brominated flame retar-

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M. Huerta-Fontela (✉) and F. Ventura
AGBAR-Aigües de Barcelona, Av. Diagonal 211, 08018 Barcelona, Spain
e-mail: mhuerta@agbar.es

M.T. Galceran
Department of Analytical Chemistry, University of Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain

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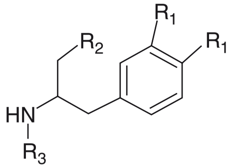
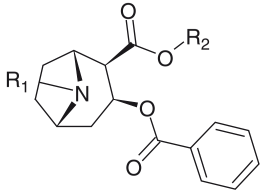
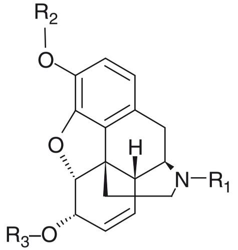
dants in water can tell us about the industrial activity on a specific area; or the analysis of pharmaceutical residues can offer a general overview on health and drug consumption patterns of certain population clusters served by specific wastewater treatment plants (WWTPs). Recently, illicit drugs have been identified as a new unexpected group of water contaminants confirming this "water squealer" ability. To date, these compounds have been already found in several water matrices around the world and the concern regarding their presence in these resources is exponentially growing due to their potent psychoactive properties and their unknown effects to the aquatic environment. The presence of illicit drugs in water resources is related to two main causes. On the one hand, most of the main consumed illicit drugs are excreted unaltered or as slightly transformed metabolites, which reach the sewage system, and can be then easily identified (Table 3.1). On the other hand, the high consumption rates reported for these compounds explain their relative high concentration levels in the aquifer. Specifically, around 200 million people in the world are estimated to have used illicit drugs at least once during the last year (United Nations Office of Drug and Crime 2007). Cannabis is the most consumed one affecting by far above 4% of the global population aged between 15 and 64 years old. Next, opiates (especially heroin) and cocaine are the two second most consumed illicit drugs at the global level (United Nations Office of Drug and Crime 2007). Nevertheless, different patterns of use can be found depending on the country/region selected. For instance, in Europe and in Asia, opiates are the most consumed illicit drugs, with percentages of use above 58% and 62% among the adult population (15–64 years), respectively. In Africa and Oceania, cannabis is the most abused drug (63% and 46% adults, respectively) while in South-America cocaine use is still predominant (48%). Finally, in North America, cocaine and cannabis are the two most consumed illicit drugs with percentages above 29% and 26%, respectively. Despite these general region percentages, different patterns of use can also be found depending on the country/area selected. For instance, in Spain, the annual prevalence levels of cocaine exceeded those in the USA and the number of users is four times higher than the European average (among the adult population 15–64 years), demonstrating important local differences in the drug use panorama among countries.

3.1.1 Wastewaters

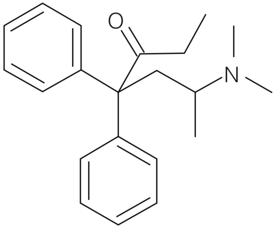
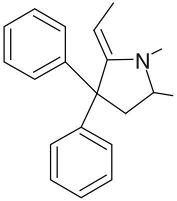
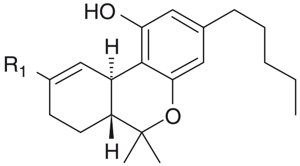
An alternative method to determine illicit drug consumption by measuring these drugs in wastewaters was first proposed by Daughton (2001). Few years later, this theory was put into practice in two works related to the determination of some illicit drugs in water resources (Jones-Lepp et al. 2004; Zuccato et al. 2005). The first one reported the presence of methamphetamine (0.8 ng/L) and 3,4-methylenedioxymethamphetamine (MDMA) (0.5 ng/L) in effluent samples of three WWTPs in the USA. But it was in 2005 when scientists from the Mario Negri Institute in Italy centered their efforts to exclusively look for illicit drugs in water resources

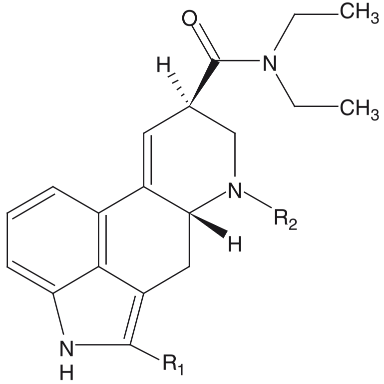
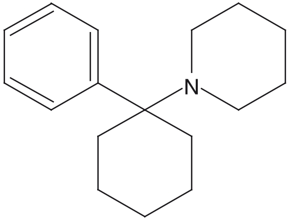
Table 3.1 Illicit drug classification and structures.

Classification	Structure		Compound (abbreviation)	CAS #
Amphetamine-type-stymulants		R_1=H R_2=H R_3=H	Amphetamine	[300-62-9]
		R_1=H R_2=H R_3=CH_3	Methamphetamine	[537-46-2]
		R_1=O-CH_2-O- R_2=H R_3=H	MDA	[4764-17-4]
		R_1=O-CH_2-O- R_2=H R_3=CH_3	MDMA	[42542-10-9]
		R_1=O-CH_2-O- R_2=H R_3=CH_2-CH_3	MDEA	[82801-81-8]
		R_1=O-CH_2-O- R_2=H R_3=CH_2-CH_3	MBDB	[103818-46-8]
Cocainics		R_1=CH_3 R_2=CH_3	Cocaine	[50-36-2]
		R_1=H R_2=CH_3 R_1=CH_3 R_2=H	Norcocaine	[61585-22-6]
		R_1=H R_2=H	Benzoylecgonine (BE)	[519-09-5]
		R_1=CH_3 R_2=CH_2-CH_3	Norbenzoylecgonine (norBE)	[60426-41-7]
			Cocaethylene	[529-38-4]
Opiates		R_1=CH_3 R_2 =$COCH_3$ R_3= $COCH_3$	Heroin	[561-27-3]
		R_1=CH_3 R_2 =H R_3= $COCH_3$	6-Acetylmorphine	[2784-73-8]
		R_1=CH_3 R_2 =H R_3=H	Morphine	[57-27-2]
		R_1=H R_2=H R_3=H	Normorphine	[466-97-7]

(continued)

Table 3.1 (continued)

Classification	Structure	Compound (abbreviation)	CAS #
		Methadone	[76-99-3]
		EDDP	[1095-90-5]
Cannabinoids	 $R_1 = CH_3$ $R_1 = COOH$ $R_1 = CH_2\text{-}OH$	D9-Tetrahydrocannabinol (THC) D9- carboxytetrahydrocannabinol (THC-COOH) D9- hidroxytetrahydrocannabinol (THC-OH)	[1972-08-3] [56354-06-4] [36557-05-8]

LSD		R_1=H R_2=CH R_1=O R_2=CH_3 R_1=H R_2=H	LSD 2-oxo-3-hydroxy LSD(LSD-OH) Nor-LSD	[50-37-3] [N/A] [35779-43-2]
PCP			PCP	[77-10-1]

(Zuccato et al. 2005). In this work, the presence of cocaine and its major metabolite, benzoylecgonine, was reported for the first time in wastewaters and in the Po River. Cocaine was found in four WWTPs at concentrations ranging from 42 to 120 ng/L and the levels of benzoylecgonine were in accordance with the metabolic excretion ratios (0.15 ± 0.03) giving concentrations ranging from 390 to 750 ng/L. Additionally, both compounds were also found in Po River with concentrations of 2 and 25 ng/L, respectively. Few months later, an extended study from the same research group (Castiglioni et al. 2006) confirmed the presence of cocaine together with other illicit drugs, such as amphetamine type stimulants, morphine or methadone in influent and effluent samples from two Italian WWTPs. The occurrence of illicit drugs was also confirmed in Germany (Hummel et al. 2006) and Spanish (Huerta-Fontela et al. 2007) wastewaters. These results not only established the presence of illicit drugs in water resources but also suggested incomplete removal during the wastewater treatment. A more extensive work was then published regarding the presence of stimulatory illicit drugs in 42 WWTPs in Spain (Huerta-Fontela et al. 2008a). Most of the studied illicit drugs were found in both influent and effluent wastewaters. Cocaine and its metabolite were detected in wastewaters at concentrations ranging from 4 to 4,700 ng/L and from 9 to 7,500 ng/L respectively, while concentrations of amphetamine type stimulatory (ATS) drugs ranged from 2 to 688 ng/L. Additionally, their removal was also studied in eight WWTPs, showing variable percentages of elimination depending on the compounds and on the influent concentration levels. For instance, cocaine and benzoylecgonine removal percentages were higher than 88% while those for ATS varied, ranging from 40% to more than 99%. The persistence of illicit drugs during wastewater treatments has been also confirmed, for the time being, in surveys performed in Ireland (Bones et al. 2007), Belgium (Gheorghe et al. 2008; van Nuijs et al. 2008) and in Spain (Boleda et al. 2007; Postigo et al. 2008). In Table 3.2, a summary of the results published regarding the detection of illicit drugs in water is given.

Daily variations were also evaluated during seven consecutive days in WWTP from Italy (Zuccato et al. 2008a). Concentrations of THC-COOH were constant during the week suggesting steady use of cannabis. For benzoylecgonine, maximum values were detected on Saturday, corroborating previous results obtained from a survey performed in Spain (Huerta-Fontela et al. 2008a). However, different results between both studies were obtained when variations in ATS were evaluated. While constant values were obtained all through the week in Italian wastewaters, in Spain significant maximums were observed at weekend suggesting different patterns of use during the week.

3.1.2 Surface Waters

The non-quantitative elimination of illicit drugs in WWTPs has a direct effect in rivers, lakes, or seas where the treatment plants discharge their effluents. Therefore, once the presence of illicit drugs is demonstrated in wastewater effluents, surface

Table 3.2 Occurrence of illicit drugs in water resources

Drug	Source	Concentration (ng/L) (influent; effluent)	Loads (g/day)	Samples	Country	Reference
Cocaine	WW	42-120	-	4 WWTPs	Italy	Zuccato et al. 2005
	WW	218-421;11	-	2 WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	79; 17	-	16 WWTP	Spain	Huerta-Fontela et al. 2007
	WW	489; 47-138	1.17-224	1 WWTPs (=6)	Ireland	Bones et al. 2007
	WW	22-457	-	5 WWTPs (n=10)	Belgium	Gheorghe et al. 2008
	WW	316-861; 6.2-105	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	0.4-4700; 0.1-100	0.003-56	42 WWTP	Spain	Huerta-Fontela et al. 2008a
	WW	10-758	-	37 WWTPs	Belgium	van Nuijs et al. 2008
	WW	10-860	-	7 WWTPs	USA	Chiaia et al. 2008
	Surface	1.2	0.70	1 River	Italy	Zuccato et al. 2005
	Surface	6	-	1 River (n=6)	Spain	Huerta-Fontela et al. 2007
	Surface	25-33	-	1 River (n=6)	Ireland	Bones et al. 2007
	Surface	nd	-	1 River (n=4)	UK	Kasprzyk-Hordern et al. 2007
	Surface	nd	-	1 River (n=2)	Poland	Kasprzyk-Hordern et al. 2007
	Surface	7-26	-	3 Streams	Belgium	Gheorghe et al. 2008
	Surface	4-183	1.9-60	4 Rivers	Italy	Zuccato et al. 2008a
	Surface	4-6	-	1 River	UK	Zuccato et al. 2008a
	Surface	9-60	0.02-10	1 River (n=24)	Spain	Huerta-Fontela et al. 2008b
	Surface	1-115	0.1-55.2	28 Rivers	Belgium	van Nuijs et al. 2008
	Surface	1-7	1.2 *	2 Rivers (n=6)	UK	Kasprzyk-Hordern et al. 2008
	DW	nd	-	1 DWTP (n=24)	Spain	Huerta-Fontela et al. 2008b
Norcocaine	WW	4.3 ; 14 ; 0.7	-	2 WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	4-50	-	7 WWTPs	USA	Chiaia et al. 2008
	Surface	0.1-3.6	-	4 Rivers	Italy	Zuccato et al. 2008a
Cocaethylene	WW	6 -12 ; 0.2	-	2 WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	49-89; 1.7-6.8	-	4 WWTPs	Spain	Postigo et al. 2008
	Surface	0.1-1.3	-	4 Rivers	Italy	Zuccato et al. 2008a

(continued)

Table 3.2 (continued)

Drug	Source	Concentration (ng/L) (influent; effluent)	Loads (g/day)	Samples	Country	Reference
BE	WW	390-750	0.9-2.6	4 WWTPs	Italy	Zuccato et al. 2005
	WW	1132; 100-547	-	2 WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	78;49		1 WWTP	Germany	Hummel et al. 2006
	WW	0.9-7500; 0.1-1500	-	16 WWTPs	Spain	Huerta-Fontela et al. 2007
	WW	290; 22-31	-	1 WWTP (n=1)	Ireland	Bones et al. 2007
	WW	164-1898	-	5 WWTPs (n=10)	Belgium	Gheorghe et al. 2008
	WW	1020-4226;30-318	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	0.9-7500; 0.1-1500	0.02-175	42 WWTPs	Spain	Huerta-Fontela et al. 2008a
	WW	23-2258	-	37 WWTPs	Belgium	van Nuijs et al. 2008
	WW	110-2800	-	7 WWTPs	USA	Chiaia et al. 2008
	Surface	25	2.7	1 River	Italy	Zuccato et al. 2005
	Surface	3	-	1 River (n=1)	Germany	Hummel et al. 2006
	Surface	77	-	1 River (n=6)	Spain	Huerta-Fontela et al. 2007
	Surface	nd	-	6 samples	Ireland	Bones et al. 2007
	Surface	nd	-	4 samples	UK	Kasprzyk-Hordern et al. 2007
	Surface	nd	-	2 samples	Poland	Kasprzyk-Hordern et al. 2007
	Surface	44-191	-	3 Rivers	Belgium	Gheorghe et al. 2008
	Surface	0.5-44	8-391	4 Rivers	Italy	Zuccato et al. 2008a
	Surface	4-16	-	1 River	UK	Zuccato et al. 2008a
	Surface	15-150	3-25	1 River (n=24)	Spain	Huerta-Fontela et al. 2008b
	Surface	1-520	0.3-249	28 rivers	Belgium	van Nuijs et al. 2008
	Surface	1-123	2.6-39	2 Rivers (n=6)	UK	Kasprzyk-Hordern et al. 2008
	DW	3-130	-	1 DWTP (n=24)	Spain	Huerta-Fontela et al. 2008b
Norbenzoylecgonine	WW	19 ; 37; 7.5	-	2 WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	14-170	-	7 WWTPs	USA	Chiaia et al. 2008
	Surface	1.6-8.4	-	4 Rivers	Italy	Zuccato et al. 2008a
Amphetamine	WW	15	-	2 WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	3-688; 4-210	-	16 WWTPs	Spain	Huerta-Fontela et al. 2007
	WW	6.5-41;0.5-3.3	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	3-688; 4-210	0.0003-9	42 WWTPs	Spain	Huerta-Fontela et al. 2008a
	WW	80-220	-	7 WWTPs	USA	Chiaia et al. 2008

	Surface	nd	-	1 River (n=6)	Spain	Huerta-Fontela et al. 2007
	Surface	6-9	-	1River (n=4)	UK	Kasprzyk-Hordern et al. 2007
	Surface	nd	-	1River (n=2)	Poland	Kasprzyk-Hordern et al. 2007
	Surface	nd	-	4 Rivers	Italy	Zuccato et al. 2008a
	Surface	nd	-	1 River (n=5)	UK	Zuccato et al. 2008a
	Surface	5-90	-	1 River (n=24)	Spain	Huerta-Fontela et al. 2008b
	Surface	9-50	0.1-8	2 Rivers (n=6)	UK	Kasprzyk-Hordern et al. 2008
	DW	nd	-	1 DWTP (n=24)	Spain	Huerta-Fontela et al. 2008b
Methamphetamine	WW	0.8-1.3	-	3 WWTPs	USA	Jones-Lepp et al. 2004
	WW	16; 3.5	-	2WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	3-18; 1.5-6.3	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	3-277; 3-90	0.003-14	42 WWTP	Spain	Huerta-Fontela et al. 2008a
	WW	10-2000	-	7 WWTPs	USA	Chiaia et al. 2008
	Surface	1.7-2.1	-	4 Rivers	Italy	Zuccato et al. 2008a
	Surface	nd	-	1 River (n=5)	UK	Zuccato et al. 2008a
	Surface	1-2	0.1-0.4	1 River (n=24)	Spain	Huerta-Fontela et al. 2008b
	DW	nd	-	1 DWTP (n=24)	Spain	Huerta-Fontela et al. 2008b
MDEA	WW	1.5;	-	2 WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	27;	-	16 WWTPs	Spain	Huerta-Fontela et al. 2007
	WW	6-114; 12	0.01-0.7	42 WWTPs	Spain	Huerta-Fontela et al. 2008a
	WW	nd	-	7 WWTPs	USA	Chiaia et al. 2008
	Surface	nd		1 River (n=6)	Spain	Huerta-Fontela et al. 2007
	Surface	nd	-	1 River (n=24)	Spain	Huerta-Fontela et al. 2008b
	DW	nd	-	1 DWTP (n=24)	Spain	Huerta-Fontela et al. 2008b
MDMA	WW	0.8-1.3	-	3 WWTPs	USA	Jones-Lepp et al. 2004
	WW	49;41	-	16 WWTPs	Spain	Huerta-Fontela et al. 2007
	WW	47-134; 30-376	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	2-598; 2-267	0.003-16	42WWTP	Spain	Huerta-Fontela et al. 2008a
	WW	2.7-70	-	7 WWTPs	USA	Chiaia et al. 2008
	Surface	3	-	1 river (n=6)	Spain	Huerta-Fontela et al. 2007

(continued)

Table 3.2 (continued)

Drug	Source	Concentration (ng/L) (influent; effluent)	Loads (g/day)	Samples	Country	Reference
	Surface	1.1-1.7	0.1-30 (total AMP)	4 Rivers	Italy	Zuccato et al. 2008a
	Surface	2-6	-	1 River (n=5)	UK	Zuccato et al. 2008a
	Surface	1-40	0.2-7	1River (n=24)	Spain	Huerta-Fontela et al. 2008b
	DW	nd	-	1DWTP (n=24)	Spain	Huerta-Fontela et al. 2008b
MDA	WW	3-266; 1-200	0.005-6	42 WWTPs	Spain	Huerta-Fontela et al. 2008a
	WW	2-6	-	7 WWTPs	USA	Chiaia et al. 2008
	Surface	1.2	-	4 Rivers	Italy	Zuccato et al. 2008a
	Surface	nd	-	1 River (n=5)	UK	Zuccato et al. 2008a
	Surface	10-20	0.08-3	1 River (n=24)	Spain	Huerta-Fontela et al. 2008b
	DW	nd	-	1 DWTP (n=24)	Spain	Huerta-Fontela et al. 2008b
MBDB	WW	nd	-	7 WWTPs	USA	Chiaia et al. 2008
Heroin	WW	2.3-24; 1.2	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	nd	-	5 WWTPs	Spain	Boleda et al. 2007
Morphine	WW	820;111	-	12 WWTP	Germany	Hummel et al. 2006
	WW	83-204;55	-	2 WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	452-874		1 WWTP (n=6)	Ireland	Bones et al. 2007
	WW	63-163;12-30	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	26-97;21-81	-	5 WWTPs	Spain	Boleda et al. 2007
	Surface	10 *	-	4 Rivers	German	Hummel et al. 2006
	Surface	nd	-	3 Rivers	Ireland	Bones et al. 2007
	Surface	3-38	1.5-4	4 Rivers	Italy	Zuccato et al. 2008a
	Surface	5-42	-	1 River (n=5)	UK	Zuccato et al. 2008a
Normorphine	WW	31	-	5 WWTPs	Spain	Boleda et al. 2007
6-AM	WW	10; 12	-	2 WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	6-13;2-3.6	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	nd	-	5 WWTPs	Spain	Boleda et al. 2007
	Surface	nd	-	4 Rivers	Italy	Zuccato et al. 2008a
	Surface	nd	-	1 River (n=5)	UK	Zuccato et al. 2008a

Methadone	WW	nd	-	12 WWTPs	German	Hummel et al. 2006
	WW	12- 50; 9.1-36	-	2 WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	4-24 ;4-25	-	5 WWTPs	Spain	Boleda et al. 2007
	WW	4.9-62	-	7 WWTPs	USA	Chiaia et al. 2008
	Surface	nd	-	4 Rivers	German	Hummel et al. 2006
	Surface	3.4-8..6	1.2-196 (+ EDDP)	4 Rivers	Italy	Zuccato et al. 2008a
	Surface	nd	-	1 River (n=5)	UK	Zuccato et al. 2008a
EDDP	WW	20-91; 23-72	-	2WWTPs (n=8)	Italy	Castiglioni et al. 2006
	WW	9-206	-	1 WWTP (n=6)	Ireland	Bones et al. 2007
	WW	4.5-41;5-57	-	5 WWTPs	Spain	Boleda et al. 2007
	Surface	nd	-	3 Rivers	Ireland	Bones et al. 2007
	Surface	4.3-18	-	4 Rivers	Italy	Zuccato et al. 2008a
	Surface	nd	-	1 River (n=5)	UK	Zuccato et al. 2008a
THC-COOH	WW	14-39;13-21	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	38-96;14-48	-	5 WWTPs	Spain	Boleda et al. 2007
	Surface	0.5-7	0.9-38	4 Rivers	Italy	Zuccato et al. 2008a
	Surface	1	-	1 River (n=5)	UK	Zuccato et al. 2008a
THC	WW	14-39;13-21	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	11-32 ;	-	5 WWTPs	Spain	Boleda et al. 2007
THC-OH	WW	4.3-33;4-19	-	4 WWTPs	Spain	Postigo et al. 2008
PCP	WW	nd	-	16 WWTPs	Spain	Huerta-Fontela et al. 2007
	WW	nd	-	42 WWTPs	Spain	Huerta-Fontela et al. 2008a
	WW	5	-	7 WWTPs	USA	Chiaia et al. 2008
LSD	WW	nd	-	16 WWTPs	Spain	Huerta-Fontela et al. 2007
	WW	nd	-	42 WWTPs	Spain	Huerta-Fontela et al. 2008a
	WW	1.4-4.7;0.2-1.6	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	nd	-	7 WWTPs	USA	Chiaia et al. 2008
	Surface	nd	-	1 River (n=24)	Spain	Huerta-Fontela et al. 2008b
	DW	nd	-	1 DWTP (n=24)	Spain	Huerta-Fontela et al. 2008b
LSD-OH	WW	2.6-5.6; 0.7-0.8	-	4 WWTPs	Spain	Postigo et al. 2008
	WW	nd	-	7 WWTPs	USA	Chiaia et al. 2008
Nor-LSD	WW	4.3-22; 0.6-4	-	4 WWTPs	Spain	Postigo et al. 2008

*Median values; WW: wastewater; WWTP: wastewater treatment plant; DW: drinking water; nd: non detected waters should be analyzed. Several studies have been published analyzing the presence of illicit drugs in rivers from Italy (Zuccato et al. 2005, 2008a; Castiglioni et al. 2006), Spain (Huerta-Fontela et al. 2007, 2008b; Boleda et al. 2007), Ireland (Bones et al. 2007), UK (Kasprzyk-Hordern et al. 2007, 2008; Zuccato et al. 2008b), Poland (Kasprzyk-Hordern et al. 2007) and Belgium (Gheorghe et al. 2008; van Nuijs et al. 2008). For instance, in a recent work published by van Nuijs et al. (2008), 28 rivers from Belgium were sampled and analyzed for cocaine and two metabolites, benzoylecgonine and ecgonine methyl ester (which was not detected). Results showed the extended occurrence of the parent compound (0.1–55.2 g/day) and of benzoylecgonine (0.1–249.7 g/day) in 15 and 20 of the sampled rivers, respectively. In this study, the variation in cocaine loads at the sampled rivers was also evaluated, showing an increasing trend when going downstream. This behavior was also described in previous reports (Zuccato et al. 2008a; Huerta-Fontela et al. 2008a) and it is probably related to the continuous discharges of wastewaters along the rivers with a consequent accumulation effect. As regards other illicit drugs, one study performed in four Italian rivers and one from UK revealed different concentration levels of twelve and six illicit drugs, respectively. For instance, cannabis (THC) was detected as its main carboxylic metabolite (THC-COOH) at concentrations ranging from 0.5 to 7 ng/L in the Italian rivers and at 1 ng/L in one UK River. However, cocaine (by means of its metabolite benzoylecgonine) was the compound found at higher concentrations, followed by methadone and EDDP, codeine, cannabis (in the form of THC-COOH), and amphetamine related compounds (cocaine > methadone > codeine > THC > ATS).

Some seasonal studies have been also performed in surface waters; however extrapolations are more difficult to perform since concentrations depend not only on the excretion of the compounds but also on weather conditions (mainly water temperature and rainfall episodes), proximity of WWTPs and natural attenuation processes. In order to obtain comparable results, the seasonal surface survey should be performed always in the same sampling point, at the same time/day, avoiding rainfall episodes, measuring the river flow rates (in order to normalize concentrations), and evaluating water temperature effect. Additionally, ratios between concentrations of the parent compounds and their metabolites should be always checked since they provide information about natural degradation processes. Kasprzyk-Hordern et al. (Kasprzyk-Hordern et al. 2008) studied the seasonal variations through six consecutive months (from January to August 2007) and the results reported showed higher loads for amphetamine and benzoylecgonine in August. Another study performed in one river from Spain during 1 year showed maximum loads for amphetamine during the summer season. For cocaine, ecstasy and methamphetamine high loads were also detected in summer but maximum values were found in winter. A more detailed study of this period was performed by collecting samples more frequently (from December 14, 2006 to January 30, 2007). This survey revealed an important increase in the concentrations of these compounds during the last days of December and the first days of January, corresponding to the Christmas and New Year holidays. In Fig. 3.1, the results obtained during this seasonal survey are displayed.

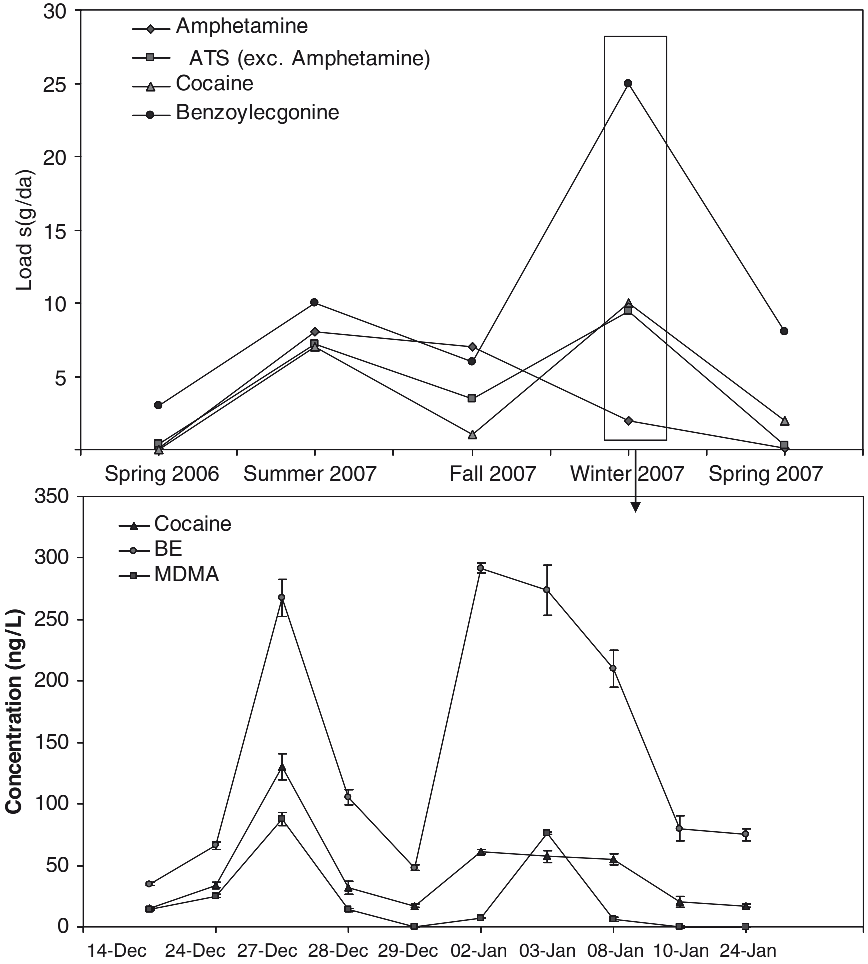


Fig. 3.1 Seasonal variation of illicit drugs in surface waters from NE-Spain. (Huerta-Fontela et al., 2008b)

3.1.3 Drinking Water

It is important to consider that often, surface waters are used as raw sources for drinking water production and the presence of illicit drugs can have a negative impact on the quality of the final tap water. Recently, one study has been published describing for the first time the presence and removal of illicit drugs through drinking water treatment (Huerta-Fontela et al. 2008b). Amphetamine-type stimulants (except MDMA) were completely removed during prechlorination, flocculation, and sand filtration steps. Granulated activated carbon (GAC) filtration removed cocaine (100%), MDMA (88%) and benzoylecgonine (72%). Post-chlorination achieved the complete elimination of MDMA and only benzoylecgonine persisted throughout treatment, although reductions of 90% were obtained.

3.2 Consumption Estimation

The estimation of the percentages of illicit drug users and trends established in national and international annual reports are usually based on population surveys and statistical approximations. For instance, the percentages published in the World Drug Report 2007 (summarized in the previous section) are based primarily on the results obtained from the "Annual Reports Questionnaire (ARQ)" returned by Governments to UNODC (United Nations Office of Drug and Crime 2007). This questionnaire mainly depends on self-reports (in-house surveys) and also considers the number of treatment demands, arrests, and drug production and seizure rates declared by the Governments. Therefore, a general overview of the extent of the drug use is given by these reports but the margins of error are considerable.

The analysis of illicit drugs in water resources represents a novel and cheaper approach to determine more realistically the consumption rates and the patterns of use. In order to extrapolate illicit drug concentrations to consumption percentages, the first premise to take into account is that these drugs are hardly metabolized with known parent/metabolite excretion rates (pharmacokinetic data) and that they are stable in wastewaters (environmental transformation rate data) (Daughton 2001). Therefore, the normalization of the concentration values found in wastewaters can be easily performed by using the measured daily flow rates entering the WWTP and the number of inhabitants served. In general, the steps performed to extrapolate these results are as follows. First, concentration values are multiplied by daily influx, obtaining daily loads (e.g., g/day), which are divided by the population served (e.g., g/day × 1,000 inhabitants). Then, a correction factor is applied to these loads to obtain the number of doses per day and population. This correction factor includes excretion ratios together with official dose contents. In Table 3.3, a summary of the correction factors is displayed.

3.2.1 *Cocaine*

The first works published using these approximations extrapolate cocaine wastewater concentrations to consumption rates (Zuccato et al. 2005, 2008a; Huerta-Fontela et al. 2008a, b; Bones et al. 2007; van Nuijs et al. 2008). In Table 3.4, a summary of these results is displayed. In most of these works, cocaine estimations were performed by using benzoylecgonine concentration data since this compound

Table 3.3 Excretion parameters for illicit drugs consumption calculations

Drug	Dose (of parent drug)*	Excreted Compounds	Description	% Excreted (Baselt, 2004)	$t_{1/2}$ (h) (Baselt, 2004)	Correction Factor
Cocaine	100 mg	Benzoylecgonine	Major Excretion Product	35-54%	4.5	2.33
		Ecgonine methylester	Major Excretion Product	32-49%	3.1	
		Cocaine	Parent drug	1-9%	0.8	
		Cocaethylene	Excreted when consumed with ethanol	1-10%	1.7	
		Norcocaine	Minor Excretion Product	Traces	-	
		Norbenzoylecgonine	Minor Excretion Product	Traces	-	
Amphetamine	30 mg	Amphetamine	Parent drug-Major Excretion Product	30%	24	3.3
Methamphetamine	125 mg	Methamphetamine	Parent drug-Major Excretion Product	34%	24	2.9
		Amphetamine	Minor Excretion Product-not exclusive	4-7%	24	
MDMA	100 mg	MDMA	Parent drug-Major Excretion Product	72%	24	3.8
		MDA	Minor Excretion Product-not exclusive	1%	24	
MDEA	100 mg	MDA	Major Excretion Product-not exclusive	28%	24	
		MDEA	Parent drug-Minor Excretion Product	19%	24	5.3
Methadone		Methadone	Parent drug-Major Excretion Product	35-60%	24	
		EDDP	Major Excretion Product	35-60%	24	2.2 (50%)
Heroin	30 mg	Morphine-Glucuronides	Major Excretion Products-not exclusive	38 %	7	
		Morphine	Major Excretion Product-not exclusive	4.2%	7	

(continued)

Table 3.3 (continued)

Drug	Dose (of parent drug)*	Excreted Compounds	Description	% Excreted (Baselt, 2004)	$t_{1/2}$ (h) (Baselt, 2004)	Correction Factor
		6-acetylmorphine	Excretion Product-exclusive	1.3%	40	68
		Heroin	Parent drug-Minor Excretion Product	0.1%	40	
Morphine	100 mg	Morphine-3-glucuronide	Major Excretion Products-not exclusive	75 %	72	2.16
	(non th.)	Morphine	Major Excretion Product-not exclusive	10%	7	10
		Normorphine	Minor Excretion Product	1%		
THC	500 mg	THC-COOH	Major Excretion Product	1%	2-72	109
		THC-OH	Minor Excretion Product	Traces	72	

*(United Nations Office of Drug and Crime, 2007); non th.=therapeutic

Table 3.4 Estimations of cocaine consumption

Extrapolation	Country	Loads per capita (mg/day/ 1000inh)	Number of Doses (doses/ day/1000inh)	Users %	Reference	Official %[a]
From BE loads	Italy	210-730 900-2700[*]	2-7 9-27[*]	0.2-0.7% 0.9-2.7%[*]	(Zuccato et al., 2005)	0.8-2.1%[**] 1.2%[*]
From BE loads	Spain	1400[**] 3300	14[**]33[*]	1.4%[**] 3.3%[*]	(Huerta-Fontela et al., 2008a)	1.6-3%[**] 2.8%[*]
From BE loads	Belgium	700-1000	7-10	0.7-1%	(van Nuijs et al., 2008)	0.9%
From COC loads	Ireland	180-1440	2-14	0.2-1.4%	(Bones et al., 2007)	0.5-1.1%[**]

[a] Percentage of users considering last month prevalence. (European Monitoring Center for Drugs and Drug Addiction, 2008; United Nations Office of Drug and Crime, 2007).

[*] young adults: 15-34 years old;[**] adults: 15-64 years old

comes entirely from the metabolic degradation of cocaine and therefore from human consumption. Cocaine loads are not included in the calculations to avoid the effects of any sporadic direct discharge. Moreover, in a recent work published by Gheorghe et al. (2008), it was demonstrated that cocaine is not stable. For instance, at pH 6 and 20°C degradation percentages of 40% and 75% after 5 h and 1 storage day were found respectively. Therefore, benzoylecgonine loads are recommended to be used when cocaine consumption calculations are performed. To relate benzoylecgonine with cocaine, the percentage of intranasal cocaine excreted in urine as benzoylecgonine (30–50%) and the molar mass ratio of cocaine/BE (1.05) are considered, giving a factor of 2.3 (Zuccato et al. 2005) or 2.7 ± 0.6 (Huerta-Fontela et al. 2008a) depending on the excretion percentages considered. The total equivalents of cocaine are then obtained, and they can be converted to the total number of doses assuming a typical consumption unit/dose (at street purity) of 0.1 g of cocaine (United Nations Office of Drug and Crime 2007). The number of doses per 1,000 inhabitants described in the literature range from 2 to 14 and these values rise above 27 doses/1,000 inhabitants (in Italy) and 33 doses/1,000 inhabitants (in Spain) when only young adults (from 16 to 34 years old) are considered.

A raw comparison between the official prevalence data published and the percentages from these surveys can be also performed. As can be observed in Table 3.4, similar percentages of cocaine users are obtained with both estimations. It must be taken into account that the official rates are calculated by considering only adult population (from 15 to 64 years old) and a time frame of use of 1 month (or 1 year) while in these surveys, the population age range differs from one study to another and the time frame of use is mainly of 1 day or 1 week. Further work needs to be performed in order to optimize and standardize the "sewage epidemiology"(Zuccato et al. 2008b) approach to drug consumption; however, it can be stated that these first approximations provide similar orders of magnitude than those so far provided by the "standard estimation methods".

3.2.2 *Heroin*

For heroin, additional figures must be taken into account before calculating consumption from wastewater concentrations. In one hand, only one exclusive metabolite of heroin can be found in wastewater samples, 6-acetylmorphine. This metabolite is a minor excretion product and up to now, it has not been considered for wastewater calculations since it is supposed to be present at fluctuating concentrations (Zuccato et al. 2008b). On the other hand, heroin, major excretion products, morphine, and conjugated morphine glucuronides (Table 3.3), are not specific or exclusive metabolites of this parent drug since they are also excreted after morphine or codeine consumption. According to previous studies (Baselt 2004; Zuccato et al. 2008b), codeine contribution to wastewater morphine can be neglected due to the low excretion percentages. Morphine concentrations in wastewater can then come from therapeutic morphine consumption or from heroin use. Additionally, morphine glucuronides are extensively hydrolyzed to morphine by enzymatic mechanisms in fecal waters (Baselt 2004; Zuccato et al. 2008a). Therefore, in order to calculate heroin consumption, corrections in morphine wastewater concentration must be performed to compensate the extensive contribution from therapeutic morphine use. These therapeutic contributions can be calculated by using official or published data regarding local consumption values (amount of therapeutic morphine per time per capita) which are changed to daily amounts of morphine metabolite by considering excretion rates (85% for therapeutic morphine). Next, these amounts are subtracted from the total morphine wastewater loads, giving to a residual morphine amount which can be considered to come mostly from heroin consumption. Finally, taking into account these morphine amounts, heroin consumption can be calculated by considering the excretion percentage (42%) and the molar mass ratio (1.3) (Table 3.3).

Zuccato et al. (2008b) firstly proposed this approximation in order to estimate heroin consumption from morphine wastewater concentrations. The calculated heroin consumption was of 70 mg/day per 1,000 inhabitants in Italy, 100 mg/day per 1,000 inhabitants in Switzerland and 200 mg/day per 1,000 inhabitants in UK. Considering that a typical intravenous dose of heroin has an average content of pure active drug of 30 mg, the number of doses consumed daily ranged from 2 to 7 doses. Additionally, in a recent work performed in 15 WWTPs in Spain (Boleda et al. 2009), similar approximations were used in order to calculate heroin consumption. An average value of 5 doses/day per 1,000 inhabitants was obtained which represents 0.67% of the population aged between 15 and 64 years old.

3.2.3 *Other Illicit Drugs*

Extrapolation from wastewater concentrations to drug consumption can be also performed for other illicit drugs. For instance, in a study published in 2007, wastewater concentrations of MDMA were directly used to estimate ecstasy consumption since this compound is mainly excreted unaltered (Table 3.3). Total loads of MDMA (26 mg/day per 1,000 inhabitants) were corrected by considering the excretion percentages (72%) and the estimated local use of ecstasy was calculated by taking into consideration that a typical dose of MDMA is 0.1 g (unit/dose) (United Nations Office of Drug and Crime 2007). One dose of ecstasy per day per 1,000 habitants was obtained for population aged between 15 and 64 years old. Finally, these results were also extrapolated to population aged between 15 and 34 years old, since the use of this drug in Spain is nearly exclusively restricted to young adults group, giving an estimated consumption of four doses of ecstasy per day per 1,000 habitants. Lower loads were found in Italy (Milano), Switzerland (Lugano), and England (London) with values ranging from 3.4 to 7.3 mg/day per 1,000 inhabitants (adult population). The extrapolation to consumption rates gives values ranging from 0.12 to 0.28 doses/day per 1,000 inhabitants which are ten times lower than those reported in Spain. Finally, in a recent study performed in seven WWTPs around USA (Chiaia et al. 2008), higher variability in loads was found, with values ranging from 2 to 40 mg/day per 1,000 inhabitants which correspond to 0.1 to 1.5 doses/day per 1,000 inhabitants. Unlike cocaine use, these studies demonstrate important variations in ecstasy consumption depending on country/regions and age ranges.

THC consumption can be also calculated from wastewater concentrations by using THC-COOH since it is the major metabolite of cannabis and it has been ubiquitously found in wastewaters sampled (Table 3.2). For instance, Zuccato et al. (2008b) found load levels ranging from 20 to 50 mg/day per 1,000 inhabitants of the cannabis metabolite which can be extrapolated to 2180 to 5450 mg/day per 1,000 inhabitants of the parent compound. Considering a typical smoked dose of 125 mg (14% of pure THC), these values correspond to 124–311 doses/day per 1,000 inhabitants. According to this study cannabis was the most used drug among the studied ones, and results agreed with official figures.

3.3 Concluding Remarks

The presence of illicit drugs in water resources has been discovered in the last few years. Since this fact was firstly uncovered in 2005, a number of increasing works dealing with this topic have been published.

In this chapter, a summary of the works published regarding the occurrence of illicit drugs from wastewater to tap water has been performed. Results can be considered and processed from two different points of view. In one hand, from an environmental point of view, illicit drugs or their slightly transformed metabolites have been detected in water matrices at relatively high concentrations. This fact not only confirms the effect of human habits and activities in the environment but also suggests the introduction of new psychoactive agents into the aquatic system. For instance, cocaine, amphetamine, ecstasy, heroin, or cannabinoids among others have been detected entering to water resources by means of sewage waters from different countries such as Italy, Germany, Spain, Belgium, UK, or USA. Wastewater treatments showed not to be effective enough to remove these drugs and therefore they were also found, at lower concentrations, in receiving surface waters which at the same time can be used for drinking water production. Drinking water treatments showed the complete removal of all the illicit drugs or metabolites detected in the raw water except for benzoylecgonine (cocaine metabolite), methadone, and EDDP (methadone metabolite). Considering all the surveys performed and the results obtained it can be concluded that the presence of illicit drugs in the "water cycle" far from being a temporary or a national problem has become a stationary problem of global concern. On the other hand, from a forensic point of view, illicit drug concentrations in wastewater can be also used to backward calculate the amount of drugs consumed by a specific population. Several studies perform these calculations by considering excretion pathways and percentages; parent compounds (ecstasy, methadone) or main excretion metabolites (benzoylecgonine or THC-COOH) have been used to estimate consumptions. Results obtained from these approximations provide similar magnitude orders than those obtained from classical estimation methods. Therefore, this kind of sewage approximations can become a powerful and reliable tool for enforcement agencies and to obtain epidemiologic and consumption tendency data.

Finally, it must be emphasized that much more data are needed in order to improve the knowledge of the behavior and occurrence of illicit drugs in wastewaters and surface waters as well as their toxicological impact in both aquatic life and human beings. Additionally, validation protocols should be established in order to improve backward calculations and to incorporate general and agreed guidelines to perform representative and reproducible surveys.

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Chapter 4
Precious Metals in Urban Aquatic Systems: Platinum, Palladium and Rhodium: Sources, Occurrence, Bioavailability and Effects

Nadine Haus, Sonja Zimmermann, and Bernd Sures

Abstract The platinum group elements (PGE) belong to the rarest metals on our planet. During the last three decades three of the six PGE (platinum (Pt), palladium (Pd) and rhodium (Rh)) are found in increasing concentrations in different terrestrial and aquatic matrices. Anthropogenic sources of PGE are industrial discharges, road runoff as well as waste waters from hospitals and dental surgeries. As anthropogenic PGE are mostly emitted in elemental form, they were initially thought to be not relevant for biota. Laboratory studies, however, revealed that aquatic plants and animals are able to take up and accumulate PGE. Effect studies showed that animals exposed to PGE respond with increased levels of stress markers.

The most important factors influencing the bioavailability of PGE tend to be time, metal concentration in the medium, the chemical speciation of the metal and the presence of complexing agents. This chapter summarizes the present knowledge on the introduction of PGE into urban aquatic ecosystems and the behavior within these habitats. It draws attention to the increase of PGE contamination in different matrices, summarizes current PGE concentrations in the field, discusses the different bioavailability of Pt, Rh and Pd and evaluates the effects of PGE on aquatic organisms.

4.1 Introduction

Platinum group elements (PGE) are a group of six metals: iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), ruthenium (Ru), and rhodium (Rh). They belong to the rarest elements on earth as their proportion of the upper Earth crust is about $10^{-6}\%$ to $10^{-7}\%$ (Hoppstock and Sures 2004). Nowadays, these metals are of

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N. Haus (✉), S. Zimmermann and B. Sures
Applied Zoology/Hydrobiology, University of Duisburg-Essen, Universitätsstr. 5, 45141 Essen, Germany
e-mail: nadine.haus@uni-due.de

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high interest for industrial purposes because of their special characteristics with regard to corrosion resistance, high melting points and catalytic properties, especially in their metallic form. The global demand in particular of Pt, Pd, and Rh is steadily rising, due to new applications in the industry (i.e. organometallic chemistry, surfaces-, materials- and crystal engineering, photo- and electrochemistry, catalysis and organic synthesis), whereas the demand for Ir, Os and Ru is currently still lower (Hoppstock and Sures 2004). Consequently, the extended usage of noble metals in several industrial branches resulted in an increase of PGE emitted into the environment (reviewed in Ek et al. 2004; Hoppstock and Sures 2004; Ravindra et al. 2004). The distribution of PGE in urban aquatic ecosystems and their effects on biota, however, gained less attention. Therefore, this chapter represents the first comprehensive review of the current state of research on effects of PGE in urban aquatic ecosystems.

4.2 Sources

As for most heavy metals, there are several routes through which PGE can enter urban aquatic ecosystems. These include the direct discharge from the industry, from sewage systems, and municipal sewer systems as well as the diffuse discharge via wind and abrasion mainly from roads. Approximately 50% of the global PGE production will end up in the automobile industry (Matthey 2008). The noble metals are used for automobile catalytic converters in order to reduce the emission of nitrogen oxides, hydrocarbons and carbon monoxides as part of the exhaust fumes. Mostly due to mechanical abrasion, PGE break off the catalyst converter and are emitted into the environment as particles, attached to aluminium oxides (Schlögl et al. 1987; Rauch and Morrison 2008). Emission rates of an individual car for all three PGE are in the low ng km^{-1} range for gasoline vehicles. In diesel catalysts, however, mostly Pt is used and emission rates are around 100 ng km^{-1} (Moldovan 2007). Traffic related PGE can be introduced into aquatic systems via atmospheric transport or via road runoff through sewers or municipal sewage systems (Laschka and Nachtwey 1997).

A variety of industries use PGE in their production lines, including the application of PGE in process catalysts for manufacturing chemical products (e.g. nitric acids, hydrogen peroxide), in the glass industry for producing glass fibres or LCD glass (only Pt) or in the electronic industry, where Pd competes with gold in electroplating processes (Matthey 2008). In discharge water of different industrial companies, Schwesig et al. (2006) found Pd to be the predominant PGE. It was detected in the particulate phase of effluents and only a small part was present in the soluble fraction. Three-quarter of the PGE discharged in industrial effluents is released by the chemical industry. Herein, concentrations were found to range between <2 to 73 ng L^{-1} for Pd, <1 to 22 ng L^{-1} for Pt and 8–81 ng L^{-1} for Rh. The production of chemical fibres yielded the second largest PGE emission in industrial effluents (IWW 2004).

Other sources of PGE emitted into aquatic systems with discharges into municipal sewer systems are effluents from hospitals and dental clinics. In hospitals especially Pt is used as part of anticancer drugs in the form of cisplatin [cis-diaminedichloroplatinum (II)] and carboplatin [diamine (1,1-cyclobutanedicarboxylato) platinum (II)]. Patients treated with these drugs excrete platinum via urine, even years after their chemotherapy (Hohnloser et al. 1996). Kümmerer et al. (1999) estimated the concentration of Pt released from medical institutions into the environment as relatively low compared with other sources like road runoff.

Dental laboratories use Pt and Pd for dental inlays. Their input of PGE into the municipal sewer systems is estimated to be lower compared to PGE input from industrial sources. For the state of North Rhine Westphalia (Germany) IWW (2004) estimated a total emission rate of 780 g Pt, 55 g Pd and <10 g Rh/year into the effluents of dental laboratories.

Due to these different sources it is not surprising that PGE can be detected in the effluents of municipal treatment plants. In a study containing 33 different municipal treatment plants IWW (2004) found concentrations usually below 10 ng L^{-1} in the effluent water. Occasionally, permanent emissions of 20–50 ng L^{-1} were found, with the concentrations of Pt always being the highest followed by nearly equal concentrations of Pd and Rh, which never reached concentrations higher than 10 ng L^{-1}. Laschka and Nachtwey (1997) have already shown that Pt concentrations in the effluent of a municipal sewage treatment plant in Munich (Germany) were dominated by industrial discharges during dry seasons, whereby in rainy seasons Pt loads were increased due to road runoff. Investigations on the Pt elimination rate in a sewage treatment plant in Munich revealed that only 70% of Pt is eliminated before the treated wastewater is discharged into the river Isar.

As the PGE loads of some entrance routes into aquatic systems are still not quantified (e.g. diffuse discharge), there is still discussion about the major sources for PGE in urban rivers and lakes. Most authors believe that emission through automobile catalytic converters is the main source of PGE in aquatic systems (due to stormwater drainage, municipal sewer systems and diffuse entrance due to atmospheric transport) (e.g. Kümmerer et al. 1999; de Vos et al. 2002; Rauch and Hemond 2003). Other authors state, however, that industrial sources play the major role in PGE discharge, and assume that hospital discharges and automobile PGE emissions tend to be negligible (Schwesig et al. 2006). Regardless of the significance of these sources, it is clear that a mixture of different chemical species for each PGE can be found in urban aquatic systems. Information on the speciation of PGE is still missing (Turner et al. 2006).

4.3 PGE in Urban Aquatic Habitats

As most of the PGE are emitted in particulate form (especially in road runoff and discharge of the chemical industry), they are thought to accumulate in the sediment of aquatic systems. This is reflected in a high number of field studies on PGE, which are solely focused on PGE concentrations in sediments. In the recent literature PGE data of approximately 100 different sampling sites (most of them in European urban regions) can be found (summarized in Table 4.1).

Unfortunately, PGE were analyzed in different grain size fractions of the sediment samples and the studies are therefore not comparable in all aspects. Nevertheless, some of the authors provide a detailed description of the conditions at the sampling sites and data can be divided into sampling sites which are highly polluted, like those which are in short distance to inlets of sewer systems or mine drainage systems, or lightly polluted (e.g. in urban surroundings, but not directly affected by discharge with PGE containing waters, or upstream/downstream of such discharges). In highly polluted sediments, concentrations are above 20 ng g^{-1} for Pt and Pd and above 3 ng g^{-1} for Rh (Moldovan et al. 2001; Whiteley and Murray 2005, Prichard et al. 2008). In lightly polluted sediments Pt and Pd concentrations are usually below 10 ng g^{-1}, whereby Rh is often not detectable or in the range of 1–2 ng g^{-1} (de Vos et al. 2002; Haus et al. 2007; Prichard et al. 2008).

It should be pointed out that PGE concentrations in sediments are still very low (ng g^{-1} range) in comparison to other heavy metals (µg g^{-1} range, see e.g. Haus et al. 2007).

Rauch and Hemond (2003) and Rauch et al. (2004a) investigated if the introduction of automobile catalytic convertes is the main source of PGE in sediments. In sediment cores of the Upper Mysthik Lake in Boston they investigated retrospective concentrations of Pt, Pd and Rh. Concentrations prior to the introduction of automobile catalytic converters ranged between 0.5–2.3 ng g^{-1} for Pt, approximately 2 ng g^{-1} for Pd and 1 ng g^{-1} for Rh. Starting in the 1980s, concentrations increased to 29,

Table 4.1 Field data on PGE concentrations in water (ng L^{-1}), sediments (µg g^{-1}), and animal tissue samples (ng g^{-1}, wet weight) sampled in different lake and river systems

Sample	Pt			Pd			Rh		
	N	min	max	N	min	max	N	min	max
Water[a]	5	<d.l.	0.8	4	0.4	10.2	4	<d.l.	<d.l.
Sediments[b]	126	<d.l.	85	94	<d.l.	57	94	<d.l.	9.6
Asellus aquaticus[c]	8	<d.l.	1,295	2	76.9	284.2	2	3.6	48.2
Amphipoda[d]	6	<d.l.	1.3	n.a.	–	–	n.a.	–	–
Dreissena polymorpha[e]	1	0.1	0.1	1	1.0	1.0	1	<d.l.	<d.l.
Barbus barbus[f]	3	0.1	0.8	3	<d.l.	7.1	3	<d.l.	0.4

n.a.: not analyzed <d.l.: below limit of detection.

[a] Eller et al. (1989); Rauch and Morrison (1999); Hoppstock and Alt (2000); Moldovan et al. (2003).

[b] Wei and Morrison (1994); Rauch and Morrison (1999); Tuit et al. (2000); Moldovan et al. (2001); de Vos et al. (2002); Rauch and Hemond (2003); Whiteley and Murray (2005); Haus et al. (2007); Jackson et al. (2007); Prichard et al. (2008).

[c] Rauch and Morrison (1999); Moldovan et al. (2001); Haus et al. (2007).

[d] Haus et al. (2007).

[e] Zimmermann et al. (2002).

[f] Sures et al. (2005).

21 and 3 ng g^{-1}, respectively. Levels of the three metals were positively correlated and Pt/Rh and Pd/Rh ratios resembled ratios found in catalyst converters. The Pt/Pd ratio was higher than expected if one assumes traffic to be the main source of PGE. Similar results are also available from other studies (de Vos et al. 2002; Jackson et al. 2007; Prichard et al. 2008). A possible explanation is the higher mobility of Pd than of Pt, which was described in several solubility studies, in which Pd in road dust samples showed a higher solubility than Pt (Moldovan et al. 2002; Colombo et al. 2007).

Generally, PGE concentrations in water samples are close to or even below detection limits of approximately 0.1–0.9 ng L^{-1}. Only Pd could be detected in water samples of the river systems Rhine and Schwarzenbach in Germany and a river in Gothenburg, Sweden (Eller et al. 1989; Moldovan et al. 2003). While Eller et al. (1989) did not describe their sample area, Moldovan et al. (2003) took the samples near a highly frequented parking lot and therefore found the highest amount of Pd in water samples is reported so far (10.4 ng L^{-1}). In the same study Pt concentrations remained below the detection limit. Rh has not yet been detected in water samples of urban river or lake systems.

PGE analyses from animal tissues of aquatic organisms collected in the field are random and scarce (summarized in Table 4.1). As there is still no reference material for PGE in biota samples, only a few analytical methods have been developed for PGE determination in organic matrices, all of them are very time consuming (Zimmermann et al. 2001; Haus et al. 2009). From the limited number of studies available it emerged that PGE are bioavailable, although they are mostly emitted in a particular form. The concentrations in which PGE were detected in these studies vary considerably and assumptions about general PGE loads are difficult to make. In the field study of Moldovan et al. (2002) the uptake of Pt, Pd and Rh by *Asellus aquaticus* could be proven, with highest concentrations for Pd, followed by Pt and Rh. Differences were found in PGE tissue concentrations when asellids were sampled on different days. These differences were interpreted by asellid individual physiological variations (Rauch and Morrison 1999; Moldovan et al. 2002). Furthermore, Rauch and Morrison (1999) showed that asellids store 50–75% of their Pt load in the exoskeleton as it is also known for other heavy metals and other crustaceans (Zauke 1982). Thus, variations in the PGE concentrations could be due to the moulting status of individual asellids. In comparison to other heavy metals, concentration factors (CF) of Pt (as the ratio between animal and sediment concentration) were high with a CF of 14.3 (Rauch and Morrison 1999). In contrast, Haus et al. (2007) described CFs of 0.1 for *Asellus aquaticus* and 0.16 for *Gammarus pulex*. Although being much lower than the values reported by Rauch and Morrison (1999), the latter values were in-between the CFs for the essential metal Zn (0.7 and 0.48, respectively) and the toxic metal Cd (0.07 and 0.05, respectively) (Haus et al. 2007). The direct comparison between the concentration of Pt and other heavy metals, however, revealed that Pt concentrations in invertebrates are still three orders of magnitude lower than those of other heavy metals like Pb and Cd and five orders of magnitude lower than those of essential metals like Zn or Cu (Haus et al. 2007). In addition to information on PGE in invertebrates PGE levels in vertebrates collected from the field are only available from one study. Sures et al. (2005) performed an exposure experiment with barbel (*Barbus barbus*) originating from the river Danube. Also in the tissues of the control fish, which were not experimentally exposed to PGE, Pt, Pd and Rh could be detected. This indicates that the input of PGE into the river Danube downstream from Budapest is high enough to cause a detectable pollution with these metals in the fish tissues.

4.4 Uptake and Bioaccumulation of PGE by Aquatic Organims

For a better understanding of the uptake and bioavailability of PGE by aquatic organisms exposure studies were conducted with different plant and animal species (see Table 4.2).

As there is still a great uncertainty about the chemical speciation of PGE in aquatic habitats, the exposure experiments were performed with different metal sources, which can be classified into soluble PGE (eg. soluble salts or standard solutions for analytical purposes), or particle bound PGE like ground catalytic material, road dust or river sediments. In exposure studies with aquatic plants, however, only soluble PGE species were used so far. Farago and Parsons (1994) demonstrated that PGE uptake by the water hyacinth increased with rising PGE concentrations in the respective culture medium. The same was found for the willow moss *Fontinalis antipyretica* (Veltz et al. 1994) and for Pt (II) and Pt (IV) uptake by periphyton communities (Rauch et al. 2004b). PGE were offered as a solution of

Table 4.2 Organisms tested in bioaccumulation studies

Organism tested in bioaccumulation experiments	Literature
Eichhornia crassipes (Water hyazinth)	Farago and Parsons (1994)
Lemna minor (Common duckweed)	Veltz et al. (1994)
Fontinalis antipyretica (Willow moss)	Veltz et al. (1994)
periphyton communitie	Rauch et al. (2004b)
Asellus aquaticus (Water louse)	Rauch and Morrison (1999)
	Moldovan et al. (2001)
Dreissena polymorpha (Zebra mussel)	Sures et al. (2002)
	Zimmermann et al. (2002, 2004a)
	Singer et al. (2005)
	Sures and Zimmermann (2007)
	Frank et al. (2008)
Lumbriculus variegatus (Blackworm)	Veltz et al. (1994, 1996)
Lebistes reticulates (Guppy)	Veltz et al. (1994)
Danio rerio (Zebra fish)	Jouhaud et al. (1999a, b)
Anguilla anguilla (European eel)	Sures et al. (2001, 2003)
	Zimmermann et al. (2004a, b, 2005b)
Barbus barbus (Barbel)	Sures et al. (2005)

chlorocomplexes and uptake of PGE by the water hyacinth was highest in the roots. Pt (II) uptake was the highest, followed by Pd (II) and then Rh (II) (Farago and Parsons 1994). The treatment of the duck weed *Lemna minor* with H_2PtCl_6 resulted in a decrease of growth with increasing Pt concentration in the culture medium (0; 0.5 and 300 μg L^{-1}) and a fast yellowing of the leaves at a Pt concentration of 300 μg L^{-1} (Veltz et al. 1994).

Exposure studies with animals showed that the uptake of PGE depends on various factors such as PGE concentration in the exposure medium and exposure period. Another crucial factor influencing the bioaccumulation of PGE is the chemical speciation in which the metals are offered.

In studies with *Asellus aquaticus* Rauch and Morrison (1999) demonstrated that uptake of Pt (IV) was significantly higher than the uptake of Pt (II) after 96 h. Studies with *Dreissena polymorpha*, on the contrary, revealed a ten fold higher uptake of Pt (II) compared to Pt(IV) after an exposure period of 6 weeks (Zimmermann 2002). Several studies demonstrate that PGE are bioavailable, irrespectively if they are offered in a soluble state or bound to particles: Zimmermann (2002) exposed *D. polymorpha* to soluble PGE salts, road dust and ground catalyst material. It could be demonstrated that PGE uptake was highest for soluble metals, followed by catalyst material and then by road dust. Similar results were found for the isopod *Asellus aquaticus*: Exposure to soluble metals resulted in the highest uptake rates, followed by uptake from road dust, river sediments and tunnel dust (Moldovan et al. 2001). These findings resemble the results of solubility studies, which demonstrate a higher solubility of PGE from road dust than from catalytic material (Jarvis et al. 2001; Moldovan et al. 2002). Therefore, the bioavailabilty of PGE tends to increase with increasing solubility from the metal source provided.

Independently of the available metal source, the accumulation rate of Pt, Pd and Rh is varying. In almost all studies comparing uptake of Pt, Pd and Rh, Pd showed the highest accumulation in animal tissues, followed by Pt and then Rh (Moldovan et al. 2001; Sures et al. 2002, 2005; Zimmermann et al. 2002, 2004a, b, 2005a, b; Sures and Zimmermann 2007). The only exception is presented in the study of Singer et al. (2005), in which the uptake of Pt (IV) by *D. polymorpha* was higher than the uptake of Pd (II) and Rh (II). Once again, the usually higher bioavailability of Pd can be explained by a higher solubility of Pd from solid phases compared to the solubility of Pt and Rh, as demonstrated for catalyst material (Moldovan et al. 2002) and road dust (Jarvis et al. 2001). This is also supported by results of Turner et al. (2006), who showed that Pd deriving from road dust has the lowest affinity to sediment particles and the highest exchangeability followed by Pt and Rh. Pd has therefore the greatest potential for bioaccumulation in the aquatic environment. On the other hand, Pd concentrations in animal tissues are also increased compared to Pt and Rh, if the three PGE are provided in the same concentration in the exposure medium (Moldovan et al. 2001; Sures and Zimmermann 2007). In conclusion, the current findings suggest that Pd accumulates to a higher degree in animal tissues than Pt or Rh, either due to higher uptake or lower elimination rates by the animals.

Another factor influencing the bioavailability of PGE is the presence of humic substances or other complexing agents (Zimmermann et al. 2003). In studies with *D. polymorpha* exposed to road dust and ground catalyst material, Zimmermann et al. (2002, 2005a) discovered higher PGE accumulation in mussel tissue after exposure in water containing humic substances compared to an exposure in tap water. Using soluble salts instead of road dust, Sures and Zimmermann (2007) could confirm an elevated Pd uptake by *D. polymorpha*. However, in the same study a lower bioavailabilty was shown for Rh, while the accumulation of Pt did not show a significant difference between mussel exposure in water containing humic substances or in tap water. Eels also tend to accumulate less soluble fractions of PGE when humic substances are present in the exposure tank (Zimmermann et al. 2004b).

The different effects of humic substances on PGE uptake of particulate and soluble metals are explained by different solubility processes. While the water solubility of particulate PGE is enhanced by humic substances (Bowles et al. 1995; Lustig et al. 1998), soluble PGE show varying reactions in the presence of humic acids. Sures and Zimmermann (2007) attribute this phenomenon to different reactions of soluble Pt, Pd and Rh to the fractions of humic substances: Whereas soluble Pt forms insoluble Pt-humic acid complexes in the presence of humic substances, Pd is bound in soluble fulvic acid complexes. These fulvic acid complexes prevent the precipitation of Pd which could otherwise be observed in water which does not contain any humic substances.

Organ-specific PGE uptake was investigated in exposure studies with fish (Sures et al. 2001, 2005; Zimmermann et al. 2004a, b, 2005b). The highest PGE concentration could be found in the metal target organs liver and kidney after exposure to soluble PGE salts, ground catalytic material or road dust. High Pt concentrations could also be found in the intestine of eels after 6 weeks of exposure to Pt (IV) (Zimmermann et al. 2004a). Concentrations in muscle tissues were low or even below detection limit in all studies mentioned above.

As has already been demonstrated for other heavy metals (e.g. Pb and Cd, reviewed in Sures 2008), also for PGE the highest concentrations and concentration factors can been found in acanthocephalans; a group of parasites living in the intestine of their fish hosts (Sures et al. 2003, 2005; Zimmermann et al. 2005b), see also Table 4.3. Due to their exceptional metal accumulation potential, acanthocephalans are considered as potential biomonitoring organisms also for PGE (Sures et al. 2003, 2005).

In exposure studies using road dust, the accumulation of PGE could be compared with those of other traffic related heavy metals. Transfer factors from road dust into the soft tissue of *D. polymorpha* decreased in the following order: Cu > Cd > Ag > Pd > Sb > Pb > Fe > Pt > Rh after an exposure period of 26 weeks (Zimmermann et al. 2002). Again, a high bioavailability was found for Pd, with a transfer factor of Pd only about four times lower compared to Cd, but three times higher compared to Sb and Pb. Transfer factors of Pt and Rh were five and eight times lower compared to Pb (Zimmermann and Sures 2004).

Table 4.3 Concentration factors (tissue concentration [μg kg^{-1}, wet weigth]/water concentration [μg L^{-1}]) of eel and barbel tissues after exposure to different PGE according to Zimmermann et al. (2004a, 2005b) and Sures et al. (2005)

	Liver	Kidney	Bile	Intestine	Muscle	Parasite
Exposure of *Anguilla anguilla* with soluble metals						
Pt	2.6	5.3	6.7	8.7	<d.l.	n.a.
Rh	1.2	0.5	0.3	0.7	<d.l.	n.a.
Exposure of *Anguilla anguilla* with ground catalyst material						
Pt	0.002	0.002	n.a.	<d.l.	<d.l.	0.083
Pd	0.12	0.12	n.a.	0.028	0.003	0.48
Rh	<d.l.	<d.l.	n.a.	<d.l.	<d.l.	<d.l.
Exposure of *Barbus barbus* with ground catalyst material						
Pt	180	150	n.a.	80	30	4,000
Pd	310	280	n.a.	110	20	4,900
Rh	57	39	n.a.	89	32	4,000

<d.l.: below detection limit; n.a.: not analyzed.

4.5 Toxicological Effects of PGE on Aquatic Organisms

The toxicity of PGE on aquatic organisms was mainly proven by using soluble PGE species in exposure and toxicity studies with different organism groups (crustaceans and fish). Results of the acute toxicity tests are summarized in Table 4.4. They reveal that Pt is the most toxic of the three PGE (Borgmann et al. 2005). Toxicity of Pt, however, was far behind the toxicity of e.g. Cd, Cr, Hg and Pb with LC_{50} values ranging between 0.57–8.4 μg L^{-1} after exposure in soft water and 1.05–159 μg L^{-1} after exposure in tap water. It was assumed to be as toxic as Se, Ce and Lu (Borgmann et al. 2005).

Besides the acute toxicity of PGE, also sublethal effects of Pt were investigated. An EC_{50} value of 62 μg L^{-1} was conducted for *Daphnia magna* (Biesinger and Christensen 1972) after exposure with Pt (IV). They found significant reduction of wheight and proteins of the animals and a reduction in glutamic oxaloacetic transaminase (GOT) activity. *Danio rerio* showed reversible intestinal changes after an exposure of 16 μg L^{-1} Pt (IV) (Jouhaud et al. 1999a, b). Rauch et al. (2004b) investigated the influence of Pt (IV) and Pt (II) on the photosynthetic activity of a natural grown periphyton community. No significant difference could be found for periphyton exposed in river water that contained the different Pt speciations in comparison to the control group. However, differences were found for periphyton exposed in reference water. Here, photosynthetic activity decreased. The effect of Pt (II) was found to be greater than the effect of Pt (IV).

All these studies were conducted with PGE concentrations which are far above concentrations found under environmental conditions. Therefore, it is unlikely to find acute or sublethal PGE-induced toxicity under field conditions for aquatic organisms. Unfortunately, only little information is available on chronic effects of aquatic organisms exposed to PGE. Singer et al. (2005) and Frank et al. (2008)

Table 4.4 Acute toxicity of PGE on aquatic species

Organism	Duration of exposure	LC_{50}	Literature
Hyallela azteca	1 week in soft water[a]	Pt: 110 μg L^{-1} Rh: 804 μg L^{-1} Pd: survival of 87%	Borgmann et al. (2005)
Hyallela azteca	1 week in tap water[b]	Pt: 221 μg L^{-1} Rh: survival of 71% Pd: 570 μg L^{-1}	Borgmann et al. (2005)
Daphnia magna	3 weeks	Pt(IV): 520 μg L^{-1}	Biesinger and Christensen (1972)
Oncorhynchus kisutch	24 h	Pt(IV): 15.5 mg L^{-1}	Ferreira and Wolke (1979)
Oncorhynchus kisutch	96 h	Pt(IV): 2.5 mg L^{-1}	Ferreira and Wolke (1979)

[a] Hardness 124 mg L^{-1}, carbonate alkalinity 84 mg L^{-1}, Ca 35 mg L^{-1}, Mg 8.7 mg L^{-1}, Na 13 mg L^{-1}, K 1.6 mg L^{-1}, SO4 32 mg L^{-1}, Cl 25 mg L^{-1}.

[b] Hardness 18 mg L^{-1}, carbonate alkalinity 14 mg L^{-1}, Ca 5.6 mg L^{-1}, Mg 0.90 mg L^{-1}, Na 1.4 mg L^{-1}, K 0.15 mg L^{-1}, SO4 3.4 mg L^{-1}, Cl 2.5 mg L^{-1}.

investigated the effects of PGE on stress biomarker in *D. polymorpha* in studies that lasted about 10 weeks. Singer et al. (2005) demonstrated that PGE can induce the production of heat shock proteins (hsp70). These proteins have important functions in terms of protein folding, protein transport and cell stabilisation (Schröder et al. 1999; Werner and Hinton 1999). They were already used as biomarkers of adverse effects of other heavy metals, eg. Pb and Cd (reviewed in Sanders 1993). In the study of Singer et al. (2005) the threshold levels for hsp70 induction decreased in the order: Cd > Pt > Pb ≥ Pd >Rh after exposure of *D. polymorpha* to diluted standard metal solutions (500 μg L^{-1}). The increase of hsp70 was time dependent. Highest hsp70 values were found for mussels exposed to Pd, followed by Pt and Rh. Hsp70 values were 25-fold higher for Pd and 19-fold for Pt and Rh in comparison to control mussels. With a 6- and 12-fold increase of hsp70 due to Cd and Pb exposure, respectively, these metals showed a much lower effect than the PGE.

Frank et al. (2008) investigated the induction of metallothioneins. Theses proteins are involved in detoxification processes of heavy metals (e.g. Cd) and are therefore used as biomarkers for metal pollution. The exposure of *D. polymorpha* to different concentrations of Pd (II) (5, 50, and 500 μg L^{-1}) resulted in a linear increase of metallothioneins. Compared to initial metallothionein concentrations, an increase up to 600-, 160- and 27-fold after an exposure with 500, 50 and 5 μg L^{-1} was found, respectively. These results reveal that chronic effects after PGE exposure even in lowest concentrations can not be excluded.

4.6 Conclusions

PGE are widespread in aquatic systems. They can be found in water, sediment and biota samples in the field. While it is still unclear in which chemical speciation PGE occur in aquatic systems, exposure studies with different sources of PGE (i.e. ground catalyst material, road dust, river sediments, soluble salts) could demonstrate that PGE are bioavailable in all relevant speciations. Several studies confirm that Pd tends to be the most bioavailable PGE. The acute and sublethal toxicity of PGE were proven to be low, however, chronical effects to low concentrations of PGE can not be excluded. The monitoring of PGE concentrations in relevant matrices (sediments, biota) of aquatic systems with special emphasis on Pd and further ecotoxicological tests are therefore highly recommended.

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Chapter 5
Fate and Effects of Little Investigated Scents in the Aquatic Environment

Richard Bolek and Klaus Kümmerer

Abstract The sense of smell is our most emotional sense. Although not always being aware of it, it plays an important role in our everyday live. Scents are widely used in Personal Care Products (PCPs) such as shampoo, washing lotions or make up. They give a pleasant smell, mask unpleasant scents and may even bind consumers to a specific brand. As a result, scents are being applied more and more and in turn are being introduced in increasing volumes into the environment. Their fate and effect in the environment are to date mostly unclear. Because many organisms rely on scents as means of communication, the emerging amount of scents emitted by our civilization can cause disturbances, known as "infochemical effect".

In this chapter, we give a short overview on the current usage and regulation of scents for Europe and the United States of America and possible risks of the introduction into the environment. For the University Medical Center Freiburg, we calculated the amount of used scents for the year 2006 from manufacturers' information and give examples for used scents which also act as infochemicals.

5.1 Introduction

Man has used substances for scenting purposes since the dawn of humanity. Flowers were found in a Neanderthal tomb in Shanidar Cave in northern Iraq (Leroigourhan 1975). In ancient Egypt, scented oils were used as perfumes and the process of perfume making is documented on ancient Egyptian wall paintings. In ancient Greece and Rome, natural scents, derived from rare flowers and woods, were used for religious and personal purposes. Through medieval ages the art of scenting was lost in Europe but preserved in the Arabic countries. In the sixteenth century the art of scenting was reintroduced to Europe. With the emerging industrialization of

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R. Bolek and K. Kümmerer (✉)
Section for Applied Environmental Science, University Medical Center Freiburg,
Freiburg, Germany
e-mail: klaus.kuemmerer@uniklinik-freiburg.de

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society, more and more people could afford buying scented products due to increasing wealth. Also, due to progress in chemistry, scents themselves could be produced industrially at lower costs. This led to a large increase in the amount of used scents. Because today, differences in the quality of the everyday Personal care Products (PCPs) are very small, scents are one important criterion for choosing a special brand. Therefore, marketing takes efforts to find scents which match the product image or even enhance it (Knoblich et al. 2003). Additionally they even influence the perception of the result (Holland et al. 2005). As a result, not only PCPs are scented but also whole shops or even offices in order to enhance corporate identity.

Today, the production of scents is a global business. For 2008, a study of Business Insights lists ten companies which account for 66% of the global flavor and fragrance market (Business Insights 2008). In Europe's cosmetic industries, fragrances account for approximately €5.25 × 10^9 and the market is still growing. According to their annual report of 2007, the world leading company for flavors and fragrances, Givaudan, states its earnings before interest, taxes, depreciation and amortization (EBITDA) in 2007 for fragrances as €274 × 10^6. This means an increase in earnings of nearly 20% compared to the year 2006 earnings (Givaudan 2007). According to data from the German Umweltbundesamt, the consumption of scents in laundry detergents has doubled from 3,200 t in 1992 to 6,948 t in 2004 whilst the total consumption of laundry detergents has decreased from 522,732 t in 1992 to 368,637 t in 2004 as can be seen Fig. 5.1. This means, the content of scents per ton laundry detergent has tripled.

Another effect of increasing use of scents is a increase in allergies against them. Many natural scents or their oxidation products, e.g. tetrahydrolinalool, are

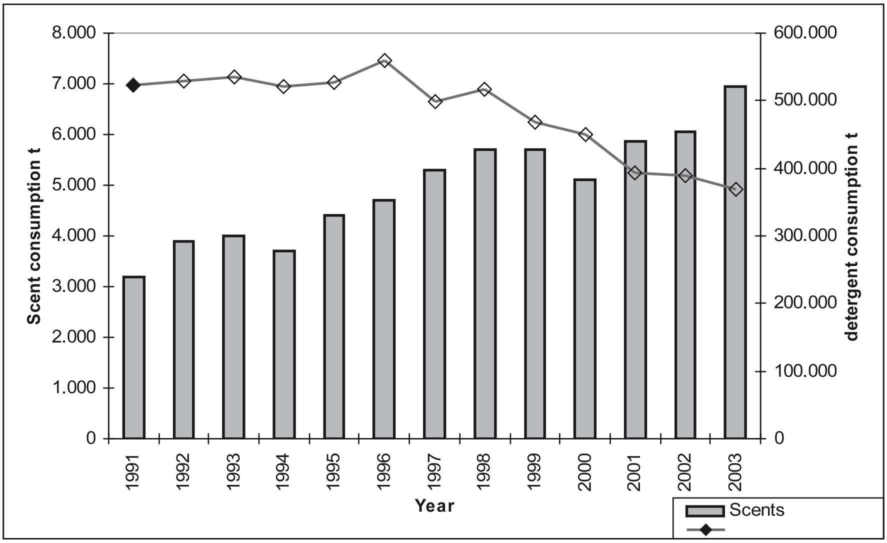

Fig. 5.1 Total consumption of laundry detergents (*line*) and consumption of scents in laundry detergents (*bars*) (Source: www.umweltbundesamt-umwelt-deutschland.de)

potent allergens. To date, scent-induced contact allergies are very common (e.g. Johansen 2003). For the European Union, the former Scientific Commitee on Cosmetic Products and Non Food Products intended for Consumer (SCCNFP) published an opinion on 24 scents and two mixtures which have sensitizing properties (SCCNFP 1999).

Together with the increase in production and sale, the emissions into the environment also increased. Many PCPs like shampoos, showering gels and laundry detergents are emitted via the household into the sewage. Being volatile, some are emitted into the air too. The main part of used scents ends up unaltered in the environment. For some scents, such as synthetic musk compounds, it is already known that they are bioaccumulating and not biodegradable (Bester et al. 1998; Gatermann et al. 2002a, b). They have been found in a wide variety of fish, mussels and shrimp (e.g. Rimkus and Wolf 1994). Their impact on the environment is not known to date.

5.2 Sources and Use

5.2.1 Natural Sources and Roles

There are many ways living beings gather information on their environment, however, use of (volatile) chemicals is one of the most widespread ways to gather informations. These chemicals can transport and preserve information through time and space and are therefore used by organisms in a wide context e.g. Table 5.1 (Klaschka 2009a). In 2004, Linda B. Buck and Richard Axel won the Nobel Prize in medicine for their discoveries of odorant receptors and the organization of the olfactory system. Most known organisms are much more dependant on their sense of smell and the information they can gather than man. Every dog owner knows that dogs use urine marking to convey information on gender, sexual maturity, health and social dominance in a particular area (Pal 2003). The social behavior of many insects, e.g. ants and bees, strongly depends on scents (Fraberger and Ayasse 2007). Fish use scents to find their prey and plants communicate via green leaf volatiles (Reddy and Guerrero 2004; Gardiner and Atema 2007). Even bacteria have a kind of “olfactory” sense, i.e. they communicate by chemicals and use it for quorum sensing, an ability according to which the concentrations of specific chemicals emitted by bacteria affects the behavior of these and other bacteria (Waters and Bassler 2005). Because of the role in information exchange these substances are called infochemicals.

One of the first infochemicals found was the pheromone bombycol (Butenandt et al. 1959). Since then, a vast number of different chemicals that transfer information have been identified. Today, one can distinguish several classes of infochemicals. Pheromones transfer information in which the sender and the receiver are both from the same species, whereas allelochemicals contain interspecific information. Allelochemicals are further divided into allomones (only the sender takes advantage from the information), kairomones (only the receiver takes advantage from the information) and synomones (sender and receiver take advantage from the information)

Table 5.1 Scents used in PCPs and their roles in nature

Compound	CAS No.	Role as infochemical in nature
Anethole	104-46-1	Food attractant
Anisaldehyde	135-02-4; 123-11-5	Food attractant
Benzaldehyde	100-52-7	Sex pheromone
Benzoic acid	65-85-0	Phytoalexin
D-Bornylacetate	5655-61-8	Sex pheromone
Camphene	79-92-5	Food attractant
Camphor	76-22-2	Food attractant Allelopathy Irritant Insect repellent
Citral	5392-40-5; 624-15-7	Antiseptic Defense Food attractant Signal for egg deposition
Citronellal	106-23-0	Defense Antiseptic
p-Cresol	106-44-5	Defense
Isopentenylacetate	5205-07-2	Warning pheromones
Linalool	78-70-6	Antiseptic Food attractant Signal for egg deposition
Methylisoeugenol	93-16-3	Food attractant
Ocimene	13877-91-3	Food attractant
alpha-Pinene	7785-26-4	Repellent
beta-Pinene	18172-67-3	Defense Allellopathy repellent Irritant
Salicylaldehyde	90-02-8	Defense Hygiene (to keep the body surface clean and allow breathing under water)
Terpinyl acetate	80-26-2	Antiseptic Food attractant Signal for egg deposition
Terpinolene	586-62-9	Food attractant Warning pheromones
Tridecanone	593-08-8	Repellent Various other responses

(Dicke and Sabelis 1988). The relationship between the different infochemicals can be seen in Fig. 5.2.

To understand the various opportunities of interference, one has to understand how information transfer takes place via infochemicals. A generalized scheme of the perception of infochemicals is shown in Fig. 5.3. A cascade of sophisticated reactions starts when infochemicals dock at receptors in the receiving organ. They

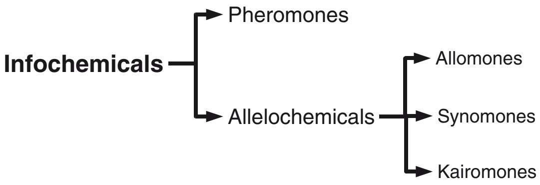

Fig. 5.2 Infochemical terminology (Dicke and Sabelis 1988)

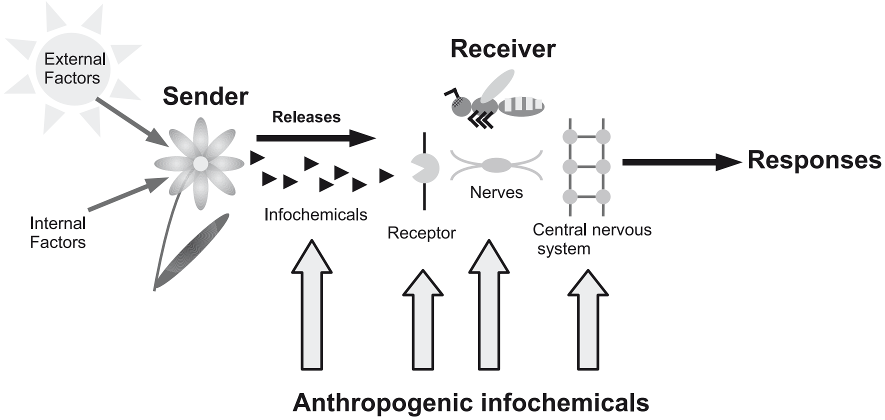

Fig. 5.3 Simplified model of the reaction chain of the chemical communication by infochemicals. The possible sites of action of anthropogenic infochemicals are indicated by *black framed arrows*

release an electric stimulus to the central nervous system that can trigger various reactions from behavioral responses to morphological changes. Both can be influenced by internal and external factors such as concentration of the infochemical, time of day or the reproductive status of the receiver.

5.2.2 *Anthropogenic Use*

Although unaware of it, humans are also affected by human infochemicals (Bhutta 2007). They still play a role e.g. in mate choice. Another example is the regulation of the female ovulation (Stern and McClintock 1998).

Additionally to their natural odors, humans also use alien scents. Every substance which can be smelled by the human nose can be used as a scent (DVRH 2008). It is assumed that humans can distinguish up to 10,000 different scents. From these 10,000 compounds, more than 2,100 substances representing 22 chemical groups are listed as scents in the Research Institute for Fragrance Materials (RIFM) database (Salvito et al. 2002, 2004).

Scents are manufactured in comparatively small amounts. For 2005, the German association of fragrance manufacturers (DVRH) state that 30 substances are listed as high volume production chemicals (HPVC[1]) (DVRH 2008). The substances themselves are not mentioned, there are only hints that they have a vanillin, mint and citrus note.

Many scents used by humans have naturally occurring archetypes, like linalool or limonene examples for natural infochemicals which are also used by humans is given in table 5.1 (Klaschka 2009a). However, there are also artificial substances as lilial (2-(4-tert-butyl benzyl) propionaldehyde), lyral (4-(4-Hydroxy-4-methylpentyl)-3-cyclohexen-1-carboxaldehyd) or synthetic musk compounds. As different as they are with regard to their chemical structure, they also differ in their physical and chemical properties such as vapor pressure, water solubility or partition coefficient between octanol and water ($\log P_{OW}$). These different properties are well known and used by fragrance manufacturers.

In most cases, mixtures of several scents are used in a product with combinations ranging from a few to hundreds of scents. This multitude of compounds may react with each other, mask unwanted scents and can even influence each others' physical properties. For example, diethyl phthalate is used in fragrance formulations as a solvent and to influence the volatility of other scents (RIFM 2007). These combinations of substances bring new challenges in balancing and assessment because there are no tools currently available through which to determine the hazards of mixtures.

5.2.3 Introduction into the Environment

Scents are emitted into the environment by way of several pathways. Scents from washing, cleansing and disinfecting products (e.g. shampoos, washing lotions, laundry detergents) are emitted primarily into the wastewater. Estimation of the use of scents in cleansing and disinfecting products can be done using the Technical Guidance Document on Risk Assessment (TGD) of the Institute for Health and Consumer Protection (European Chemicals Bureau 2003). In Part IV, mean consumption values for several PCPs are listed in gram per day and per capita. Because these values are applicable for HPVC and scents are mostly Low Production Volume Compounds (LPVC), they can only deliver a crude estimate. Because manufacturers just have to list scents which are classifed as allergens by the former SCCNFP and don't have to list the used amounts, determination of the amount of used scents is very difficult.

As an example, we estimated the consumption of scents in washing, cleansing and disinfecting agents for the University Medical Centre Freiburg for 2006. Consumption for washing, cleansing and disinfecting agents, were obtained by the central supply management. The data listed 120 PCPs, of which, according to the information given by the manufacturers, 33 contained scents. We could identify ten different scents from manufacturers' information, which are listed in Table 5.2.

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[1] Annual production volume exceeding 1,000 t.

Table 5.2 Scents identified in cleansing, washing and disinfecting products at the University Medical Centre Freiburg (2006) (From IFRA Code of Practice February 2009)

Name	CAS-No.	HPVC/LPVC	Natural sources/target organisms	IFRA standards	Estimated use 2006 (kg)
Alpha-Isomethylionone	127-51-5	HPVC	Found in nature/none	–	3.00×10^{-3}
Amylcinnamonaldehyde	122-40-7	LPVC	Soya bean, black tea/none	R	1.17×10^{-2}
Lilial	80-54-6	HPVC	Not found in nature/none	R	1.57×10^{-2}
Citronellal	106-23-0	HPVC	Produced by several plants/behavioral function on several insect species	–	4.13×10^{-1}
Citronellol	106-22-9	HPVC	Produced by several plants/behavioral function on several insects	–	9.69×10^{-2}
Coumarin	91-64-5	LPVC	Found in several plants (e.g. cinnamon/none	–	1.17×10^{-2}
Hexylcinnamaldehyde	101-86-0	HPVC	Found in nature/none	R	1.17×10^{-1}
Isoeugenol	97-54-1	LPVC	Produced by several plants/behavioral function on several insects	R	3.10×10^{-2}
Limonene	5989-27-5	HPVC	Produced by several plants/behavioral function on several insects	S	2.35×10^{-1}
Linalool	78-70-6	HPVC	Widely present in the environment	S	4.52×10^{-1}

R = restricted, – = no recommendations, S = specifications.

Natural occurrence and behavioral function according to www.pherobase.net and www.thegoodscentscompany.com.

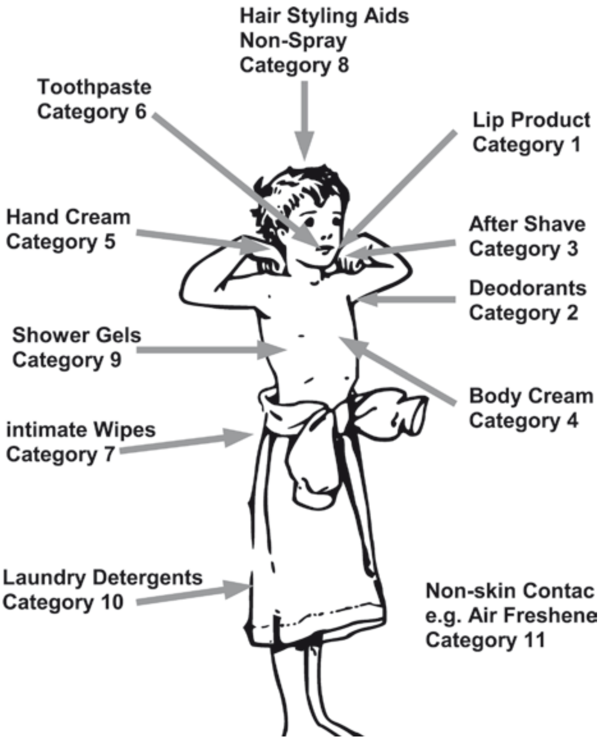

Fig. 5.4 Examples for Categories according to IFRA QRA Booklet

According to law, a scent which is listed by the SCCNFP has to be declared when exceeding a minimal content of 0.01%. Other scents are not declared and there is no quantitative statement. Therefore, the estimation of the consumption data of the scents was carried out by taking the consumption data for the products and assuming a content of 0.01%, giving minimum amounts. The real amounts can only be obtained by measurements.

Additionally, we checked all scents that we found on their infochemical properties, their production volume classification in Europe and their recommended usage according to the IFRA's Code of Practice. From the ten found scents, only three were LPVC, i.e. are produced less than 1,000 t per year. All others are HPVC. According to the IFRA's code of Practice, for two of them (Linalool and Limonene) the usage was specified as the level of the oxidation products should be below a certain amount. For four (Amylcinnamonaldehyde, Lilial, Hexylcinnamonaldehyde and Isoeugenol), the usage was restricted to certain concentrations according to different categories (for the categories refer to Fig. 5.4). Whilst only one (Lilial) has no known natural source, half of the found scents are natural infochemicals.

5.3 Fate in the Environment

Once emitted into the air scents can undergo reactions e.g. with hydroxyl, nitrate and ozone radicals. For four examined fragrances (OTNE ([1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethylnaphthalen-2yl] ethan-1-one), acetyl cedrene, Galaxolide and Isochroman), life times of between 2 min (OTNE with nitrate radicals) and 11 days (acetyl cedrene with nitrate radicals) were found (Aschmann et al. 2001). An atmospheric lifetime above 10 days allows transport across 10,000 km (Schultz et al. 1999). Also, volatile scents can be oxidized and condense to secondary organic aerosols. For this mechanism, values for aerosol formation of different volatiles, including some scents, could be obtained (Pankow et al. 2001). The significance of transport by particles is not known.

According to the TGD, one can assume that nearly 100% of the products are released into the water cycle after usage. Scents will therefore primarily enter the sewage system. Once there, they can undergo different chemical, physical and biological transformations. Scents with high vapor pressure may be emitted into the air and then oxidized. Substances with low vapor pressure and a high $\log P_{OW}$ may be adsorbed by sludge. Scents with low vapor pressure and high water solubility may reach the sewage treatment plant and may be biodegraded or even pass the sewage treatment plant like other micropollutants such as pharmaceuticals (Kümmerer 2008). Data on biodegradation are rare. A not published review of manufacturer's information, literature and databases, undertaken by one of the authors showed that out of 110 scents, biodegradability data was only avaiable on 52. biodegradability was available. The same applies to ecotoxicological data.

5.4 Anthropogenic Infochemicals, Application of Infochemicals and the Infochemical Effect

The infochemical effect is the effect anthropogenic substances have on an organism's perception of infochemicals, as shown in Fig. 5.3 by black framed arrows. If the infochemical emerges from an anthropogenic source, this substance is called an anthropogenic infochemical (Klaschka 2008b). Use of repellents against insects and pheromone traps for pests are just two examples of various methods by which humans knowingly interfere with the chemical perception of organisms, thus taking advantage of the infochemical effect.

There are several ways by which an infochemical effect can take place. The basic mode is the introduction of a substance already used by an organism. Many insect traps or mating disruption methods work with synthetic pheromones as attractants, either to lure the pests into the trap or to try to "mask" a mating scent (e.g. El-Sayed et al. 2006). Many scents used in PCPs are also natural infochemicals, thus leading to unwanted effects. Japanese scientists were able to determine 2-pentenol, 3-methyl-1-butanol and 1-methylbutyl-3-methylbutanoate as allomones for *vespa mandarinia* (Ono et al. 2003). Since these substances are also present in shampoos and shower gels, their use could lead to insects attacking humans. With respect to the scents we found in our analysis at University Medical Centre Freiburg, their infochemical role is additionally mentioned in Table 5.2.

Substances with a different structure to known infochemicals might also have an effect. As outlined in Fig. 5.3, the perception of infochemicals takes place at various stages of olfactory perception. All these stages can be influenced. Anthropogenic infochemicals can act as a background signal for natural infochemicals, natural infochemicals can be masked by anthropogenic infochemicals before reaching the target organism, and anthropogenic infochemicals can block the perception sites in the cells. Within the cell, they can interfere with signal processing or alter the response itself, e.g. heavy metals such as mercury and zinc are known to damage chemosensory tissue in fish (summarized in Klaprat et al. 1992) and pesticides can alter the response to female priming pheromone in salmon (Moore and Lower 2001).

Keeping in mind the sophisticated system of information exchanged by chemicals on the one hand, and the volume of chemicals released into the environment day by day on the other, one can only surmise the extent of the disturbance caused by man, not only by introducing new infochemicals but also by altering the concentrations of natural infochemicals. As stated previously, the concentration or its change itself can be part of the information. Additionally, adequate tests for the determination of the infochemical properties of a substance are not yet established (Klaschka 2009b). Therefore, the concentrations needed for an effect might well be in the range of many anthropogenic contaminants already found in the natural environment.

5.5 Regulation

5.5.1 Europe

From 1997 to 2004 the SCCNFP, a part of the General Directorate for Health and Consumers subsection Public Health, was in charge of regulations concerning most PCPs in Europe. In opinion SCCNFP/0017/98 a list of 24 substances and two mixtures which are used as scents and have sensitizing properties was published (SCCNFP 1999). Thirty-six additional substances have been listed, which should not be used as fragrance ingredients in consumer products (SCCNFP 2000). Due to reassignment of responsibility to the European Food Safety Authority, the responsibility concerning fragrances in non-food products was reassigned to the Scientific Committee on Consumer Products (SCCP), of the General Directorate for Health and Consumers subsection Public Health.

Concerning cosmetic products, ingredient regulations were harmonized for the European Union in cosmetic Directive 76/768/EEC. In this Directive, substances which should not be used in cosmetics are listed as well as substances which are only acceptable under special circumstances. For detergents, regulation 648/2004 states that the 26 scents categorized as sensitizing according to 76/768/EEC, must be mentioned when exceeding an amount of 0.01% of the product. Other scents must only be indicated as perfume.

Since June 2007, all chemical substances within the European Union are regulated by Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). Accordingly, manufacturers have to give information concerning the toxicity and behavior of the substances used. This information from manfacturers covers approximately 750 scents (DVRH 2008). The others are produced in sufficiently low amounts so that they do not have to be registered. These are still to be handled as specified in the cosmetics Directive 76/768/EEC. Therefore, it is not expected that through REACH much more data on the environmental fate and toxicity will be available for scents (Klaschka and Kolossa-Gehring 2007).

5.5.2 United States of America

There are several institutions responsible for scents. While the major part of regulation lies in the hands of the Food and Drugs Administration (FDA) and the Consumer Product Safety Commission (CPSC), some aspects concerning environmental behavior are regulated by the United States Environmental Protection Agency (US EPA).

Scents and fragrances used in cosmetics fall under the regulation of the FDA. The FDA defines cosmetics as "articles intended to be rubbed, poured, sprinkled, or sprayed on, introduced into, or otherwise applied to the human body for cleansing, beautifying, promoting attractiveness, or altering the appearance" (US FDA 2004). Soaps fall under the legislation of the CPSC and are defined as products for cleansing whose nonvolatile matter consists mostly of fatty acids and alkali salts, without claiming another effect, e.g. deodorizing. Both authorities (FDA and CPSC) rely mainly on the selfcontrol of the manufacturers. The only applicable regulation is that the endproduct shall cause no harm to the consumer.

Due to indoor volatiles, the US EPA is more concerned about volatile substances, including scents. Again, the US EPA relies primarily on manufacturers' information, e.g. of the RIFM, to determine threats originating from scents.

5.5.3 Manufacturers' Self-Control

Manufacturers of fragrances are associated internationally by the International Fragrance Association (IFRA). This association gives advice to members concerning the use of substances. Data is acquired by the RIFM, which is sponsored by the IFRA. The RIFM carries out toxicological and when needed, ecotoxicological testing and has access to manufacturers' proprietary data. The results of these tests are incorporated into the IFRAs Code of practice. The latest version is from October 2006 with the last amendment being published in May 2007. The RIFM regularly publishes toxicology studies of substance classes. In the latest publication, from 2007, the investigated groups were those related to esters and alcohols of cinnamic acid and cinnamic alcohol, ionones and salicylates.

The IFRA uses the information obtained by the RIFM to give advice on the use of several substances in cosmetics. To date, there are 156 substances. Among these 147 substances, there are 69 the use of which is prohibited and 68 substances the use of which is restricted. From the remaining 19 scents the use of seven needs specification, such as a certain maximum peroxide level.[2] The use of three is prohibited and restricted, such as the pure substance is prohibited but essential oils, containing this substance to a certain level, are allowed.[3] The use of six is prohibited with specifications such as use is allowed from certain sources or certain purities[4] and the use of three is restricted with specifications[5] (IFRA 2008).

Additionally, all products containing scents are categorized for dermal sensitization by quantitative risk assessment (RFIM 2007). Depending on the category of the product, different maximum concentrations of scents are recommended. In these categories, very different products can be included. Category 1 for example includes all lip products and toys. Examples for products and their categories are shown in Fig. 5.4.

These regulations by IFRA are recommendations and have no legal-binding character.

5.6 Conclusion

Scents are an important part of everyday life, not only for humans, but for all living beings. Today, we can choose from a variety of different scents to use, depending on our own state of mind and preferences. However, this is a double-edged sword because not only can we choose a scent to match our feelings, but marketing and industry also tries to use scents to influence our feelings. This adds up to an increasing usage of scents in general. The disturbances which may be caused by emitting infochemicals into the environment cannot be determined to date. Although being present in low amounts, infochemicals can influence a population at whole. Influencing every part of life, they have many possibilities to disturb. Research concerning this class of pollutants is only at the beginning. To present knowledge the role and significance of man made chemicals which act as infochemicals is not yet clear.

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[2] For example, Linalool, Limonene.

[3] cis- and trans-Asarone, Safrole, Styrax.

[4] For example, Birch wood pyrolisate.

[5] Farnesole, Oakmoss extracts and Treemoss extracts.

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Chapter 6
Sources and Occurrence of Cyanotoxins Worldwide[1]

Miguel Pelaez, Maria G. Antoniou, Xuexiang He, Dionysios D. Dionysiou, Armah A. de la Cruz, Katerina Tsimeli, Theodoros Triantis, Anastasia Hiskia, Triantafyllos Kaloudis, Christopher Williams, Mark Aubel, Andrew Chapman, Amanda Foss, Urooj Khan, Kevin E. O'Shea, and Judy Westrick

Abstract The eutrophication of water resources, mainly attributed to antrophogenic activities such as sewage and agricultural runoffs, has led to a worldwide increase in the formation of cyanobacterial harmful algal blooms (Cyano-HABs). Cyano-HABs have the ability to produce and release toxic compounds, commonly known

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M. Pelaez, M.G. Antoniou, X. He and D.D. Dionysiou (✉)
Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati, Ohio, 45221-0071, USA
e-mail: dionysios.d.dionysiou@uc.edu

A.A. de la Cruz
Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH, 45268, USA
e-mail: delacruz.armah@epa.gov

K. Tsimeli, T. Triantis and A. Hiskia
Laboratory of Catalytic - Photocatalytic Processes (Solar Energy – Environment), National Center of Scientific Research "Demokritos", 153 10Agia Paraskevi, Athens, Greece
e-mail: hiskia@chem.demokritos.gr

T. Kaloudis
Organic Micropollutants Laboratory, Athens Water Supply and Sewerage Company (EYDAP SA), Oropou 116, 111 46 Galatsi, Athens, Greece
e-mail: t_kaloudis@ath.forthnet.gr

C. Williams, M. Aubel, A. Chapman and A. Foss
GreenWater Laboratories/CyanoLab, Palatka, FL, USA
e-mail: chriswilliams@greenwaterlab.com

U. Khan and K.E. O'Shea
Department of Chemistry and Biochemistry, Florida International University, Miami, FL, 33183, USA
e-mail: osheak@fiu.edu

J. Westrick
Department of Chemistry, Lake Superior State University, Marie, MI, 49783, USA
e-mail: jwestrick@lssu.edu

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[1] All authors have contributed equally to this chapter.

D. Fatta-Kassinos et al. (eds.), *Xenobiotics in the Urban Water Cycle: Mass Flows, Environmental Processes, Mitigation and Treatment Strategies*, Environmental Pollution, Vol. 16,
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as cyanotoxins, which comprise a potent threat for human and animal health as well as negative economical impacts. This chapter presents an overview on the sources and occurrence of species of cyanobacteria and their association with the production of cyanotoxins throughout the world. The main bloom-forming cyanobacteria that have been detected include *Microcystis, Cylindrospermopsis, Anabaena, Aphanizomenon,* and *Planktothrix*. The main cyanotoxins related to these cyanobacteria are microcystins, cylindrospermopsin, anatoxin-a and saxitoxins.

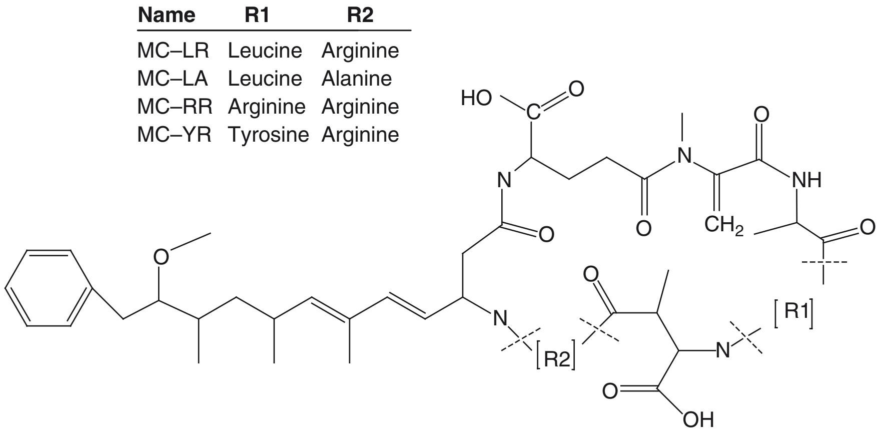
6.1 Introduction

Cyanobacteria are ubiquitous organisms found in all types of habitats, including hydrothermal vents, sulfur springs, arid deserts, acidic tropical soils, and Antarctic lakes. They primarily make up, but are not limited to, the planktonic members of the water column in marine and freshwater environments. Special adaptations such as the presence of accessory pigments, nitrogen fixation, ability to regulate buoyancy, and differentiated cell types for reproduction and dormancy, have provided cyanobacteria a competitive edge over other organisms that may lead to harmful blooms. During favorable environmental conditions, cyanobacteria can form dense growth known as “algal blooms” or “scum”. Cyanobacterial blooms occur globally as a result of naturally- and artificially-induced water eutrophication. Some lakes typically undergo natural maturation and become enriched in dissolved nutrients. Eutrophication is exacerbated by human wastes such as sewage, industrial discharges, fertilizers from farms, homesteads, golf courses and concentrated animal feeding operations referred as CAFOs in the United States. Only some cyanobacterial blooms produce cyanotoxins and these are referred to as Cyano-HABs. Cyanotoxins are released into the surrounding medium via secretory pathways, senescence or lyses of the blooms creating a significant risk to public and environmental health.

6.2 Sources and Occurrence of Cyanotoxins in North America, the Arctic and Antarctica

6.2.1 General

The most commonly occurring cyanotoxins reported in North American water bodies are microcystins (see Fig. 6.1). The occurrence of anatoxins, saxitoxins and cylindrospermopsins (see Fig. 6.2 for a representative chemical structure of each cyanotoxin) has also been reported, on a limited basis. Monitoring programs recently put into place are now beginning to provide more information about their distribution.



Name	R1	R2
MC–LR	Leucine	Arginine
MC–LA	Leucine	Alanine
MC–RR	Arginine	Arginine
MC–YR	Tyrosine	Arginine

Fig. 6.1 General structure of a microcystin (MC)

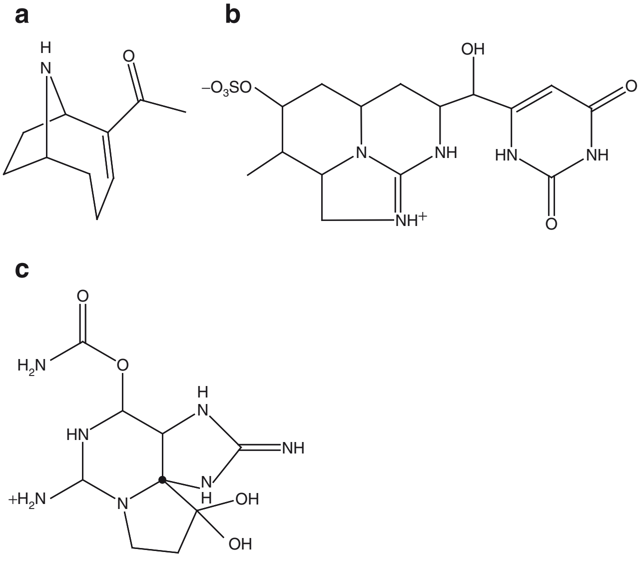


Fig. 6.2 Structures of (**a**) anatoxin-a, (**b**) cylindrospermopsin and (**c**) saxitoxin

Cyanobacterial harmful algal blooms have been documented in 49 out of 50 states in the USA from a wide range of habitats (Fristachi et al. 2008). Maryland, Massachusetts, Minnesota, Nebraska, and New York have reported the presence of cyanotoxins in their water bodies and have closed waters used for recreation due to cyanobacterial harmful algal blooms. The states of Iowa, Minnesota, Nebraska, Wisconsin, California and Oregon in the USA, and Alberta and Manitoba in

Canada, have performed monitoring programs and routinely issue alerts for cyanobacterial harmful algal blooms.

The first documented link between gastroenteritis and cyanotoxins in the USA was reported in 1931 when a large gastrointestinal outbreak occurred in Charleston, Virginia which coincided with a cyanobacterial bloom in the Ohio River (Veldee 1931). A similar event occurred in Pennsylvania where 62% of the population served by the Sewickley water utility suffered severe gastroenteritis due to cyanobacteria (Lippy and Erb 1976). In 1959 in Saskatchewan, Canada a number of people developed gastroenteritis after swimming in lakes experiencing algal blooms that contained species of *Microcystis* and *Anabaena* (Dillenberg and Dehnel 1960). *Microcystis* and *Anabaena spp.* were detected in stools of all patients.

A cyanobacterial bloom survey in the U.S. was undertaken in Wisconsin waters in the summer of 1987 and revealed that approximately 28% of the water sampled contained cyanobacterial toxins. *Microcystis, Anabaena*, and *Gloeotrichia* were the predominant cyanobacteria identified in these samples (Repavich et al. 1990). In a later study (McDermott et al. 1995), also performed in Wisconsin, 87% of water samples from northeastern lakes and ponds collected during cyanobacterial blooms contained 200–200,000 ng/L microcystin and *Microcystis spp.* were the most commonly identified microcystin-producing algae present. Seasonal variation in microcystin LR concentrations was observed in samples collected from Buffalo Springs Lake (BSL) and Lake Ransom Canyon (LRC) in western Texas collected in 2003–2004. The highest concentration observed was >1 μg/L microcystin-LR and was collected in the spring in 70% of BSL and 33% of LRC samples (Billam et al. 2006). Davis et al. (2008) reported the frequent occurrence of cyanobacterial blooms, dominated by *Microcystis spp.*, in four lakes in the Northeast USA and that the microcystin synthesis gene, *mcyD*, is a better predictor in quantifying toxic species than was total cyanobacteria or chlorophyll *a* concentrations previously used by the World Health Organization (WHO). The first cyanobacterial harmful bloom in western Washington occurred in American Lake in 1998 (Johnston and Jacoby 2003). Since then, toxic blooms have occurred in Great Lakes, Lake Waughop, Steilacoom Lake and Lake Sammamish resulting in recreational closures. A survey of 24 public water utilities in the USA and Canada from June 1998 to January 1998 showed 80% of the water samples were positive for microcystin LR and 4.3% contained >1 μg/L (Billam et al. 2006). In a limited study conducted in the summers of 2001 and 2002 in the USA, weekly source and finished water samples showed <0.2 μg/L microcystin, quantified by ELISA (Sinclair et al. 2005). Microscopic examination revealed cyanobacteria genera that can possibly produce microcystins and anatoxin-a.

In general, cyanobacterial species that produce microcystins are predominatly planktonic. Recently, however, more and more benthic cyanobacteria (mostly filamentous) are being identified to produce microcystins. Benthic microbial mats are dominated by cyanobacteria in many lakes, ponds, and streams in the Arctic and Antarctica (Vincent 2000). Samples from meltwater ponds on the McMurdo Ice Shelf, Antarctica, collected in the summers of 1997–1999, showed cytotoxic properties, phosphatase inhibiting activity and the presence of nodularin and microcystin LR (Hitzfeld et al. 2000). Benthic mats of algae in Ward Hunt Lake, located at the northern limit of the Canadian High Arctic, were comprised predominantly of filamentous cyanobacteria (*Leptolyngbya, Pseudoanabaena, Tychonema, Lyngbya, and Oscillatoria spp.*) while the water column also contained cyanobacteria, primarily *Synechococcus* and *Anabaena spp.* (Bonilla et al. 2005). Benthic microcystin-producing filamentous cyanobacteria have been isolated in four drinking water reservoirs in southern California (Izaguirre et al. 2007). Cultured isolates were identified as *Oscillatoria sp.* and *Phormidium ambiguum* based on morphology and partial 16S rRNA sequence comparison. Other members of *Oscillatoriales* as well as *Cylindrospermum* and *Merismopedia spp*. were also common.

Seasonal monitoring of cyanobacterial blooms in the Bay of Quinte and Maumee Bay, Canada revealed differences in the cyanobacterial genotypic community from early to late summer in 2005 and 2006. Four eutrophic lakes in the eastern townships in Quebec, Canada showed peak cyanotoxin levels in late summer and in spring (Rolland et al. 2005). The toxins present were attributed to the abundance of *Microcystis* and *Anabaena spp*.

6.2.2 Sources and Occurrence of Cyanotoxins in the Great Lakes

The Laurentian Great Lakes are located in the mid-eastern part of the United States, with four out of the five having shores in Canada. They are a global treasure from an ecological, economic, and social perspective. The Great Lakes consists of five lakes; Lake Superior, Lake Huron, Lake Michigan, Lake Erie, and Lake Ontario. Lake Superior is the most rural and Lake Erie has the most human impact. Containing one-fifth of the world's freshwater, and providing drinking water to over 24 million Canadian and U.S. citizens allude to the human significance of these freshwater resources. With the Great Lakes encompassing 95% of the surface water supply in the United States, the Great Lakes Region strives to set the example for controlling anthropogenic practices that impact water quality such as toxin producing cyanobacteria blooms. A comprehensive review by Watson et al. (2008) reported harmful algal blooms at six locations on Lake Ontario, seven locations in Lake Erie, three locations in Lake Huron, two locations in Lake Michigan, and none in Lake Superior. These data were collected from published papers, United States Environmental Protection Agency Area of Concern reports, and unpublished drinking water treatment records. Since there are no published reported harmful algal blooms in Lakes Michigan and Superior, the focus of this review was on Lakes Huron, Erie and Ontario.

The second largest great lake is Lake Huron spanning 205 miles from north to south and 183 miles across. This lake has two of the largest freshwater bays; Georgian and Saginaw Bays. Both Georgian and Saginaw Bays have reported measurable amounts of microcystin (Watson et al. 2008; Vanderploeg et al. 2001).

The dominant microcystin congener was microcystin LR and the second most abundant was microcystin LA (Dyble et al. 2008). The more recent cyanobacterial blooms in Lake Huron's Saginaw Bay and Lake Erie have been correlated to the invasion of the zebra mussels. Since the invasion of zebra mussels, there have been an increased number of blooms in Saginaw Bay (Vanderploeg et al. 2001) as well as Lake Erie (Murphy et al. 2003; Rinta-Kanto et al. 2005). With zebra mussels found in each of the Great Lakes there is concern that other bays will have cyanobacterial blooms.

Lake Erie is 241 miles across and 57 miles from north to south and is the smallest of the lakes with respect to water volume. Its watershed includes parts of Indiana, Michigan, Ohio, Pennsylvania, New York, and Ontario. It is also exposed to anthropogenic effects from urbanization and agriculture. By the mid 1960s, seasonal cyanobacterial blooms were reported in the western basin of Lake Erie due to high influx of nutrients. Several potential cyanotoxin producing genera were reported: *Anabaena, Aphanizomenon*, and *Microcystis*. During the 1970s annual cyanobacterial blooms occurred with the predominate genera being *Aphanizomenon*. No massive cyanobacterial blooms were reported in the 1980s and when a bloom did occur the predominate genera was *Aphanizomenon*. By the late 1980s both zebra and quagga mussels were reported. In 1995 and 1998 the western part of Lake Erie experienced large cyanobacterial blooms of *Microcystis*. In the late 1990s, Brittain et al. (2000) reported microcystin levels as high as 3.4 μg/L and the isolation of toxic *Microcystis* from Lake Erie. During a 2004 study (Dyble et al. 2008), research reported the dominant congener from the group of microcystins was microcystin LR and the second most abundant congeners was microcystin RR that accounted for up to 25% of the total microcystin concentration. A recent paper by Rinta-Kanto and Wilhelm (2006) suggested that the microcystin-producing communities may not be limited to *Microcystis*. The identities and phylogenetic relationships of microcystin-producing communities for Lake Erie were assessed by the analysis for the mcyA gene carried by microcystin-producing *Anabaena, Planktothrix*, and *Microcystis*. Distinct populations of potentially toxin-producing *Microcystis* and *Planktothrix* were found in spatially isolated locations, suggesting diverse populations may be responsible for the microcystin levels reported in western Lake Erie. Wilson et al. (2008) determined the tissue and liver microcystin concentrations from yellow perch (*Perca flavescens*) and particulate-bound microcystin concentrations from water samples at 11 locations in the western basin of Lake Erie. While particulate microcystin concentrations fluctuated between 0.16–4,282 ng/L, the liver microcystin concentrations ranged from 17 to 1,182 ng/g dry weigh tissue, and the muscle tissue microcystin concentrations ranged from 0.12 to 4.02 ng/g dry weigh tissue. This study suggests that the muscle of yellow perch is safe for human consumption, while the liver is not. With this announcement, Lake Erie became a high priority research area of concern.

The smallest of the Great Lakes with respect to surface area is Lake Ontario with a surface area of 7,340 square miles. It is the last of the chain and has shores on Ontario, Canada and New York State. With 80% of the water flowing into Lake Ontario being downstream effluent for the other Great Lakes, it is impacted by the human activities throughout the Great Lakes Basin. The southern shore of Lake Ontario reported levels below 1.0 μg microcystin/L with the highest values from bays and rivers (Makarewicz et al. 2006). Hotto et al. (2007) investigated the occurrence and diversity of microcystin genotypes and of microcystin variant composition from embayments and lakeside water samples from the southern and eastern shores of Lake Ontario in 2001 and 2003. The genotype distribution was in agreement with the earlier studies indicating that the embayments and harbor contained toxigenic cyanobacteria. The genotype compositions within embayments were relatively homogenous compared to those for the shoreline and tributary samples suggesting that the embayments were impaired. Several microcystin congeners RR, YR, LR, LA, and LY were reported.

From 2000–2004 a large scale cyanotoxin monitoring took place by annual cruises in Lakes Erie and Ontario (Boyer 2008). Three hundred and eight and 736 samples were collected from Lake Erie and Ontario, respectively. Subsets of these samples were analyzed for microcystins, anatoxin-a, cylindrospermopsin and saxitoxins. The cruises were scheduled on availability of the ship; not based on the seasonal trends of cyanobacterial blooms. Lakes Erie and Ontario microcystin concentrations were analyzed by protein phosphatase inhibition assay and were reported in microcrystin-LR equivalents concentration. The Lake Erie microcystin monitoring yielded 4% of the samples were greater than 1.0 μg/L, 29% of samples were between 1.0 and 0.1 μg/L, and 40% of the samples were between 0.1 and 0.01 μg/L. Anatoxin-a, saxitoxin, and cylindrospermopsin were reported with 6% of the samples between 0.01 and 1.0 μg/L, 1% of the samples having greater than 0.01 μg/L, and 3% of the samples having greater than 0.01 μg/L, respectively. The most toxic bloom was reported in August of 2003, when levels of microcystins were 21 μg/L. Several beaches and recreational boating areas were closed because surface scum had washed ashore. Three regions of the lake were reported to have microcystins, two in the western portion at the mouths of the Maumee River and Sandusky Harbor, and one in the northeastern region, Long Point Bay. Lake Ontario microcystin monitoring yielded 1% of the samples were greater than 1.0 μg/L, 11% of samples were between 1.0 and 0.1 μg/L, and 28% of the samples were between 0.1 and 0.01 μg/L. Anatoxin-a and cylindrospermopsin were reported with 2% of the samples between 0.01 and 1.0 μg/L and 3% of the samples having greater than 0.01 μg/L, respectively.

6.2.3 Prevalence of Cyanotoxins in Florida

Cyanobacteria are commonly found in Florida's springs, lakes, and estuaries. Many of Florida's largest and most important lakes, rivers, and estuaries, such as Lake Okeechobee, the St. Johns River, the St. Lucie River and the Caloosahatchee River are increasingly impacted by large cyanobacterial blooms. In 1998, the Florida Legislature organized the Florida Harmful Algal Bloom Task Force which initiated a study to identify if cyanobacterial toxins were prevalent in Florida's surface waters.

Samples were collected throughout Florida and of the 167 samples analyzed, 88 samples from 75 individual sample sites contained cyanotoxins (Detection Limit (DL) ≥0.1 µg/L). The algal toxins that were positively identified were microcystins, anatoxin-a, and cylindrospermopsin (Williams et al. 2001).

As explained in the introduction, cyanotoxins are naturally produced metabolites that tend to be produced in warm, slow moving, eutrophic water bodies. Major toxins of concern include the microcystins, cylindrospermopsin, anatoxin-a, saxitoxins, beta-methyl amino alanine (BMAA) and toxins associated with *Lyngbya* species (lyngbyatoxins and aplysiatoxins). All of these compounds, except for BMAA and the lyngbyatoxins, have been positively identified in Florida freshwater systems. The Florida Harmful Algal Bloom Task Force reported microcystins (12.5 µg/L), cylindrospermopsin (97 µg/L) and anatoxin-a (8 µg/L) at concentrations significantly greater than accepted guideline levels in post-treatment drinking water (Williams et al. 2006) indicating a potential for human health risks. The suggested guideline levels in drinking water for microcystin LR, cylindrospermopsin and anatoxin-a are 1 µg/L (World Health Organization 1998), 1 µg/L (Humpage and Falconer 2002) while none is currently formulated (although it is assumed to be ≤1 µg/L), respectively. Although greater attention has been given to these freshwater toxins over the past 10 years, there still exists a limited amount of information, on a national basis, regarding the prevalence, magnitude, duration and actual health implications of these compounds.

Microcystins are the most frequently reported and exhibit the highest environmental concentrations of any of the cyanotoxins in Florida. However, very little information is available concerning the effects of microcystins on environmental and human health (acute or chronic exposure). In Florida, microcystins are common components of surface waters and can be present year-round, but predominantly at low concentrations (0.5–3.6 µg/L) (Lake County Water Authority 2005). Recent work by the St. Johns River Water Management District in 2008 showed microcystins to be present throughout the freshwater section of the Lower St. Johns River Basin from June through early September at concentrations that ranged between non-detectable to 3.21 µg/L (analyses were not performed before June or after October, Williams et al. 2008, unpublished data). In general, *Microcystis* spp. (specifically *Microcytsis aeruginosa*) is responsible for microcystin production in Florida but *Anabaena* spp. and *Planktothrix* spp. can also contribute.

In Florida, microcystin containing bloom events may occur within a given lake at multiple times per year and can result in concentrations that reach the ppm range (mg/L) (Lake County Water Authority 2005). Major bloom events tend to occur during the summer and early winter (usually November and December) and can have a duration of 30–60 days depending on weather conditions (Green Water Laboratories/CyanoLab 2008). Early winter blooms can exhibit extremely high microcystin concentrations and can be the highest concentrations observed during a given year (Lake County Water Authority 2005). Concentrations as high as 12 mg/L have been recorded via enzyme linked immunosorbent assay in a south Florida lake by GreenWater Laboratories (Williams et al. 2007, unpublished data). Highest concentrations are typically found at the windward shoreline and only in the upper surface waters (0–0.5 m) due to the positively buoyant nature of *Microcystis* cells and the intracellular compartmentalization (90–95% intracellular) of toxin in healthy thriving populations. As blooms senesce, higher concentrations of extracellular microcystins can be found in the water column.

The St. Johns River, near Jacksonville Florida (northeast Florida), has experienced three large *Microcystis* blooms (1999, 2000 and 2005) over the past decade. Bloom formations extended over 100 km of river surface, were extremely dense in localized areas (5–15 cm in depth) and persisted for up to 3 months (C. William's personal observation). Major bloom events have consistently developed in specific stretches of the St. Johns River and have been associated with bird and fish mortality events. Concentration levels can be highly patchy with specific areas void of microcystins while windward shorelines, embayments, tributaries or small canals can reach concentrations in excess of 1,000 μg/L. High concentrations usually persist throughout the bloom where cell concentrations are dense and are normally terminated by storm events. Data from the St. Lucie River and the St. Johns River during simultaneous but separate *Microcytsis aeruginosa* blooms in 2005, showed toxin concentrations that ranged from 0–278 and 0.2–1,413 μg/L, respectively. (Williams et al. 2007). Microcystin data from the Calooshatchee River during a major *Microcystis* bloom displayed concentrations that ranged between 1,000 and 5,000 μg/L for nearly 60 days (Williams et al. 2007).

In 1999, the Florida Harmful Algal Bloom Task Force was the first to positively identify the compound cylindrospermopsin in Florida waters with environmental concentrations as high as 202 μg/L (Williams et al. 2006). Since this time, toxin concentrations in the same lakes have been found infrequently (18%) and only at concentration levels between 0.05–0.2 μg/L even though cell concentrations of *Cylindrospermopsis raciborskii* remained consistently high (>100,000 cells per mL) (Lake County Water Authority 2005). A recent publication by Yilmaz et al. (2008) suggests that *C. raciborskii* may not be the source of cylindrospermopsin in Florida waters but that other cyanobacteria, namely *Aphanizomenon ovalisporum*, might be the causative agent of toxin production. Data collected by the Florida Department of Health showed that specific lakes do exhibit consistent cylindrospermopsin production. Lake Jesup surface water was found to contain 0.5–1.6 μg/L from July–October, 2005 (Aubel et al. 2006). Recent work conducted by the St. Johns River Water Management District (2008) reported cylindrospermopsin to be consistently present (0.05–0.44 μg/L) in water samples collected from June through October in the St. Johns River (Williams et al. 2008, unpublished data).

Anatoxin-a is the third most prevalent of the cyanotoxins found in Florida phytoplankton. Monitoring performed between 2002 through 2006 in central and northeast Florida showed that anatoxin-a, analyzed via LC/MS/MS, was not reported (n = 90, DL ≥ 0.1 μg/L) (Lake County Water Authority 2005). Conversely, recent work conducted by the Florida Department of Health, Aquatic Toxins Program (2007/2008) showed a small recreationally utilized lake in central Florida to contain low levels (0.1–1.0 μg/L) of anatoxin-a throughout the year. In general, *Anabaena circinalis* is the primary blue-green algae of concern for the production of anatoxin-a.

In 2000, the Florida Harmful Algal Bloom Task Force identified a very large bloom of *A. circinalis* that developed in the St. Johns River and contained 156 μg/L of anatoxin-a. Unfortunately, toxin analyses were not performed over the duration of the bloom event. This bloom extended over 40 km of river surface and was associated with a major fish mortality event near Jacksonville, Florida. In the same year, a mortality event with white pelicans was observed in a small northeast Florida lake. *C. raciborskii* was the dominant algae present in the lake but a high level of anatoxin-a was reported in the liver of one specimen by Carmichael et al. (Williams et al. 2006). Microcystins and cylindrospermopsin were analyzed for but were not found in the same tissue.

The Florida Department of Health, Aquatic Toxins Program (2007/2008) recently initiated the collection and analysis of filamentous algae and cyanobacteria in Florida's freshwater spring systems. Debromoaplysiatoxin (DAT) and saxitoxins (STX) have been identified in algal mats collected. Although multiple algal species were present in these collections, mats dominated by the cyanobacteria *Oscillatoria limosa* exhibited concentrations of DAT from 2–10 μg/g (dry weight). Mats dominated by the cyanobacteria *Lyngbya wollei* have exhibited concentrations of STX greater than 1,000 μg/g (dry weight) (Green Water Laboratories/CyanoLab 2008, unpublished data).

To date, analyses for the presence of saxitoxins or BMAA have not been performed on Florida lake water and their associated phytoplankton. Saxitoxins have been reported from the tissues of shellfish collected from the St. Johns River (J. Landsberg, 2008 personal communication) but the source of these toxins were not identified.

6.3 Sources and Occurrence of Cyanotoxins in Europe and the Middle East

Cyanobacteria blooms are known to occur in the waterbodies of European countries and in some extent in the Middle East. The range of water bodies in which cyanobacteria develop includes fresh waters (natural lakes, rivers, ponds, man-made reservoirs and canals) and brackish waters. Monitoring programs and/or research studies have been performed in most European countries (Chorus 2005). Moreover, UNESCO has implemented a network for cyanobacterial blooms and toxin risk management (International Hydrological Program) which aims to establish a relatively uniform approach to assess the occurrence and toxicity of cyanobacterial mass populations in European waters (Codd et al. 2005a and 2005b). Information on the occurrence of cyanobacteria species from water sources in Europe and Middle East are given below.

Microcystins were identified in water samples taken from freshwater and brackish water locations in SW Finland from 1999 to 2001. The most likely microcystin producers were *Planktothrix agardhii, Microcystis aeruginosa and Anabaena lemmermannii*. The most common toxins found were microcystin RR, LR and YR with different degrees of demethylation (non-, mono- or didemethylated) (Spoof et al. 2003). Cyanobacterial bloom samples from the Gulf of Finland (northern Baltic Sea) were analyzed for microcystins and nodularins, cyanobacterial peptide hepatotoxins. The blooms consisted mainly of the genera *Nodularia, Anabaena* and *Aphanizomenon*. The main hepatotoxin in the samples was nodularin-R (Nod-R). The presence of demethylnodularin-R and microcystin-LR was also confirmed. *Anabaena* was the likely producer of microcystin-LR in the samples (Karlsson et al. 2005).

The most frequently appearing cyanobacterial genera in Danish lakes and coastal areas are *Microcystis, Anabaena, Aphanizomenon, Planktothrix*, and *Nodularia*. The most frequent toxins are microcystins, but other types have also been found, including anatoxin, nodularin and saxitoxin. A recent survey on a large number of Danish lakes showed that the toxin content on a volumetric basis can easily exceed the 1 μg/L guideline as suggested by WHO (Christoffersen 2005).

Recent studies suggest the occurrence of microcystins in the aquatic environment of the Czech Republic. Median annual concentrations in water bloom biomass ranged from 150 to 600 μg/g (1993–2005) with maximum (extreme) concentrations about an order of magnitude higher. Concentrations of microcystin-LR formed only about 50% of total microcystins. Results of filtered water samples collected during 2004–2005 from surface waters of Czech Republic showed median concentration of 0.212 μg/L. In samples from drinking water supplies, a median of 0.2 μg/L was recorded (in both 2004 and 2005) with a maximum of 17 μg/L. About 75% of analysed samples had concentrations below the WHO limit for microcystin LR (Blahova et al. 2008).

The occurrence of cyanotoxins in relation to species dominance and environmental factors has been studied in the frame of a research project in Germany. It showed that *Microcystis* and *Planktothrix* appear to be the two genera of toxic cyanobacteria most frequently occurring in Germany and that field samples of these almost always contained microcystins, with *Planktothrix* usually containing more microcystins than *Microcystis*. The neurotoxins investigated (anatoxin-a and saxitoxins) were rarely detected and if so, at low concentrations (Chorus 2002). According to a study concerning the occurrence of microcystins and anatoxin-a in Berlin water bodies, it was found that concentrations of total microcystins (cell-bound and dissolved) varied between 0.14 and 119 μg/L; nearly 74% of the samples showed values above 1 μg/L, 38% above 10 μg/L and 2% above 100 μg/L. (Fromme et al. 2000). On the other hand, the cyanobacterial toxin cylindrospermopsin is widely spread in German lakes. Recent studies showed that the widespread native Nostocales species *A. gracile* is a potential cylindrospermopsin producer in German lakes (Rucker et al. 2007).

A survey of the distribution of cyanobacterial blooms in the southern part of Belgium, in Luxembourg as well as in bordering northeastern France was carried out for four years (1997, 1999–2001). *Microcystis* as well as *Planktothrix* were the most frequently encountered dominant bloom formers, followed by *Anabaena, Woronichinia* and *Aphanizomenon*. Mycrocystins were found in 53% of the analysed blooms and their presence was mainly assigned to *Microcystis* dominance.

The highest microcystin concentration of 2.231 μg/g seston as dry weight was recorded in a sample dominated by *Woronichinia naegeliana*. Among the six investigated microcystin variants, microcystin LR was the most frequently detected whereas microcystin-LY was never detected (Willame et al. 2005).

The occurrence and concentration of microcystins were analysed in samples from water reservoirs in the Madrid region (Spain) between July and November in 2002 and 2003. The data collected indicated that microcystins were present in both years in all the reservoirs studied. In many cases, microcystin concentrations were higher than the WHO recommended limit for drinking water (1 μg microcystin LR/L) and in one of the reservoirs, Santillana, its concentration was extremely high (up to 70 μg/L). *Microcystis aeruginosa* was the main producer of microcystins in freshwaters from the Madrid region (Carrasco et al. 2006).

Toxic cyanobacterial bloom samples collected in natural lakes, reservoirs and rivers of Portugal were analysed. The main bloom species present in the samples were *Microcystis aeruginosa, Microcystis wesenbergii, Anabaena flos-aquae* and *Nostoc* sp. Microcystin LR was the most common and its proportion in each sample ranged from 45.5% to 99.8% of the total microcystin contents. Microcystins RR, YR and [D-Asp3] LR were also identified in the samples. Total microcystin concentration varied from 1.0 to 7.1 μg/mg as dry weight of cyanobacteria (Vasconcelos et al. 1996).

Phytoplankton and LC/MS/MS toxin analyses were performed in surface water samples collected from several Italian lakes from 1989 to 2006. The most widespread species associated with toxin production belonged to the genera *Microcystis, Planktothrix* and *Anabaena*. Extracellular concentrations varied from traces (minor than 0.004 ng/L) up to 226.16 μg/L for microcystins (sum of all variants), to 126 ng/mL for total cylindrospermopsin and to 100 mg/g (dry weight) for anatoxin-a. (Messineo et al. 2009).

Cyanobacterial water blooms were observed in Greek surface water. Cyanobacterial genera (*Microcystis, Anabaena, Anabaenopsis, Aphanizomenon, Cylindrospermopsis*) with known toxin producing taxa were present. According to existing data it would appear that Mediterranean countries are more likely (a) to have toxic cyanobacterial blooms consisting of *Microcystis* spp. and (b) to have higher intracellular microcystin concentrations. Several microcystins variants have been identified in the cyanobacterial blooms. The most abundant variants are microcystins LR and RR, while microcystin LA, YR and demethylated derivatives of microcystins LR and RR have also been found. In addition, other bioactive peptides (anabaenopeptins A and B) have been identified and quantified in some Greek lakes (Gkelis et al. 2005). There is no evidence to date for the occurrence of neurotoxic cyanobacterial blooms in Greece (Cook et al. 2004). In a recent study (May 2007–December 2008) in Marathonas Lake, a drinking water reservoir in the area of Athens, microcystins RR, LR and YR were detected at concentrations up to 0.060, 0.029 and 0.009 μg/L, respectively. However, no cyanotoxins were detected in drinking water samples of the area of Athens (Tsimeli et al. 2008).

Excessive development of planktonic cyanobacterial species can frequently be observed in the warm season in Romanian freshwaters, leading to massive blooms. Cyanobacterial bloom material collected in the summer of 2001 from the Gheorgheni recreational water body (Cluj-Napoca, Romania) during a bloom period was dominated by *Microcystis aeruginosa* and *Microcystis viridis*. Different microcystins, such as microcystins LR, RR, YR and WR, were detected for all extracts of cyanobacterial material (Boaru et al. 2006).

The Kucukcekmece Lagoon is in the European part of the city of Istanbul, Turkey. It was considered a drinking water reservoir in the 1980s; however, the lagoon has shown some eutrophication, as indicated by cyanobacterial blooms and deterioration in water quality. The occurrence of microcystins in the Kucukcekmece Lagoon, was investigated from October 2000 to June 2003. Water samples were collected from surface waters at three sites. Most bloom samples were dominated by *Microcystis aeruginosa*. The major microcystin variants detected were microcystins YR and LR. Microcystin concentrations increased dramatically from early summer to early autumn and thereafter tended to decrease. The toxin concentration found in the filtered samples from surface waters varied between 0.06 and 24.2 μg/L, microcystin LR equivalents. Each year, extensive fish mortality was recorded between mid-June and early October, coinciding with heavy algal blooms (Albay et al. 2005).

6.4 Sources and Occurrence of Cyanotoxins in Asia and Australia

Freshwater cyanobacteria harmful algal blooms, as well as benthic marine cyanobacteria have been observed in Australian waters (Sinclair et al. 2008; Codd et al. 1994). The first instance scientifically correlating the presence of cyanobacteria harmful algal blooms with wild life fatalities was reported in Australia (Codd et al. 1994; Francis 1878). The favorable conditions (i.e., water temperature, stagnant waters, nutrient levels) for algal growth have resulted in the formation of numerous species in Australian waters including *Anabaena, Cylindrospermopsis raciborskil* and *Phillipinensis, Lyngbya, Microcystis*, and *Nodularia spumigena* (Sinclair et al. 2008; Australian Drinking Water Guidelines 2008). In addition to the presence of toxins, water supply problems associated with cyanobacteria include undesired taste and odour in water (Australian Drinking Water Guidelines 2008).

Based on the Fact Sheet of the Australian Drinking Water Guidelines (ADWG) in Southeastern Australia, the hepatotoxic microcystins are considered to be the most important drinking water contaminant related to cyanobacteria. Cylindrospermopsin has been found in many water supply reservoirs in northern, central and southern Queensland and the Murray-Darling River system (Australian Drinking Water Guidelines 2008).

The hospitalization of 148 people (including children) after consuming water from the Solomon Dam on Palm Island (Queensland, Australia) in 1979 was associated with cylindrospermopsin. A toxic *Cylindrospermopsis raciborskii* bloom in the Dam was treated with copper sulfate causing cells to break increasing the extracellular concentration of cylindrospermopsin (Australian Drinking Water Guidelines 2008; Griffiths and Saker 2003). In Moreton Bay benthic blooms of *Lyngbya majuscule* have caused skin, eye, and respiratory effects to swimmers (Burch 2008). So far, no human fatalities have been reported in Australia; however deaths of animals such as cattle are believed to be caused by cyanotoxins (Griffiths and Saker 2003).

Australia has been one of the pioneers in setting limits on cyanotoxin concentrations in drinking (1.3 μg/L total microcystins) and recreational waters (10.0 μg/L total microcystins). Australia has also developed Livestock Drinking Water Guidelines for Cyanobacteria based on the chronic and toxic effects of cyanobacteria and their toxins on animals. In addition to that, the state of Victoria has adapted a "health alert" for microcystins and nodularins in seafood (Burch 2008). Treatment processes proposed for the cyanotoxins microcystins and cylindrospermopsin include chemical oxidation with ozone and chlorine as well as adsorption to granular activated carbon. It is noted that boiling the water is insufficient to remove microcystins (Australian Drinking Water Guidelines 2008). The next step for Australia will be to establish a best available technology for the treatment of cyanobacteria and their toxins in drinking water.

Toxic cyanobacterial blooms have been frequently detected and studied in drinking and recreational water sources of Japan such as Lakes Sagami, Tsukui, Kasumiguara, and the Ariake Sound (Tsuji et al. 1996; Seki et al. 1980; Ishizaka 2003). Tsuji et al. determined the intracellular and extracellular microcystin levels in the water environment during 1992–1995. Microcystin RR, LR, and YR were detected at 0.02–2.64 μg/L in cell-free water and at 0.02–378 μg/L in the cells. Only in one sampling event the extracellular microcystins concentration exceeds the WHO provisional limit of 1 μg/L (Tsuji et al. 1996; Falconer et al. 2006). Studies in Japan have also focused on the persistence of cyanotoxins in natural environment and the natural routes (i.e., dilution, adsorption, thermal decomposition, photolysis and biological degradation) that can assist in their decomposition (Harada and Tsuji 1998).

In China, algal blooms of the commonly found worldwide species of *Microcystins, Anabaena* and *Planktothrix* as well as more rare ones such as the cylindrospermopsin producing *Raphidiopsis* have been detected (Li et al. 2008). Persistent blooms in vital water bodies of China such as Lake Tai (which until recently served 2 million people) has been troubling the Chinese environmental services (Xie et al. 2008). Therefore a number of studies that investigated the causes of eutrophication and plankton formation in Chinese lakes and seas are currently available. Determination of water quality parameters and nutrient levels (i.e., biological oxygen demand, BOD; chemical oxygen demand, COD; total phosphorus, TP; total nitrogen, TN; dissolved oxygen, DO) along with satellite imaging were employed to investigate the spatial and temporal distribution events of algal blooms in water bodies (Wei et al. 2008; Wu Wu and Ma 2008; Tang et al. 2003). In the case of Lake Tai, high ammonia concentrations from the direct discharge of manure and sewage were the main sources of contamination (Xie et al. 2008). Another study on red tide events in the South China Sea occurring from 1980 to 2004 attributed their preferential formation (77%) around the coastal area of the cities Shen Zhen, Zhu Hai and Hui Zhou to the geology of the ground and water quality. Currently the Chinese government has committed to a 5 year restoration plan of Lake Tai that is estimated to cost 14.4 billion dollars (Yardley 2007). Since recent studies have related the elevated levels of primary liver cancer in specific parts of China to the exposure to hepatotoxic microcystins (Yu et al. 2001), monitoring, treatment and mitigation of the affected areas are essential.

6.5 Sources and Occurrence of Cyanotoxins in South America

Water bodies in Central and South America have started to receive greater attention as field studies become necessary to estimate the environmental and sanitary importance of cyanobacteria in the region. However, only few publications on the occurrence of cyanobacteria species from water sources are available from Argentina (Amé et al. 2003; Ruibal Conti et al. 2005), Uruguay (De Leon and Yunes 2000; Vidal and Kruk 2008), Brazil (Magalhães et al. 2003; Deblois et al. 2008; Azevedo et al. 2002; Branco and Senna 1996) and Chile (Gaete et al. 1994). All of the reservoirs examined in these studies are considered tropical or subtropical and are important sources of drinking water, power generation, aquaculture and recreational activities where urbanization of the surrounding areas has impacted the water quality. Surveys carried out in Argentina, Uruguay and Brazil were performed in man-made reservoirs which are ecosystems, in general, more susceptible for the development of cyanobacterial blooms due to their large water volume, long water retention time and shallow configuration.

Amé et al. (2003) studied the variation of water quality parameters of the San Roque Reservoir in Córdoba, Argentina. Environmental factors such as high temperature promote the presence of toxic strains of microcystins and high concentrations of ammonia-nitrogen and iron disfavored its presence during bloom periods. Spatial distribution analysis indicated that summer and early autumn were the seasons when proliferation of cyanobacterial blooms occurred, in agreement with other studies conducted in the same and different regions in South America (Ruibal Conti et al. 2005; De Leon and Yunes 2000; Vidal and Kruk 2008; Magalhães et al. 2003; Deblois et al. 2008; Gaete et al. 1994). The analysis of the extracts showed the presence of microcystin LR and RR in 97% of the blooms sampled. The total amount of microcystins ranged between 5.8 and 2,400.0 μg/g of the freeze-dried bloom material weight obtained (Amé et al. 2003).

La Plata River Basin in Uruguay has also shown presence of cyanobacteria (De Leon and Yunes 2000). As expected from previous studies, *Microcystis aeruginosa* was dominant compared to other phytoplankton species during sampling in

February where lack of rainfalls, slow winds and other environmental factors favoured bloom development. MC levels range between 101.7 and 1,074.3 μg/g dry weight. In a more recent publication, Vidal et al. (Vidal and Kruk 2008) reported the presence of *Cylindrospermopsis raciborskii* in a wide variety of subtropical lakes in Uruguay during summer time. *Cylindrospermopsis raciborskii* ranged from 9.9% to 50% of total phytoplankton abundance up to becoming the dominant species in a determined system.

Microcystis aeruginosa and *Cylindrospermopsis raciborskii* are the most widespread toxic cyanobacteria in Brazil. In the Sepetiba Bay, in Rio de Janeiro, Brazil, three main phytoplanktonic classes were observed in the sampling sites where cyanobacteria species were dominant (Magalhães et al. 2003). The Funil and Furnas reservoirs, located in southern Brazil, were determined to be eutrophic in the stations sampled (Deblois et al. 2008). In the Funil reservoir, phytoplankton biomass containing microcystins producers was the dominant group whereas at Furnas reservoir, it represented a smaller fraction of the total biomass (including *Microcystis aeruginosa*) (Deblois et al. 2008). Different studies have reported periodic occurrence of blooms of *Microcystis aeruginosa* in the Paranoa reservoir. Moreover, *Cylindrospermopsis raciborskii* was found to be dominant during raining season in summer (Azevedo et al. 2002). A monitoring program after the human incident in Caruaru, Brazil in 1996, where 52 of 131 patients in a dialysis clinic died after consumption of water contaminated with cyanotoxins, was conducted (Branco and Senna 1996). The results revealed that the dominant specie of phytoplankton from water supply of the city (Tabocas reservoir) during sampling in March was cyanobacteria species, predominantly *Microcystis, Anabaena* and *Cylindrospermopsis*. In Chile, cyanobacteria blooms resulting in microcystins species dominance and massive fish death have been reported in Aculeo Lake (Gaete et al. 1994).

Data on the occurrence of toxic cyanobacteria suggests that tropical and subtropical environments in South America are adequate for the formation of cyanobacterial blooms but currently only selected studies are found in the literature. More detailed work related to the frequency, intensity and geographic distribution of harmful and toxic cyanobacteria occurrence from inland fresh water are required in South America, which opens a new field of collaborative effort to evaluate established guidelines, implement risk assessment and management policies in the region.

6.6 Sources and Occurrence of Cyanotoxins in Africa

Cyanobacterial toxins have been found nearly in all the countries of the African continent; however, occurrence information is barely available, except for South Africa (Ballot et al. 2003; Codd et al. 2005; Haande et al. 2007). The dominated cyanobacterial bloom species in South African Lakes are usually *Microcystis* and *Anabaena*. A four month study showed that *Microcystis aeruginosa* was the most abundant cyanobacteria in Lake Krugersdrift, Hartbeespoort, Klipvoor, Rietvlei and Roodeplaat (Oberholster et al. 2009; Recknagel et al. 2008). *Microcystis aeruginosa* and *Planktothrix sp.* were also shown to be prevailing in the dams studied in 2005/2006 winter and summer seasons. The microcystin concentration was as high as 28,930 μg/L in some hypertrophic dams (Masango et al. 2008). *Microcystis* was the dominant cyanobacteria species in Lake Midmar, South Africa. Even during winter time when the temperature was around 10.1°C, a cyanobacterial bloom of *Microcystis* was observed (Obergikster and Botha 2007).

About 70% of the reservoirs in Tigray, Northern Ethiopia were found to have very dense cyanobacteria bloom (Dejenie et al. 2008). Cyanotoxin producing bacteria were found in Lakes Momela, Embagai and Manyara in Tanzania, with *Arthrospira fusiformis* as the dominant microalgae in the first two lakes (Lugomela et al. 2006). In Lake Chivero in Zimbabwe, a concentration of 19.86 μg/L microcystin LR was also found in 2003 (Ndebele and Magadza 2006).

Kotut et al. (2006) collected samples from various water bodies across Kenya. Cyanobacteria were found in 12 out of more than 46 water bodies, mainly *Microcystis* and *Anabaena* in freshwaters, and *Anabaena* and *Anabaenopsis* in alkaline lakes. In Lake Victoria, Lake Baringo, Lake Bogoria and Lake Nakuru, 310–19,800 μg microcystin LR equivalents and 270–1,260 μg anatoxin-a/g dry weight were determined. The extracellular microcystins and anatoxin-a were below 1 μg/L, compared to calculated values from 0.1 to 3.3 μg microcystin-LR equivalents/L in water samples in Lake Baringo (Ballot et al. 2003; Kotut et al. 2006).

In Egypt, one of the northern Delta lakes, Lake Burullus, cyanobacteria constituted about 9.52% to 32.43% to the total phytoplankton count, generally *Merismopedia, Anabaenopsis* and *Anabaena* (Okbah and Hussein 2006). In a fish farm, the microcystins concentration in a fish species was estimated to be from 102 ng/g to 821 ng/g fresh organ weight (Mohamed et al. 2003), and in the sediments of Nile River and irrigation canals, microcystins were also detected (Mohamed et al. 2007).

Cyanobacteria were the most abundant species in the 12 out of 13 stations studied, including the Dakar Bango reservoir and Lake Guiers in Senegal, covering for more than 50% (54–89%), among which *Anabaena spp.*, *Cylindrospermopsis raciborskii* and *Microcystis aeruginosa* accounted for 35–62% of the total cyanobacteria species (Mendoza-Vera et al. 2008).

In Algeria, the dominated cyanobacteria communities were found to be of the genera *Microcystis* in Lake Oubeira. The concentration of microcystins was as high as 29,163 μg microcystin LR equivalents/L, and 4,590 μg microcystin LR equivalents/g dried weight in August 2001 (Nasri et al. 2004, 2008).

El Herry et al. (2008) studied the occurrence of two dominant cyanobacterial species in Lebna Dam, Tunisia. They found concentrations at 9 m depth of the dam to be between 0.005 and 5.57 μg total microcystin LR (particulate and dissolved) equivalents/L, compared with that at the surface between 0.008 and 1.73. The highest microcystin concentration in mass was 3.23 μg microcystin LR equivalents/g dried cyanobacterial sample material (El Herry et al. 2008).

Table 6.1 summarizes the main cyanobacteria species, the cyanotoxins identified and the location of the reported occurrence.

Table 6.1 Cyanobacteria species, their toxins and occurrence

Cyanobacteria	Toxin	Location	Reference
Anabaena spp.	Microcystins	Canada, USA, Finland, Denmark, Belgium, Luxemburg, France, Italy, Greece,	Dillenberg and Dehnel 1960; Repavich et al. 1990; Bonilla et al. 2005; Spoof et al. 2003; Karlsson et al. 2005; Rucker et al. 2007; Vasconcelos et al. 1996; Messineo et al. 2008; Gkelis et al. 2005
		Australia, China, South Africa, Kenya, Egypt, Senegal	Albay et al. 2005; Francis 1878; Harada and Tsuji 1998; Oberholster et al. 2009; Kotut et al. 2006; Okbah and Hussein 2006; Mendoza-Vera et al. 2008
A. circinalis	Anatoxin-a	USA	Aubel et al. 2006
A. lemmermannii	Microcystins	Finland	Codd et al. 2005
A. flos-aquae	Anatoxin-a	Portugal	Carrasco et al. 2006
Anaebaenopsis millerii	Microcystins	Greece, Kenya, Egypt	Messineo et al. 2008; Gkelis et al. 2005; Kotut et al. 2006; Okbah and Hussein 2006
Aphanizomenon spp.		Denmark, Greece, Finland	Karlsson et al. 2005; Messineo et al. 2008; Gkelis et al. 2005; Spoof et al. 2003
A. ovalisporum	Cylindrospermopsin	USA	Williams et al. 2007
A. gracile	Cylindrospermopsin	Germany	Fromme et al. 2000
Arthrospira fusiformis	Microcystins	Tanzania	Dejenie et al. 2008
Cylindrospermopsis phillipinensis	Saxitoxins	Australia	Albay et al. 2005; Francis 1878
Cylindrospermopsis raciborskii	Cylindrospermopsin	USA, Greece, Australia, Uruguay, Brazil, Senegal	Humpage and Falconer 2002; Messineo et al. 2008; Gkelis et al. 2005; Albay et al. 2005; Francis 1878; De Leon and Yunes 2000; Vidal and Kruk 2008; Deblois et al. 2008; Mendoza-Vera et al. 2008
Cylindrospermum spp.		USA	Izaguirre et al. 2007
Gloeotrichia		USA	Repavich et al. 1990

Leptolyngbya		Canada	Bonilla et al. 2005
Lyngbya		Canada, Australia	Bonilla et al. 2005; Albay et al. 2005; Francis 1878
L. wollei	Dermatotoxins	USA	Aubel et al. 2006
L. majuscula	BMAA	Australia	Griffiths and Saker 2003
Merismopedia spp.		USA, Egypt	Izaguirre et al. 2007; Okbah and Hussein 2006
Microcystis ssp.			
M. aeruginosa	Microcystins	Canada, USA, Finland, Denmark, Germany, Spain, Portugal, Italy, Greece	Dillenberg and Dehnel 1960; Repavich et al. 1990; Rolland et al. 2005; Codd et al. 2005; Karlsson et al. 2005; Blahova et al. 2008; Willame et al. 2005; Carrasco et al. 2006; Vasconcelos et al. 1996; Messineo et al. 2008; Gkelis et al. 2005
		Belgium, Luxemburg, France, Romania,Turkey, Australia, China, Argentina,	Rucker et al. 2007; Tsimeli et al. 2008; Boaru et al. 2006; Albay et al. 2005; Francis 1878; Harada and Tsuji 1998; Yu et al. 2001
		Uruguay, Brazil, Chile, South Africa, Kenya, Senegal, Algeria	Ruibal Conti et al. 2005; Vidal and Kruk 2008; Magalhães et al. 2003; Branco and Senna 1996; Haande et al. 2007; Kotut et al. 2006; Mendoza-Vera et al. 2008; Nasri et al. 2004
	Anatoxin-a	USA, Italy	Hotto et al. 2007; Vasconcelos et al. 1996
M. wesenbergii		Portugal	Carrasco et al. 2006
M. viridis	Microcystins	Romania	Tsimeli et al. 2008
Nodularia spumigena		Denmark, Australia, Finland, Denmark	Karlsson et al. 2005; Albay et al. 2005; Francis 1878; Spoof et al. 2003
Nostoc sp.	Microcystins	Portugal	Carrasco et al. 2006
Oscillatoria spp.		Canada, USA	Bonilla et al. 2005; Izaguirre et al. 2007
Phormidium ambiguum		USA	Izaguirre et al. 2007

(continued)

Table 6.1 (continued)

Cyanobacteria	Toxin	Location	Reference
Planktothrix spp.		USA, Germany, Belgium, Luxemburg, France, Italy, China, Denmark,	Rinta-Kanto and Wilhelm (2006); Blahova et al. 2008; Rucker et al. 2007; Vasconcelos et al. 1996; Harada and Tsuji 1998; Karlsson et al. 2005
P. agardhii		Finland	Codd et al. 2005
Pseudoanabaena		Canada	Bonilla et al. 2005
Raphidiopsis spp.	Cylindrospermopsin	China	Harada and Tsuji 1998
Synechococcus		Canada	Bonilla et al. 2005
Tychonema		Canada	Bonilla et al. 2005
Woronichinia			
W. naegeliana		Belgium, Luxemburg, France	Rucker et al. 2007

6.7 Conclusions

A worldwide increase in the occurrence and duration of cyanobacterial harmful algal blooms in natural and artificial water bodies is evident. Cyano-HABs have occurred in North America, Europe, Australia, Asia, the Middle East and South America. The dominant cyanobacterial genera found in most of these regions includes *Microcystis, Cylindrospermopsis, Anabaena, Aphanizomenon, Lyngbya* and *Planktothrix*. The most frequently detected cyanotoxins are microcystins, cylindrospermopsin, anatoxin-a and saxitoxins. The concentration of microcystins, cylindrospermopsin, and saxitoxins in many cases, has exceeded provisional guidelines for recreational and drinking waters. Since occurrence of high levels of cyanotoxins is a direct threat to human, animal and environmental health, cyanobacteria and cyanotoxins monitoring programs needed be implemented. Future research needs include improvement of analytical methods for in-situ detection of cyanobacteria and their toxins, the creation of predictive models for Cyano-HABs formation and the creation of monitoring programs on the environmental fate and transport of the toxins in recreational and drinking water sources.

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Chapter 7
Occurrence and Measurements of Organic Xenobiotic Compounds in Harbour and Coastal Sediments

Giusy Lofrano, Anastasia Nikolaou, Maria Kostopoulou, Giovanni Pagano, Vincenzo Belgiorno, and Rodolfo Maria Alessandro Napoli

Abstract The present chapter focuses on the identification of sources and fluxes of xenobiotic compounds in marine sediments to set strategies for minimizing impacts on the human life and environment. It is generally accepted that sediments constitute a sink for the more hydrophobic compounds, posing an unacceptable risk to aquatic biota, in which these compounds can bioaccumulate, and to human health through the ingestion of contaminated fish and shellfish.

Information is provided on the organic xenobiotics most frequently occurring in marine sediments, namely, polycyclic aromatic hydrocarbons (PAHs), surfactants, halogenated compounds, organotin compounds and pharmaceuticals. The development and optimization of analytical methods for the determination of those priority substances in marine sediments are discussed. Substantial improvements have been achieved in analysis performance towards optimal resolution of analytes, for example detection limits, and clean-up of environmental samples to detect low-level xenobiotics in complex mixtures such as the marine sediments.

Thus, this chapter aims at identifying the main challenges related to organic xenobiotics in marine sediments, underlying also existing gaps in legislation.

G. Lofrano (✉) and V. Belgiorno
Department of Civil Engineering, University of Salerno, I-84132, Fisciano, Salerno, Italy
Phone 0039 089969337, Fax number 0039 089969620, e-mail: glofrano@unisa.it

A. Nikolaou and M. Kostopoulou
Department of Marine Sciences, Faculty of the Environment,
University of Aegean, University Hill, GR-81100, Mytilene, Greece

G. Pagano
Hygiene Section, Federico II University, I-80134, Naples, Italy

R.M.A. Napoli
Faculty of Environmental Sciences, Parthenope University, I-80133, Naples, Italy

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7.1 Introduction

Harbour and coastal sediments can be polluted by a wide range of xenobiotics. In harbours, where exchange of water with the open sea is limited, accumulation of toxic substances can be particularly significant and raises major concerns for human health, especially when leisure shores are located nearby. The priority substances of the Water Framework Directive 2000/60/EC, such as polycyclic aromatic hydrocarbons, organotins and nonylphenol, are characterized by high toxicity, high environmental persistence and high lipophilicity, leading to bioaccumulation in food webs (IARC 1983). They can occur as mixtures, having combined adverse effects, which are yet largely unknown.

Xenobiotics can reach the environment by different routes up to their final destination in sediments (Jartun et al. 2009; la Farré et al. 2007). The physico-chemical properties of the contaminants, for example water solubility or vapour pressure and polarity, contribute to determine their distribution in the environment. Xenobiotics can be subjected to both biotic and abiotic transformation processes in the environment giving derivatives that can be more persistent and more toxic than the parent compounds (la Farré et al. 2007). Under the anaerobic or hypoxic conditions normally present in the sub-surface layers of harbour sediments, these compounds are expected to undergo low photodecomposition and biodegradation. Therefore, sediments can act as secondary contamination sources posing a long-term hazard to the environment (Lee et al. 2001). All benthic organisms are potentially exposed to them. Any exposure to sediment laden with xenobiotics may cause adverse effects at lower trophic levels and/or lead to biomagnification and more serious adverse toxic effects at higher trophic levels (Merilainen and Okari 2008; US EPA 2004; Wernersson et al. 2004). Moreover, remobilization of toxic pollutants, thus increase of their bioavailability, can occur when polluted sediments are disturbed and dredged (Eggleton and Thomas 2004; Mäenpää et al. 2003; Water Framework Directive 2000).

Persistent Organic Pollutants (POPs) are an important component of the range of xenobiotics now ubiquitous in the global environment (Dórea 2008). The best examples of these chemicals are organic substances, such as monomethyl mercury (MMHg) and various halogenated pollutants: pp'-DDT (1,1,1-trichloro-2,2,bis (4-chlorophenyl) ethane), 1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene (DDE), pp'-dichlorophenyldichlorodiene (DDD), hexachlorobenzene (HCB), hexachlorohexane (HCH), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCP), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzofurans (PCDFs), dibenzo-p-dioxins (PCDDs), polybrominated diphenyl ethers (PBDEs), and other halogenated hydrocarbons. Persistent and volatile pollutants evaporate out of the soil in warmer countries, typically under-developed countries, where they are still used and from mid- and low-latitudes reach the Arctic regions through a process known as global distillation (Corsolini 2009; Curtosi et al. 2007; Jartun et al. 2009).

POPs have a lower solubility in seawater than in freshwater and are environmentally recalcitrant (Basheer et al. 2005). Owing to their high persistence, their hydrophobic nature and their low solubility in water, they readily bind to surface plankton and other organic particulates and readily undergo sedimentation (Bard 1999)

Surfactants, drugs and organotin compounds are also released continuously into seawater through wastewater treatment plants as well as directly, or via surface runoff. Especially organotin compounds have accumulated into the sediments of harbours and marinas in global scale, due to their extended use during the last decades as antifouling agents. These compounds tend to adsorb on particulate matter and settle onto sediments and they also accumulate in marine organisms, raising concerns for the degradation of environmental quality (Bester et al. 2001; La Farré et al. 2007; Lara-Martin et al. 2008; Tolhurst et al. 2007).

Previous pollution management efforts have focused primarily on “end-of pipe” treatment methods. However, measures aimed at reducing the pollutant loadings at the sources should be taken into account in order to effectively avoid or minimize the potentially adverse environmental impacts associated with pollutants and waste. Hence, an appropriate management plan should include source control as the very first step.

Because the human impact in terms of chemicals release into the environment can no longer be considered as a local event, the hope for the future is the application of REACH (Registration, Evaluation, Authorization of Chemical) that can lead to a more accurate evaluation of chemical-associated risks and toxicity, with the consequent establishment of restrictions and a decreasing production of new chemicals (Corsolini 2009). The application of precautionary principle is urgently required. Therefore if an activity has the potential for causing harm, appropriate steps must be taken to prevent damaging consequences and any potential risk needs to be addressed even in the absence of the scientific certainty that problems will occur.

7.2 Source, Transport and Properties of Main Xenobiotic Compounds Detected in Marine Sediments

7.2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Environmental concerns about the presence of polycyclic aromatic hydrocarbons (PAHs) in sediments have often been expressed in the scientific literature (Cardellicchio et al. 2007; Curtosi et al. 2007; Men et al. 2009; Yim et al. 2007).

PAHs are released into the environment through natural and synthetic sources with emissions largely to the atmosphere. Among them, synthetic sources provide a much greater release volume than natural sources (Boonyatumanond et al. 2007; Curtosi et al. 2007). PAHs can enter surface waters through atmospheric deposition and from discharges of industrial effluents, municipal wastewater and improper disposal of used motor oil (Liu et al. 2007; Men et al. 2009). Hazardous waste sites such as abandoned wood-treatment plants (sources of creosote) and former manufactured gas sites (sources of coal tar) can also be a concentrated source of PAHs on a local scale (Boonyatumanond et al. 2006). The category of PAHs include a number of organic substances (about 100), which are divided according to the number of rings (≥2) in their basic structural unit (ATDSR 1995). Table 7.1 reports the 16 PAHs regulated by the US EPA as priority pollutants, whose mean concentrations in marine sediments are shown in Table 7.2.

Table 7.1 The 16 PAHs regulated by the US EPA as priority pollutants

PAH_S	Molecular formula	Molecular weight	Melting point	Boiling Point	Log K_{ow}	Vapour Pressure
		(g/mol)	(°C)	(°C)		(mm Hg)
Naphthalene (NAP)	$C_{10}H_8$	128.17	79	218	3.36	2.3×10^{-1}
Acenaphthylene (ACEL)	$C_{12}H_8$	152.19	92.93	279	3.98	4.47×10^{-3}
Acenaphthene (ACE)	$C_{12}H_{10}$	154.21	95	280	4.07	0.029^{a}
Fluorene (FLU)	$C_{13}H_{10}$	166.2	116	295	4.18	3.2×10^{-4a}
Phenanthrene (PHE)	$C_{14}H_{10}$	178.2	96-99	340	4.45	6.8×10^{-4b}
Anthracene (ANT)	$C_{14}H_{10}$	178.2	218	400	4.45	1.7×10^{-5b}
Fluoranthene (FLUT)	$C_{16}H_{10}$	202.26	110	384	4.90	5.00×10^{-6b}
Pyrene(PYN)	$C_{16}H_{10}$	202.3	156	393	4.88	2.5×10^{-6b}
Benzo[a]anthracene (BAA)	$C_{18}H_{12}$	228.29	161	438	5.61	2.2×10^{-8a}
Chrysene	$C_{18}H_{12}$	228.3	256	448	5.16	6.3×10^{-7b}
Benzo[b]fluoranthene (BBFT)	$C_{20}H_{12}$	252.3	168	481	6.35	5.0×10^{-7a}
Benzo[k]fluoranthene	$C_{20}H_{12}$	252.3	216	480	6.06	9.59×10^{-11}
Benzo[a]pyrene	$C_{20}H_{12}$	252.3	179	496	6.06	5.6×10^{-9}
Indeno[1,2,3-cd]pyrene (INDE)	$C_{22}H_{12}$	276.3	164	530	6.58	$10^{-11}–10^{-6a}$
Benzo[g,h,i]perylene	$C_{22}H_{12}$	276.34	273	550	6.5	1.03×10^{10b}
Dibenzo [a,h]anthracene	$C_{22}H_{14}$	278.35	262	524	6.84	1.00×10^{-10a}

[a] At 20°C

[b] At 25°C

Table 7.2 The mean concentrations of most commonly detected xenobiotics in marine sediments

Xenobiotics	Sample source	Concentration (d.w.)	Reference
Nonylphenol	Marina sediments	0.01–0.153 mg kg^{-1}	Bester et al. 2001
	Sea sediments	<0.01–0.055 mg kg^{-1}	Bester et al. 2001
	Estuary sediments	0.0004–1.08 mg kg^{-1}	Jonkers et al. 2003
	Harbour sediments	0.008–1.05 mg kg^{-1}	Petrović et al. 2002
LAS	Sea sediments	3.2–67.6 µg g^{-1}	Lara-Martin et al. 2006
AEOs	Sea sediments	1.6–9.9 µg g^{-1}	Lara-Martin et al. 2006
AES	Sea sediments	161–1,728 ng g^{-1}	Lara-Martin et al. 2006
Σ29 PCB[a]	Harbour sediments	<3.40 µg kg^{-1}	Kilemade et al. 2009
Dieldrin	Sea sediments	60–107 ng g^{-1}	Basheer et al. 2005
Aldrin	Sea sediments	4–36 ng g^{-1}	Basheer et al. 2005
Endrin	Sea sediments	17–89 ng g^{-1}	Basheer et al. 2005
ΣDDTs	Sea sediments	0.38–1,417.08 ng g^{-1}	Zhang et al. 2009
Σ23 Organochlorine pesticide (OCP)[a]	Harbour sediments	<3.25 µg kg^{-1}	Kilemade et al. 2009
Σ17 Brominated flame-retardants (BFRs)[a]	Harbour sediments	<4.70 µg kg^{-1}	Kilemade et al. 2009
Σ% Organotin (OT)	Harbour sediments	<12.50 µg kg^{-1}	Kilemade et al. 2009
ΣPCB	Harbour sediments	41–899 ng g^{-1}	Sprovieri et al. 2007
Copper	Harbour sediments	13.39–27 mg kg^{-1}	Kilemade et al. 2009
Lead	Harbour sediments	16.40–18.80 mg kg^{-1}	Kilemade et al. 2009
Cadmium	Harbour sediments	<0.10 mg kg^{-1}	Kilemade et al. 2009
Zinc	Harbour sediments	99.10–105.30 mg kg^{-1}	Kilemade et al. 2009
Naphthalene (NAP)	Harbour sediments	37.7–43.99 ng g^{-1}	Kilemade et al. 2009
Acenaphthylene (ACEL)	Harbour sediments	Below detection limit	Kilemade et al. 2009
Acenaphthene (ACE)	Harbour sediments	4.73 ng g^{-1}	Kilemade et al. 2009
Fluorene (FLU)	Harbour sediments	7.27–12.19 ng g^{-1}	Kilemade et al. 2009
Phenantrene (PHE)	Harbour sediments	58.38–92.27 ng g^{-1}	Kilemade et al. 2009
Antracene (ANT)	Harbour sediments	12.32–14.78 ng g^{-1}	Kilemade et al. 2009
Fluoranthene (FLUT)	Harbour sediments	89.85–110.63 ng g^{-1}	Kilemade et al. 2009
Pyrene (PYN)	Harbour sediments	74.29–88.25 ng g^{-1}	Kilemade et al. 2009
Benzo[a]anthracene (BAA)	Harbour sediments	41.67–50.57 ng g^{-1}	Kilemade et al. 2009
Crisene	Harbour sediments	43.47–46.97 ng g^{-1}	Kilemade et al. 2009
Benzo[b]fluoranthene (BBFT)	Harbour sediments	107.1–119.71 ng g^{-1}	Kilemade et al. 2009
Benzo[k]fluoranthene	Harbour sediments	29.58–36.71 ng g^{-1}	Kilemade et al. 2009
Benzo[a]pyrene	Harbour sediments	42.01–45.53 ng g^{-1}	Kilemade et al. 2009
Indeno[1,2,3-cd] pyrene (INDE)	Harbour sediments	73.31–76.76	Kilemade et al. 2009
Benzo[g,h,i]perylene	Harbour sediments	50.50–53.99 ng g^{-1}	Kilemade et al. 2009
Dibenzo[a,h] anthracene	Harbour sediments	8.72–9.90 ng g^{-1}	Kilemade et al. 2009
ΣPAHs priority PAHs	Harbour sediments	9–31774 ng g^{-1}	Sprovieri et al. 2007
ΣPAHs priority PAHs	Harbour sediments	924.40–1,000.7 ng g^{-1}	Kilemade et al. 2009

[a] Classified as "probable (group 2A) or possible (group 2B)" human carcinogens (IARC 1983)

The number and position of the rings as well as the number, position and nature of the atoms that can be present in the molecules affect the physical and chemical properties of PAHs, their environmental behaviour and their interactions with biota, water and sediments. Moreover, the compositional properties of PAHs can be used for source diagnosis and pollution control and management (Li et al. 2001; Liu et al. 2007).

PAHs have high melting and boiling points and low water solubilities (IARC 1983). Their solubility in water decreases, while correspondingly their boiling and melting point increases, with increasing molecular weight.

PAHs are widespread contaminants in the oceans. However, their concentrations in sediments of coastal embayments, estuaries and continental shelves are often much higher due to greater pressures of specific anthropogenic inputs (Liu et al. 2007; Yim et al. 2007), suggesting a direct influence of these sources on the pollutant distribution patterns (Sprovieri et al. 2007). In recent years, increasing attention has been paid to the environmental behaviour of PAHs in estuarine systems, as these areas act as transit zones in which contaminants are transported from rivers to oceans (Anyakora et al. 2005; Men et al. 2009).

Owing to the chemical composition of seawater, the occurrence of PAHs, which are hydrophobic compounds, will range at very low concentration levels (<1 ng/L), in contrast to other aqueous matrices such as wastewater, river water and rainwater, where the corresponding values range, depending on the study area, from 1 ng/g to or greater than 100 ng/g per dry weight (Filipkowska et al. 2005). Vessels have a significant contribution by transporting these compounds in the marine environment. Due to their hydrophobic character, PAHs tend to adsorb onto the particulate matter resulting in their transport and accumulation in the sediments. The adsorption of PAHs occurs on the surface of organic and inorganic particles. PAHs are mainly adsorbed to the smallest soil particles but it was found that they are usually metabolized at much greater extent in soils dominated by larger particles and low content of clay and silt (Curtosi et al. 2007).The rate of adsorption is positively affected by the organic matter content in the particles. PAHs accumulation can be enhanced, especially in harbours, by scarce water renewal through contact with the open sea (Anyakora et al. 2005; Bakker et al. 2000; N'Guessan et al. 2004). The final fate of PAHs is generally sedimentary deposition, after transport in the water column, as reported for material collected in sediment traps (Zaghden et al. 2007). However, in situ factors as PAHs partitioning between sorbed and aqueous phases, bioturbation and selective microbial degradation may affect the resultant PAHs composition and the absolute levels of PAHs congeners (Sprovieri et al. 2007; Yim et al. 2007). PAHs molecules adsorbed on the sediments can be subject to slow-rate biodegradation and transformation to other forms via the actions of benthic organisms. The half-life of fluoranthene in surface sediments ranges from few days to some years depending on the environmental conditions. Degradation of compounds containing more than six rings has not been documented, while no evidence of degradation exists for PAHs in deep sediments (Neff 1979).

7.2.2 Persistent Organic Pollutants

Persistent Organic Pollutants (POPs) have triggered an increasing concern for several decade years all over the world. POPs have high toxicity, last for a long time in environment, and may travel long distance far from their sources of usage, release and emission. Furthermore, they can accumulate in fatty tissues of living organism leading to undesirable effect linked to the occurrence of immunologic and teratogenic dysfunction, reproductive impairments and endocrine disruption (Boonyatumanond et al. 2007; Dórea 2008; Mäenpää et al. 2003; Zhang et al. 2009).

Eight kinds of pesticides (dieldrin, aldrin, endrin, chlordane, heptachlor, dichlorodiphenyltrichloroethane [DDT], toxaphene and mirex), as well as two kinds of industrial chemicals (polychlorinated biphenyls [PCBs] and hexachlorobenzene [HCB]) and two kinds of byproducts (dibenzo-pdioxins and dibenzofurans (PCDD/Fs) are listed as dirty dozen in Stockholm Convention (2001).

Because some of these substances are anti-androgenic or oestrogen agonists and can disrupt reproductive functions in wildlife, they are also recognized as 'endocrine disruptors' (European Workshop on the Impact of Endocrine Disrupters on Human Health and Wildlife 1996).

Polychlorinated biphenyls (PCBs) were detected in worldwide marine sediments investigated over the last 30 years (Boonyatumanond et al. 2007; Jartun et al. 2009; Sprovieri et al. 2007; Zhang et al. 2009). Basheer et al. (2005) surveyed Organic chlorine pesticides (OCPs) and PCBs concentrations in marine sediments from north-eastern and south-western regions of Singapore's coasts. The low molecular weight PCBs that is mono- and dichloro congeners were present at relatively low concentrations in comparison to the high molecular weight congeners, which predominated in the marine sediments studied whereas HCB, Dieldrin and Endrin were more abundant OCPs. This finding might be related to the fact that the low molecular compounds are more readily volatilized in the atmosphere, whereas the higher molecular weight compounds can be expected to partition onto the particulate phase and undergo sedimentation. Li et al. (2001) propose that the high PCBs level in the sediment might be related to two main point sources, which are petroleum chemical factories and coal wharfs.

The presence of brominated flame-retardants (BFRs) in marine sediments was confirmed by the study of Kilemade et al. (2009), though the real concentrations could not be assured because of their closeness to instrumental detection limits. The mean concentrations of some halogenated compounds measured in marine sediments are shown in Table 7.2.

7.2.3 Surfactants

Surfactants comprise a broad group of chemicals synthesized to exert tensioactive properties that make them useful for employment as a key ingredient of household and industrial detergents, as well as in personal care products and pesticide formulations, among other applications (Lara-Martin et al. 2008). These compounds can be classified, according to their charge, into several types, where those of the anionic and non-ionic classes show the highest volumes of production. According to the data reported by CESIO (Comité Européen des Agents de Surface et de leurs Intermediaries Organiques), 998 kt of anionics and 1,231 kt of non-ionics were manufactured during the year 2000 in the EU, these together account for about 90% of the total production of synthetic surfactants.

Urban wastewater discharges and industrial activities are identified as the main sources for the four major synthetic surfactants, that is linear alkylbenzene sulfonates (LAS), alkyl ethoxysulfates (AES), nonylphenol ethoxylates (NPEOs) and alcohol ethoxylates (AEOs) and their metabolites in the sediments (Bester et al. 2001; Boonyatumanond et al. 2007; John et al. 2000; Lara-Martin et al. 2006; Soares et al. 2008).

LAS are anionic surfactants with molecules containing a hydrophobic and a hydrophilic group. They are used in the form of commercial mixtures consisting of isomers and homologues of related compounds, differing in physicochemical properties. The commercial mixtures contain different alkyl chain lengths (C10–C13 or C14) and isomers differing in the phenyl ring positions (2–5 phenyl) (WHO 1996).

AES are primary sulfate esters manufactured from the corresponding alcohol ethoxylates, and their structure is shown below:

$$R_2 - H; R_1 = C_{10-14}; n = 1 - 4$$

Longer alkyl or ethoxylate chains can also occur (CETOX 2000).

AEOs are nonionic surfactants and their molecules consist of a hydrophobic alkyl chain (fatty alcohol), combined ethoxylate or ethylene oxide units via an ether linkage. Representative structures are given below (CETOX 2000):

Lineary primary AE, C_{13} EO7:

$$CH_3 - (CH_2)_{12} - O - (CH_2 - CH_2 - O -)_7H$$

Iso-C_{13} branched primary AE, EO7:

Nonylphenol is a hydrophobic compound consisting of a phenol ring and a nine-carbon branched chain on the para-position, with a log K_{ow} value of 4.48 and low solubility in water (John et al. 2000). While there are just few applications of the nonylphenols themselves, nonylphenol ethoxylates, which are the main source of nonylphenol to the environment, are used as industrial detergents in metal, textile and leather processing (Bester et al. 2001; Soares et al. 2008).

An investigation into the adsorption processes controlling the partitioning of nonylphenol ethoxylates to sediments demonstrated that the organic content of the sediments was one of the important determinants in the adsorption process, especially for the shorter chained nonylphenol ethoxylates that indicates the importance of their hydrophobic interactions (John et al. 2000). Further studies in sediments free of organic matter adsorption indicated that not only organic content is relevant for nonylphenol, but that there are multiple interactions to be accounted for. Therefore it is evident that nonylphenol adsorption is controlled by two major interactions: hydrophilic interaction with mineral components and hydrophobic interaction with the organic matter (John et al. 2000; Lara-Martin 2006; Soares et al. 2008).

Shang et al. (1999) estimated that the degradation half-life of nonylphenolic compounds is greater than 60 years once they enter the sediments.

7.2.4 Organotin Compounds

Leaching of biocides such as tributyltin (TBT) and triphenyltin (TPT) from boats and ships coated with antifouling paints result in 'hot-spots' of biocide contamination around marinas (Biselli et al. 2000; Tolhurst et al. 2007). Once paint particles become interspersed with bottom sediments they provide a potential long-term sink for the biocides they contain. In 2003, the Marine Environmental Protection Committee (MEPC) recommended a world-wide recommendation ban on TBT because of its potential environmental impacts. Despite the bans organotins are still present in seawater, bottom sediments and biota in large quantities (Maguire and Batchelor 2005).

A recent study has shown, as in inter-tidal and sub-tidal sediment deposits in the vicinity of boating activities, that metals may progressively leach into organic-rich interstitial waters. During disturbance or dredging of the bed sediment that is contaminated by boat paint, leaching into the overlying water column is constrained by shorter timescales but this could amount to considerable aqueous concentration (Singh et al. 2009). The mean concentrations of some organotin compounds in marine sediments are shown in Table 7.2.

7.2.5 Pharmaceuticals

Even though several publications compile occurrence data of drug residues in aquatic ecosystems, relatively scarce reports are available regarding their occurrence in marine sediments. More than 100,000 different chemical substances are recorded in the European Union, of which 30,000 products are marketed in amounts above 1 t. Drugs often have similar physico-chemical behaviour as other harmful xenobiotics that are accumulated or induce adverse effects in terrestrial or aquatic organism (Petrović et al. 2001).

Most of the drug residues data found in literature dealing with sediments concern the occurrence of oestrogens and antibiotics (Hernando et al. 2006). Given the relatively low polarity, in particular for oestrogens with K_{ow} (2.5–5), sorption to sediments appears quite likely to be a cumulative process (Beausse 2004).

However, the log K_{ow} is not sufficient for the assessment of the sorption and distribution behaviour of antibiotics. Contrary to what would be expected from log K_{ow}, Kummerer (2009) found that ciprofloxacin sorbs well onto sediments. Laboratory experiments carried out on the behaviour of oestrogens in the aquatic environment predict that bed sediments act as environmental reservoirs from where both oestrogens and progestogens (compounds also used in birth-control pills) can eventually become bioavailable especially in anaerobic conditions (Lai et al. 2000).

7.3 Legislative Aspects

Nowadays, legislation on marine sediments is still a complex matter. No European legislation exists on management of contaminated sediments such as those coming up from dredging activities. However, during the last years, several Directives on different environmental issues regarding marine environment protection have been established. Since 2000, the EU Water Framework Directive (WFD 2000/60) is the main tool to tackle the sources of sediment contamination. The quality norms were set for 33 chemicals including polycyclic aromatic hydrocarbons, pentachlorophenol and nonylphenol, which were specified as slowly degrading, having a potential to accumulate in sediments and being toxic. The Directive does not specifically address sediment management, but it offers the opportunity to improve our knowledge about the relation between sediment quality and water quality assuming that sediments and ecological status of water bodies are interconnected.

The lack of existing data is one reason that the quality norms are not established to sediments, thus there is a need to develop analytical techniques and toxicity testing. The most widely applicable international regulatory instrument on the prevention of Marine Pollution by Dredging of Wastes and Other Matter is the London Convention 1972 (LC-72), which has been in force since 1975. In 1996, the 'London Protocol' was agreed and entered into force in March 2006 (http://www.Londonconvention.org/). Under this Protocol, all dumping is prohibited, except for possibly acceptable wastes on the so called 'reverse list'. Other Conventions on regional scale are the Oslo and Paris Convention (1992) (http://www.ospar.org/), the Helsinki Convention (1974), the Barcelona Convention (1976) and MARPOL 73/78. Most of these conventions propose methods based on a 'weight of evidence' (WOE) approach. At the beginning, a simple screening is made followed by progressing in more detailed assessments. Initial assessment considers factors related to the dredged material such as the particle-size characteristics of the material, local and historic information, and the anthropogenic activities taking place. If appropriate information cannot be obtained in order to undertake the proposed management, then chemical characterization is required. In some countries, this is done in parallel with biological screening tests. National Authorities should take into consideration the specifications given in 'Guidelines for the assessment of Wastes or Other Matter Considered for Dumping', as adopted in 1997 by the 19th Consultative Meeting of Contracting Parties to the London Convention 1972, as well as 'Specific Guidelines for the Assessment of Dredged Material"'. Management design should match with London Convention 1972 as well as the 1996 Protocol, where in the latter, in Annex 2, emphasis is given to reduce the use of sea as site dumping.

The establishment of guidelines is not an easy task as many factors play a crucial role towards effects; moreover, the approach of studies should follow many steps, both encompassing chemical analyses and toxicity testing. However, the management of dredged material is an ‘end of pipe’ solution. It is urgently required to shift from dredged material management to sediment management (Vellinga 2004).

Europe has a problem of historical contamination of sediments in all developed areas; hence the sediment issue will appear more prominent on the agenda of the Water Framework Directive.

7.4 Analytical Determination of Main Xenobiotics in Marine Sediments

Towards the revision of existing legislation as well as of the establishment of regulatory limits for xenobiotic compounds in the marine environment, more information on contaminant levels in sediment samples is required. This information can be obtained through application of sensitive analytical methods that can provide accurate results, taking into account the low levels of xenobiotics in complex matrices containing a large number of organic compounds, such as marine sediments. Therefore, the optimization of current methods, as well as the development of new methods with lower detection limits and better sensitivity is very important.

The domain of xenobiotics extraction from sediments has shown a remarkable progress, starting from the initially used Soxhlet extraction (Kennicutt et al. 1992; Schlautman and Morgan 1993) and proceeding to applications of ultrasonic extraction, microwave dissolution, pressurized liquid extraction (PLE) and supercritical fluid extraction (SFE), in order to reduce the volume of harmful solvents used as well as the time required for analysis (Berset et al. 1999; Hawthorne et al. 2000; Hubert et al. 2000; Richter 2000; Richter et al. 1997; Wennrich et al. 2000; Wong and Wang 2001). Solid phase microextraction (SPME) techniques have also gained interest for sediment samples. Pino et al. (2003) combined a micellar microwave-assisted extraction technique with SPME (micellar solid-phase microextraction, MSPME) to determine PAHs in a certified marine sediment. Further information on analytical methods and their sensitivity can be found in the recent reviews on analytical methods for the determination of PAHs in marine sediments (Nikolaou et al. 2009) and for the determination of drugs and metabolites in aqueous matrices (Kostopoulou and Nikolaou 2008).

Cleanup techniques have been introduced in order to improve the quality of the extract to be analyzed (removal of interferences), and therefore to enhance the sensitivity of the analytical methods. Solid phase extraction (SPE), high performance liquid chromatography (HPLC) cleanup, and column chromatography have been utilized for this purpose, using a variety of adsorbents (e.g. acid and base modified silica gel, alumina and florisil). The disadvantage of application of such techniques was the increase of analysis time and effort, which led to studies on the combination of extraction and cleanup procedures with automated sample handling devices (Kim et al. 2003). Advances in analytical instrumentation available during the recent years, and capable of detection of xenobiotics in trace concentrations in environmental samples, include increase in the chromatographic resolution of Gas Chromatography (GC) and Liquid Chromatography (LC) columns, increase of the detection sensitivity and specificity by application of advances Mass Spectrometry (MS) techniques, and introduction of tandem MS techniques, in combination either with GC or with LC, which is utilized to identify not only the initial xenobiotics, but also many of their metabolites and transformation products (Diaz-Cruz et al. 2008; Feldmann et al. 2008; Focazio et al. 2008; Gomez et al. 2007; Kosjek et al. 2007; Perez and Barcelo 2007; Zuccato et al. 2008; Zuehlke et al. 2007). Detailed information on the recent advances of analytical instrumentation especially during the determination of drugs in environmental samples can be found in the review by Fatta et al. (2007).

However, many analytical problems, issues to clarify and optimizations to perform still remain, as the number of xenobiotics detected in the marine environment is increasing, and the metabolites and transformation products as well as their health effects are largely unknown. In this context, there are two directions towards which the analytical research needs to be addressed: (a) the increase of accuracy and sensitivity of analytical methods for the already known and analyzed xenobiotics, and (b) development of new analytical methods or optimization of existing methods in order to be able to accurately detect metabolites and transformation products of xenobiotics, especially in the complex marine sediments substrates. Both tasks need to be addressed in such way that cost, efforts, analysis time and harmful agents used are minimized, while the number of compounds that can be analyzed in a single run is maximized. Achieving a balance among these requirements is a great challenge for analytical researchers and will be very useful towards investigation and protection of the marine environment in global scale.

7.5 Strategies for Minimizing Risk

The knowledge of sources and possible transport pathways in aquatic sediments is the first step for an effective pollution control (Li et al. 2001). The proper sewage management is the key for safeguarding sensitive coastal areas being the receivers of the treated wastewater effluents. However, in many cases, the efficiency of the existing wastewater treatment systems is insufficient or even unknown for specific pollutants which can be critical for the aquatic life (e.g. endocrine disrupting substances). There is a need for the development of monitoring programs and analytical methods for such substances and their transformation products in marine ecosystems in order to optimize the sewage treatment systems in a way to minimize their release. Moreover, the development of quality indicators for the coastal waters would allow the evaluation of their status and help towards their management and application of the appropriate measures for their protection and restoration. Although no relevant regulation has yet been established, monitoring xenobiotics in sediments can provide information for assessing the potential toxic effects of these compounds as well as for the support of decision making from management authorities.

Even though chemical analyses are able to measure many of these compounds qualitatively and quantitatively, complex mixtures of these chemical pollutants cannot be fully assessed in terms of environmental impact, because of potential synergistic/antagonistic effects of complex mixtures. Therefore, the utilization of biomarkers or indicators to evaluate biological responses to pollutants must be increased.

7.6 Conclusions and Outlook

Harbour and coastal sediments behave as a sink of many xenobiotics, which are released into the environment as a consequence of increasing industrial activities. During the recent years, significant research has been devoted to the optimization of treatment methods with and 'end-of pipe' approach. On the other hand, the precautionary approach has too often been ignored by short-sighted strategies or by specific financial interests that are in conflict with long-term environmental protection and sustainability. In the light of the application of the precaution principle, further studies, also in the framework of REACH, should include the monitoring of old and new chemicals in marine sediments and the estimation of their toxicity.

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Chapter 8
Determination of Sources and Emissions of Persistent Organic Contaminants by Means of Sewage Sludge: Results from a Monitoring Network

Thomas Kupper, Luiz Felipe de Alencastro, and Jean-Daniel Berset

Abstract Sewage sludge contains a plethora of organic pollutants. In the present chapter, the experiences with respect to the applicability of sewage sludge as a matrix for the monitoring of persistent lipophilic contaminants released from the anthroposphere are reported and discussed. Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides, phthalates, UV filters, biocides, synthetic fragrances, polybrominated flame retardants (BFRs) and surfactants were analyzed in stabilized sewage sludge from more than 20 sites (wastewater treatment plants, catchment area) of a monitoring network in Switzerland. The specific loads (mg or g per connected inhabitant and year) in sewage sludge were used for characterizing the emissions of the compounds. A background contamination from private households was observed for all analyzed substances. Synthetic fragrances predominantly occurred in domestic wastewater. An important additional source for PAHs, PCBs, biocides and BFRs was runoff from impervious surfaces contaminated with substances originating from atmospheric deposition or leaching from treated materials. Industrial wastewater and mainly urban catchments were responsible for further loads. The specific loads observed complied with consumption patterns of the compounds obtained from the literature.

T. Kupper (✉)
Swiss College of Agriculture (SCA), 3052 Zollikofen, Switzerland
e-mail: thomas.kupper@bfh.ch

L.F. deAlencastro
Ecole Polytechnique Fédérale de Lausanne (EPFL), Environmental Science and Technology Institute, Central environmental laboratory (ENAC-ISTE-GR-CEL), 1015 Lausanne, Switzerland

J.D. Berset
Water and Soil Protection Laboratory (GBL), Schermenweg 11, 3014 Bern, Switzerland

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8.1 Introduction

Many pollutants which are released into the environment by human activities are found in wastewater. They enter the wastewater stream by direct release from private households and industry or by aerial deposition on impervious surfaces and subsequent runoff into the sewer system. At the wastewater treatment plants (WWTPs), persistent and lipophilic substances mainly sorb onto solids and are then transferred to sewage sludge. As a consequence, sewage sludge contains many important recalcitrant lipophilic compounds. It accumulates them over a period of several weeks to months. The utility of sewage sludge as a rapidly responding, valuable monitoring media has already been recognized (Oeberg et al. 2002; Hale et al. 2006; Ricklund et al. 2008). In order to describe the sources of pollutants and their distribution in the environment based on sewage sludge, the properties of the WWTP and its catchment must be known. Therefore, the project SEA (observation of the metabolism of the anthroposphere) was launched in order to investigate this issue. Between 1997 and 1998, a network of some 30 monitoring sites (WWTP and the corresponding catchment) in Switzerland was set up (Fig. 8.1). This monitoring network comprises three types of sites. Sites of type A include a separate sewer system and a rural catchment without industrial activities apart from a few craft industries. The sewage sludge originating from these sites comprises almost exclusively compounds which are used in private households. Sites B exhibit the same characteristics as type A but the catchment has a combined sewer system and some more craft industries. Apart from compounds

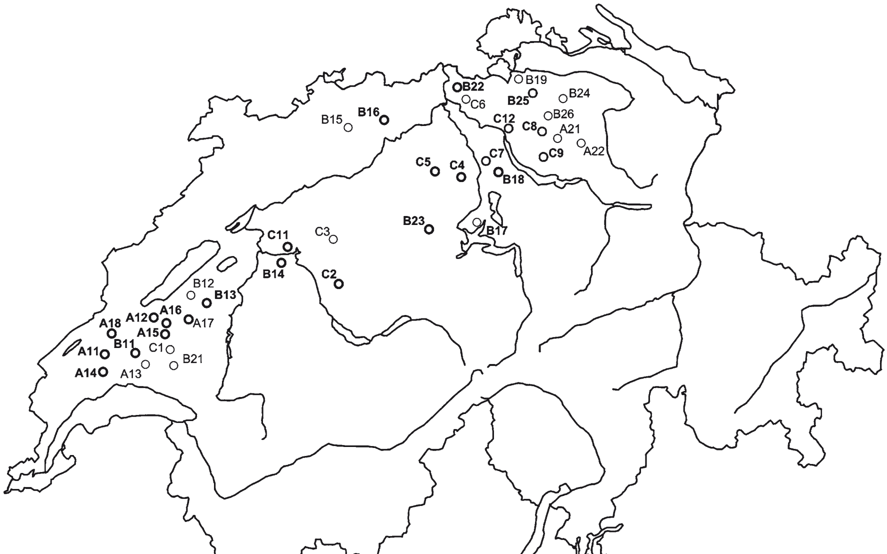

Fig. 8.1 Monitoring network of project SEA with monitoring sites A11-22, B11-26 and C1-12. Sites with *bold letters* were sampled within the studies presented in this chapter

released by private households, these sludges include compounds contained in surface runoff. Sites of type C have a combined sewer system and an urban catchment including industry and craft industry. Therefore, the sludge produced contains compounds of industrial origin besides substances originating from private households and surface runoff. Conclusively, this monitoring network can be used for the determination of the following main sources of lipophilic and persistent contaminants: private households (type A), surface runoff contaminated by atmospheric deposition or leachings from outdoor exposed surfaces or facilities (type B), industry and craft industry (type C). For this purpose, information on these monitoring sites relevant for characterizing the release of pollutants was collected, i.e. the technology of wastewater treatment, the sewer system, the socio-economic structure of the communities connected to the WWTP and the activities of industry or craft industry in the catchment. Consequently, several groups of organic contaminants were analyzed in aerobically or anaerobically stabilized sewage sludge (Berset and Holzer 1999, 2001; Plagellat et al. 2004, 2006; Kupper et al. 2004, 2008). The results were examined with respect to their applicability as an efficient and cost-effective tool for monitoring lipophilic, persistent organic pollutants. The specific issues and the aims of these studies were: (a) the determination of the specific loads of persistent organic pollutants in sewage sludge collected in different types of monitoring sites and (b) the identification of the main sources of the contaminants. In the present chapter, the experiences with respect to these monitoring purposes are reported and the applicability of the monitoring network for monitoring lipophilic persistent organic pollutants is discussed.

8.2 Materials and Methods

8.2.1 Compounds Analyzed

Within project SEA, a series of compounds was analyzed (Table 8.1).

Information on sources, applications, production volumes and ecotoxicological properties of the compounds analyzed can be obtained from Berset and Holzer (1999, 2001), Scott and Jones (2000), Plagellat et al. (2004, 2006) and Kupper et al. (2004, 2008).

8.2.2 Sampling and Analytical Methods

Samples of aerobically or anaerobically stabilized sewage sludge were collected from the storage tanks at the WWTPs of this monitoring network. This procedure provided sampling material produced over several weeks to months. It replaces continuous sampling over the same period and is likely to be much less laborious and costly. Before sampling, the sludge in the storage tank was homogenized with a stirring device. Samples were collected from the storage tank using a sampling bottle

Table 8.1 Compound classes and individual compounds analyzed

16 EPA priority polycyclic aromatic hydrocarbons (16 PAHs)
Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a*,*h*]anthracene, benzo[*ghi*]perylene
Polychlorinated biphenyls (PCBs)
Seven PCB congeners (IUPAC numbers 28, 52, 101, 118, 153, 138 and 180)
Organochlorine pesticides (OCPs)
Aldrin, *p,p’*-DDD, *p,p‘*-DDE, *p,p’*-DDT, dieldrin, α-endosulfan, endrin, β-HCH, γ-HCH, heptachlor, heptachlor-epoxide, hexachlorobenzene
Phthalates
Dimethyl phthalate (DMP), di-ethyl phthalate, (DEP), diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), bis(methoxyethyl) phthalate (DMoEP), bis(methylpentyl) phthalate (DMPP), bis(ethoxyethyl) phthalate (DEoEP), diamyl phthalate (DAP), dihexyl phthalate (DHP), butylbenzyl phthalate (BBP), hexyl-2-ethylhexyl phthalate (HEHP), bis(2-*n*-butoxyethyl) phthalate (DBoEP), bis(2-ethylhexyl) phthalate (DEHP), dicyclohexyl phthalate (DCHP), di-*n*-octyl phthalate (DnOP), dinonyl phthalate (DNP)
UV filters
3-(4-methylbenzylidene) camphor (4-MBC), octyl-methoxycinnamate (OMC), octocrylene (OC), octyl-triazone (OT)
Biocides
Organic biocides: carbendazim, diuron, Irgarol 1051, octhilinone, permethrin; organotin biocides: tributyltin (TBT), triphenyltin (TPT)
Synthetic fragrances
Polycyclic musks (PCMs): galaxolide (HHCB), tonalide (AHTN), celestolide (ADBI), phantolide (AHDI), traseolide (ATII), HHCB-lactone (metabolite of HHCB)
Brominated flame retardants (BFRs)
Polybrominated diphenyl ethers (PBDEs): 13 PBDE congeners (IUPAC numbers 28, 47, 49, 66, 85, 99, 100, 119, 138, 153, 154, 183, 209); hexabromocyclododecane (HBCD)
Surfactants
Metabolites of nonylphenol ethoxylates: nonylphenol (NP), nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO); linear alkylbenzene sulfonates (LAS): C_{10}-LAS, C_{11}-LAS, C_{12}-LAS, C_{13}-LAS

with flexible bottom and lid at several points from the rim or the bridge of the storage tank. The bottle was brought to different depths in the sludge. Samples were obtained by closing the bottom and the lid of the bottle at the adequate position. Eight to fifteen aliquots of 2 L each were collected in a container. The composite sample was cautiously homogenized before transferring the sample into glass jars. All sampling devices were of aluminum and were carefully rinsed with tap water before use. During all operations, contact of the samples with plastic materials was strictly avoided. Sampling campaigns were carried out in 1998 for PAHs, PCBs, OCPs and phthalates. Samples for analyses of UV filters, biocides, PCMs were collected in 2001 and of BFRs in 2003. Repeated sampling for the study on surfactants was conducted in 2000, 2001 and 2004. The sampling campaigns were carried out in winter or spring when the storage tanks included sludge produced over a preferably longer time period (between 30 and 300 days). For UV filters, biocides, PCMs and BFRs, the sampling was repeated within the same year during summer.

Analytical methods and properties of the WWTPs are described in Berset and Holzer (1999, 2001), Wettstein (2004), Plagellat et al. (2004, 2006) and Kupper et al. (2004, 2008).

8.2.3 Determination of the Specific Loads

The release of a substance into the wastewater might be misinterpreted if concentrations in sewage sludge are considered only. High loads of organic matter from food processing industry result in a high sludge production at the treatment plant for example. This might dilute the concentration of the analyte. The specific load in sewage sludge per inhabitant connected (capita) per year accounts for these effects and is thus a more reliable parameter. The specific load of a compound is defined as follows:

$$L_{sp(i)} = C_{ss(i)} \times P_{ss} \times cap^{-1} \tag{8.1}$$

$L_{sp(i)}$: load of substance *i* in sewage sludge per inhabitant connected per year (mg cap^{-1} $year^{-1}$) (specific load)

$C_{ss(i)}$: concentration of substance *i* in the dry matter (d.m.) of aerobically or anaerobically stabilized sewage sludge (mg kg d.m.$^{-1}$)

P_{ss}: amount of aerobically or anaerobically stabilized sewage sludge produced by the WWTP (kg d.m. year^{-1})

cap: number of inhabitants connected to the WWTP

The amount of produced stabilized sewage sludge provided by the personnel of the WWTPs was determined by recording the volume of aerobically or anaerobically stabilized sludge transported for use in agriculture or incineration and by the analysis of the dry matter (d.m.) content of each transported batch.

8.3 Results and Discussion

8.3.1 Concentrations of Organic Pollutants in Sewage Sludge

The concentrations of the analyzed organic pollutants in sewage sludge have already been reported in several papers (Berset and Holzer 1999, 2001; Plagellat et al. 2004, 2006; Kupper et al. 2004, 2008; Kupper 2008), and are only briefly summarized here. The mean content of PAHs (i.e. the sum of 16 PAHs; see Table 8.1) was 7160 μg kg d.m.$^{-1}$. The three-ring PAHs such as phenanthrene or anthracene dominated over the other compounds reaching 40% of the total amount. The mean of PCBs (sum of seven congeners; see Table 8.1) was at 93.5 μg kg d.m.$^{-1}$. The higher chlorinated congeners tended to exhibit higher contents compared to the low molecular weight PCBs. HCB, γ-HCH, aldrin, heptachlor-epoxide, α-endosulfan, DDE, DDD and DDT were found in the majority of the samples with mean contents between 2.2 μg kg d.m.$^{-1}$ (HCB) and 72.2 μg kg d.m.$^{-1}$ (heptachlor-epoxide). Dieldrin was detected in five, β-HCH in three, heptachlor in two and endrin in one sample. The concentrations were mostly in the low ppb range. Concentrations of phthalates ranged from 7.9 μg kg d.m.$^{-1}$ (mean of DMP) to 51.2 mg kg d.m.$^{-1}$ (mean of DEHP). DIBP, DBP and DEHP were found in all samples. DMP, DEP, HEHP, DCHP, DnOP and DNP occurred less frequently (in two to eight out of 11 samples). DMoEP, DMPP, DEoEP, DAP, DHP, BBP and DBoEP were not detected. The mean contents of the UV filters 4-MBC, OC and OT as of the PCMs, HHCB, AHTN and HHCB-lactone were in the order of magnitude of 10^3 μg kg d.m.$^{-1}$. The concentrations of OMC, the biocides carbendazim, diuron, permethrin, TBT and TPT as well as of the synthetic fragrances ADBI, AHDI, ATII, of PBDE and of HBCD reached approximately 10–100 μg kg d.m.$^{-1}$. All these substances occurred in every sample analyzed except for TPT and Irgarol 1051 which were found in 11 and seven samples, respectively, out of 24 samples. Octhilinone was never detected which is probably due to the rapid elimination of this compound in the sewer or during wastewater treatment (Rafoth et al. 2007).

In 2004, mean values for the sum of the metabolites of nonylphenol ethoxylates (NP, NPnEO) were in the range of 40 mg kg d.m.$^{-1}$ with NP as the most important compound. LAS showed concentrations of approximately 2,500 mg kg d.m.$^{-1}$.

It is necessary to bear in mind that the first sampling campaign of 1998 generating results for PAHs, PCBs, OCPs and phthalates, was carried out in terms of a pilot study. Sampling material allowing for multiple analyses was provided in the second phase of the project (2001–2004) only. Thus, the results obtained for the compound classes are not implicitly comparable for all years, i.e. a shift might occur for compounds such as OCPs which were phased out and which exhibit a declining burden in the anthroposphere and in the environment. However, it is assumed that a shift is limited within the time span of 6 years between the first and the last sampling campaign.

8.3.2 Specific Loads of the Compounds and Determination of the Main Pollutants Sources

The specific loads of the sum of PAHs, PCBs, OCPs, phthalates, UV filters, organic and organotin biocides, PCMs, PBDEs, HBCD and surfactants in sewage sludge are shown in Table 8.2. LAS exhibit the highest specific loads ranging between 3.2 g cap^{-1} year^{-1} (mean for sites of type A) and 87.2 g cap^{-1} year^{-1} (mean for sites of type C). This is most likely the consequence of the direct discharge into the wastewater after usage inducing the transfer of the major part of the emissions to the WWTPs. Specific loads of phthalates and NP, NPnEOs were between 0.2 g cap^{-1} year^{-1} (mean for type A) and 1.4 g cap^{-1} year^{-1} (mean for type C). PAHs, UV filters and PCMs reached loads in the range from 52.5 to 763 mg cap^{-1} year^{-1} which is higher by one or two orders of magnitude compared to the loads of PCBs, OCPs, biocides and BFRs.

The study on NP, NPnEO and LAS was repeated in 2000, 2001 and 2004. The mean specific loads of the 21 monitoring sites investigated are shown in Fig. 8.2.

Table 8.2 Specific loads (loads per connected inhabitant per year): sum of PAHs, PCBs, OCPs, phthalates, UV filters, organic and organotin biocides, PCMs, PBDEs, HBCD (mg cap^{-1} year^{-1}), surfactants (NP, NPnEO) and LAS (g cap^{-1} year^{-1}) in sewage sludge of different types of monitoring sites

	Site A[b]			Site B[c]			Site C[d]		
	Mean	Range	n[e]	Mean	Range	n[e]	Mean	Range	n[e]
Compounds[a]	(mg cap^{-1} year^{-1})			(mg cap^{-1} year^{-1})			(mg cap^{-1} year^{-1})		
PAHs	52.5	23.6–120	4	143	108–175	3	200	102–330	4
PCBs	1.2	0.8–1.6	4	1.9	1.4–2.6	4	3.0	0.9–4.0	4
OCPs	5.0	4.8–5.2	4	3.7	1.0–6.2	3	5.3	4.6–6.6	4
Phthalates	868	376–1’577	4	1’073	553–2’292	4	1’575	302–3’362	4
UV filters	61.4	27.0–105	4	200	109–281	4	262	170–389	4
Organic biocides	1.0	0.4–1.6	4	2.8	1.6–4.4	4	2.8	1.8–3.4	4
Organotin biocides	1.7	1.0–2.1	4	2.9	0.6–5.3	4	3.8	2.7–6.4	4
PCMs	524	247–884	5	540	419–668	6	763	496–975	5
PBDEs	5.8	4.6–7.2	4	7.3	5.2–11.3	4	10.3	5.7–19.8	8
HBCD	1.2	0.4–2.2	4	2.5	0.9–5.6	4	4.8	2.6–6.4	8
	(g cap^{-1} year^{-1})			(g cap^{-1} year^{-1})			(g cap^{-1} year^{-1})		
NP, NPnEOs	0.2	0.1–0.3	7	0.9	0.2–2.7	8	1.4	0.6–2.7	6
LAS	3.2	1.2–4.5	7	62.9	1.1–104	8	87.2	52.0–143	6

[a] Sum of individual compounds listed in Table 8.1

[b] Site A: Separate sewer systems with mainly domestic wastewater

[c] Site B: Combined sewer system with wastewater from private households, craft industries, and surface runoff

[d] Site C: Combined sewer system with wastewater from private households, surface runoff, industries and craft industries

[e] Number of sites

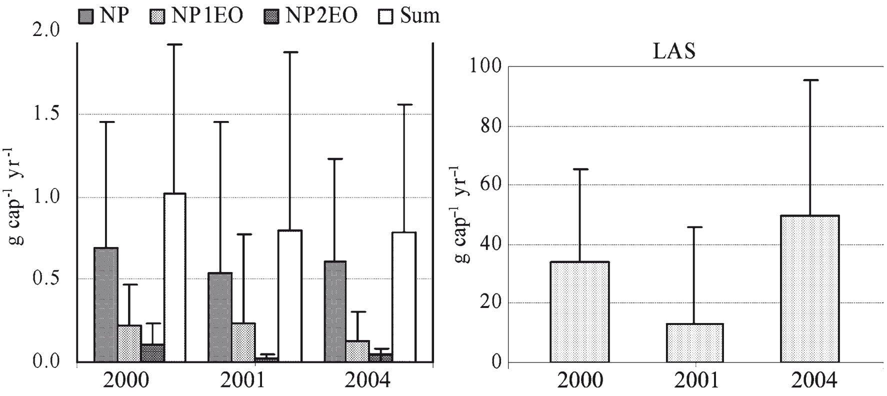

Fig. 8.2 Time series of surfactants (NP, NPnEO and LAS) in sewage sludge: mean specific load from 21 monitoring sites in g cap^{-1} $year^{-1}$ (*vertical bars*: standard deviation) for 2000, 2001 and 2004

Considering the large standard deviation, the contamination levels of sewage sludge do not show a trend. In 1986, the use of octyl- and nonylphenol ethoxylates for textile washing agents was banned in Switzerland which resulted in a strong decrease of the contents in sewage sludge and wastewater in the 1990s (Wettstein 2004). Since then, little further reduction was achieved. For LAS, constant emissions are to be expected because the consumption remained unchanged or slightly increased since the 1990s according to data obtained from De Wolf and Feijtel (1998) and Jensen et al. (2007).

For all compound classes, a background level was observed at sites of type A which results from the direct input into the sewer system by domestic wastewater. This is due to direct inputs by usage of products (e.g. household and personal care products containing PCMs, UV filters, surfactants or biocides) or due to washing and cleaning activities during which dust contaminated with compounds such as BFRs, phthalates or surfactants (Rudel et al. 2003) is collected and released to wastewater. As for BFRs, washing of textiles might contribute to the burden of some PBDEs congeners ending up in WWTPs (Anonymous, 2002). Apart from OCPs and PCMs, all compounds exhibited higher loads on sites of type B compared to sites of type A. For NP, NPnEOs and LAS, this can be explained by the wastewater treatment system. All WWTPs of type A are of an extended aeration type with a higher solids retention time of 20 days or more compared to 7–10 days of the activated sludge systems operating at the sites of type B and C. This results in a higher degradation of the surfactants during wastewater treatment. The other compounds enter the WWTPs to a significant extent indirectly through surface runoff which is likely to be responsible for the higher loads on sites of type B compared to sites of type A. These substances are emitted from the matrix in which they are incorporated by volatilization or by leaching. BFRs, for example, are covalently bound in plastics from where they are released during the lifetime of the products. They reach impervious surfaces by atmospheric deposition or leaching from treated materials and are transferred with the surface runoff into the sewer system. Biocides which are included in film preservatives or in paints might leach from treated surfaces (mainly building envelopes, i.e. facades and roof sealing membranes) and end up in surface runoff as well. In the WWTP, the compounds investigated preferentially partition onto solids and are incorporated in sewage sludge. In contrast to the compounds which are expected to originate mainly from aerial deposition OCPs do not exhibit additional loads on type B compared to type A. This observation could not be explained.

For compounds such as PCMs with emissions predominantly originating from direct inputs into domestic wastewater due to their usage in household and personal care products, the specific loads did not differ significantly at the different types of monitoring sites. Somewhat higher specific loads on sites of type C compared to sites B were observed for all compound classes (except for organic biocides). This can be explained by additional inputs which are induced by a higher extent of anthropogenic activities in the mainly urbanized catchments or due to discharges from the industry and craft industry (e.g. production of plastics commodities).

European consumption volumes of the compounds studied have been assessed in order to check the specific loads for plausibility (Table 8.3). For organic biocides and UV filters, the amounts were extrapolated from Swiss data since no figures for Europe were available from the literature. The compounds with the highest production volumes (surfactants, phthalates) exhibited the highest specific loads. Although both compound classes are degraded during wastewater and sludge treatment (Staples et al. 1997; Scott and Jones 2000), the high volumes outweighed the reduction of the loads in sewage sludge due to degradation. For substances such as UV filters, organic biocides, PCMs and BFRs which have comparable production volumes and preferentially partition onto solids in the WWTPs (Kupper et al. 2006) due to their high octanol-water partition coefficients (log K_{ow} > 5 for most of the compounds) similar loads are expected. The discrepancies observed can be explained by their different emission pathways. UV filters and PCMs are incorporated in many products (e.g. personal care products)

Table 8.3 Consumption volumes for phthalates, UV filters, organic and organotin biocides, PCMs, PBDEs, HBCD and surfactants for Europe in 1,000 t year^{-1}

	Consumption Europe[a]	
	1,000 t year^{-1}	
Phthalates	1,000	Kollotzek et al. (1998)
UV filters	3[b]	Plagellat et al. (2006)
Organic biocides	4.8[b]	Bürgi et al. (2007)
Organotin biocides	1.3	Klingmüller and Watermann (2003)
PCMs	1.8	Kupper et al. (2004)
PBDEs	8.4	Kupper et al. (2008)
HBCD	9.5	Kupper et al. (2008)
NP, NPnEOs	73.5	Soares et al. (2008)
LAS	430	Jensen et al. (2007)

[a] Figures from Europe were used since Swiss data were available for some compound classes only
[b] Figure extrapolated from Swiss data

which are directly discharged to the sewer after usage. For organic biocides and BFRs, indirect immissions are likely to dominate and therefore, only a part of the emitted amount ends up in WWTPs. For PCMs, the specific loads in sewage sludge coincide well with the consumption of the single compounds (HHCB>AHTN>>other PCMs; Kupper et al. 2004). In contrast to PCMs, this could not be observed for UV filters. The substance with the highest usage volume (OMC) exhibited the lowest specific load since it is largely degraded in the WWTP (Kupper et al. 2006).

PCBs and OCPs were still detectable due to their persistence, although low specific loads were observed. The low contamination level is plausible due to the phase out of these compounds. Interestingly, specific loads for BFRs were in the same order of magnitude as the total of organochlorines. This might indicate that the contamination of the anthroposphere and of the environment induced by these two compound classes has reached a similar level.

8.4 Conclusions

The present study provides valuable information for monitoring the release of several classes of organic contaminants (PAHs, PCBs, OCPs, phthalates, UV filters, organic and organotin biocides, PCMs, PBDEs, HBCD and surfactants) on the basis of sewage sludge collected from a monitoring network. Although degradability and emission pathways of the monitored substances as well as the wastewater treatment technology might influence the mass loads and thus hamper their conclusive interpretation, the results were consistent with production patterns of the compounds and the determination of the main sources. For surfactants, consistency between emissions trends over several years and assessed consumption volumes was obtained.

In conclusion, sewage sludge obtained from a monitoring network as outlined in this study represents an interesting matrix and allows for tracking important sources of lipophilic and persistent organic contaminants and for monitoring time trends of emissions. It provides a valuable tool for controlling the efficiency of measures dedicated to regulate mass flows of pollutants and to prevent adverse effects for receiving waters.

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Part II
Fate, Effects and Risks of Xenobiotics in Urban Waters

Chapter 9
Metabolic and Co-metabolic Degradation of Industrially Important Chlorinated Organics Under Aerobic Conditions

Ferhan Çeçen, Bilge Alpaslan Kocamemi, and Özgür Aktaş

Abstract Chlorinated organic compounds are the frequently detected xenobiotics in industrial effluents. They may enter surface water, groundwater and soil systems. Examples are presented on the level of these compounds in aquatic systems. The chapter then addresses the biological removal of these compounds by aerobic metabolism in which the substrate is used as an energy and carbon source. However, the major part of chlorinated organic compounds is resistant to metabolic removal. Yet, some can effectively be removed through aerobic co-metabolism in bioremediation of polluted groundwater and soil and in wastewater treatment systems. In aerobic co-metabolic removal of these compounds different types of substrates can be used as primary growth-substrates such as phenol, toluene, propane, methane, ammonia and others which are extensively reviewed in this chapter. The basic features of natural and enhanced bioremediation are also outlined in the chapter. The aerobic co-metabolism is exploited mainly for bioremediation of chlorinated aliphatic compounds such as trichloroethylene (TCE) in groundwater and in some cases for chlorinated benzenes and phenols. Examples of field-, pilot- and laboratory studies are documented which deal with aerobic co-metabolic removal of chlorinated compounds.

9.1 Introduction

Chlorinated aliphatic and aromatic hydrocarbons are used in various industries such as organic chemical manufacturing, pharmaceutical, metal finishing, PVC, rubber processing, paint and ink, electronics, and laundries and are released to the aquatic

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F. Çeçen (✉) and Ö. Aktaş
Boğaziçi University, Institute of Environmental Sciences, 34342 Bebek Istanbul, Turkey
e-mail: cecenf@boun.edu.tr Phone: + 90 212 359 72 56, Fax: + 90 212 257 50 33,

B.A. Kocamemi
Department of Environmental Engineering, Marmara University, 34722 Göztepe,
Istanbul, Turkey

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environment through industrial effluents, disposal by consumers, emissions from landfills, leakage from underground storage tanks and accidental spills. Significant concentrations of these pollutants have been detected in groundwaters, surface waters, drinking waters and industrial effluents. Table 9.1 lists a few examples of the detected levels of these contaminants in various media.

Due to their often carcinogenic and toxic potential and slow breakdown rates in the environment (ATSDR 2008), the removal of these compounds is of interest mainly in groundwater and soil remediation and in the treatment of municipal and hazardous landfill leachate, wastewater and drinking water. The aim of this chapter is to delineate the metabolic (direct) and co-metabolic removal of these compounds in aerobic biological systems and to present examples on bioremediation. Aerobic biodegradation often leads to full mineralization of these compounds although biotransformation is also possible depending on the type of substrate and conditions.

Table 9.1 Detected levels of industrially important chlorinated organic compounds in the environment

Compound	Detected levels/media	References
CM	3.1–500 ppt/landfill leachate	ATSDR (2008)
DCM	0–3,600 ppb/groundwater	ATSDR (2008)
	64–1,300 ppb/leachate	Sabel and Clark (1984)
	70–200,000 ppb/hazardous landfill leachate	Sabel and Clark (1984)
CF	2.1–18,90 ppb/groundwater	ATSDR (2008)
	21,800 ppb /leachate	
CT	1–720 ppb/groundwater	ATSDR (2008)
1,1-DCA	310–56,100 ppb/groundwater	ATSDR (2008)
1,2-DCA	300,000 ppb/groundwater	Dyer et al. (2000)
1,1,1-TCA	0–11,000 ppb/groundwater	ATSDR (2008)
1,1,2-TCA	700–1,800 ppb/groundwater	
	700–1,800 ppb/groundwater	Kuo et al. (2000)
VC	22,000–100,000 ppb/groundwater	ATSDR (2008)
1,1-DCE	94 ppb/groundwater	ATSDR (2008)
TCE	44–180,000 ppb/groundwater	
	7,700 ppb/leachate	ATSDR (2008)
PCE	0.2–23,000 ppb/groundwater	ATSDR (2008)
	590 ppb/leachate	
PCBs	1,200 ppb/groundwater	ATSDR (2008)
MCB	3,130–33,000 ppb/groundwater	Wünsche et al. (1999)
1,2-DCB	20–180 ppb/groundwater	Wünsche et al. (1999)
1,4-DCB	90–1,000 ppb/groundwater	Wünsche et al. (1999)
TCB	40 ppb/groundwater	Tiehm et al. (2000)
2,4 DCP	3.3 ppb/groundwater	Wünsche et al. (1999)
TCP	9.2 ppb/groundwater	Wünsche et al. (1999)

9.2 Metabolic Removal of Chlorinated Organics in Aerobic Systems

9.2.1 Aliphatic Chlorinated Hydrocarbons

Among aliphatic chlorinated hydrocarbons (ALCH) the lower chlorinated methanes having one or two chlorine atoms in the molecule, which include monochloromethane (CM) and dichloromethane (DCM), are primary growth-substrates supplying carbon and energy while higher chlorinated methanes having three or more chlorine atoms in the structure, such as chloroform (CF) and carbon tetrachloride (CT), are not utilized as such under aerobic conditions. Also, the lower chlorinated ethanes, which include monochloroethane (CA), 1,1-dichloroethane (1,1-DCA) and 1,2-dichloroethane (1,2-DCA), can be utilized as primary growth-substrates by aerobic bacteria. But, no aerobic biodegradation is yet known for the higher chlorinated ethanes, which include the trichloroethanes 1,1,1-TCA, 1,1,2-TCA, various isomers of tetrachloroethane (TeCA), pentachloroethane (PCA), and hexachloroethane (HCA) (Field and Sierra-Alvarez 2004). Lower chlorinated ethenes, which include vinyl chloride (VC) and dichloroethene (DCE), can be utilized under aerobic conditions while higher chlorinated ethenes, which include trichloroethylene (TCE) and tetrachloroethene (PCE), are not utilized as such (Bradley 2003; Field and Sierra-Alvarez 2004).

9.2.2 Aromatic Chlorinated Hydrocarbons

Microorganisms have also the capability to use aromatic chlorinated hydrocarbons (ARCH) as sole carbon and energy sources under aerobic conditions. Several bacteria were reported that can use mono-, di- and tri-chlorinated benzenes as the only source of carbon and energy (Spain 1997; Chaundry and Chapalamadugu 1991). The highly chlorinated hexachlorobenzene (HCB) is aerobically non-biodegradable. In contrast to that, the highest chlorinated phenol, which is pentachlorophenol (PCP) is aerobically mineralized because of the presence of a hydroxyl group in the molecule and seems to be better degradable aerobically than anaerobically (ICSS 2006). Both the position and the number of chlorine atoms were shown to affect biodegradability. The dichlorobenzenes 1,2-DCB, 1,3-DCB and the trichlorobenzene 1,2,4-TCB were degraded at significantly lower rates compared with monochlorobenzene (MCB) and 1,4-DCB (Dermietzel and Vieth 2002).

Puhakka et al. (1992) achieved degradation of high concentrations of various chlorophenols in anoxic and aerobic biofilm reactors with acclimated bacteria. However, only trace concentrations of chlorophenols were biodegraded in conventional municipal sewage treatment plants (Ettala et al. 1992). One way of degradation of chlorinated aromatic compounds is via an initial oxygenation of the aromatic ring. Halogenated phenols are generally more resistant to aerobic degradation compared with phenol (Fahmy et al. 1994) although some exceptional cases also exist; e.g. a chlorophenol-degrading strain could degrade 4-chlorophenol (4-CP) completely and much faster than phenol owing to different catabolic pathways (Unell et al. 2008).

The presence of one chlorinated compound can inhibit the biodegradation of another one. For example, Bae et al. (1995) found that although phenol was completely biodegraded, addition of dichlorophenol (DCP) and pentachlorophenol (PCP) resulted in incomplete biodegradation of multiple phenolic compounds. The long-term exposure of a mixed culture to chlorinated phenols resulted in a decrease in growth rates and increased substrate inhibition which was probably caused by a loss in bacterial species diversity.

Acclimation of mixed bacterial cultures to chlorophenols successfully increases their biodegradability. Aktaş (2006) showed that both phenol and 2-CP were biodegraded much more readily with phenol-acclimated microorganisms rather than non-acclimated ones. In the study of Buitron et al. (1998) an acclimated activated sludge could degrade a mixture of chlorophenols by one or two orders of magnitude faster than pure strains obtained from the acclimated consortium. This indicates that more than one strain may be involved in biodegradation of chlorophenols.

Bioaugmentation or addition of microorganisms is generally effective for one target pollutant or a group of pollutants, but has been successfully applied only in few cases (Quan et al. 2005). An activated sludge system bioaugmented with 2, 4-DCP degrading special culture could degrade both 2,4-DCP and 4-CP. The study of Lewandowski and Varuntanya (1988) showed that the use of mixed cultures is more efficient than isolated pure cultures. Rarely can a single aerobic species totally mineralize chlorinated phenols (Şahinkaya and Dilek 2005).

9.3 Co-metabolic Removal of Chlorinated Organics in Aerobic Systems

9.3.1 Basic Mechanisms in Aerobic Co-metabolism

In recent years, specific organic chemicals have become of concern and the goal is often to reduce concentrations to the low microgram per litre level, or even lower. Lower limits can also be achieved by proper design of treatment systems that base on the principle of co-metabolism. (McCarty 2000). Co-metabolism is the biological transformation of a non-growth (co-metabolic) substrate by bacteria through enzymes which can only be induced in the presence of a growth-substrate providing energy for cell growth and maintenance.

Non-growth substrates have a similar structure to growth-substrates and can bind to enzymes and be transformed due to non-specific activity.The aerobic co-metabolic transformation of chlorinated organics (Fig. 9.1) is catalyzed by non-specific oxygenase enzymes that use molecular oxygen as the electron acceptor and NAD(P)H as the reducing energy to oxidize both growth- and non-growth

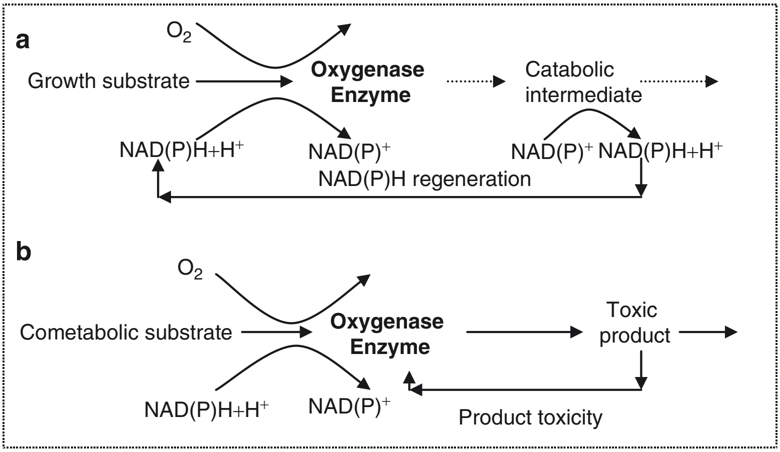

Fig. 9.1 Typical oxygenase enzyme reactions for growth-substrate and co-metabolic (non-growth) substrate (Chang and Alvarez-Cohen 1995b)

substrates (Chang and Alvarez-Cohen 1995a, b). Any organism with an active mono- or di-oxygenase enzyme has the potential for co-metabolic transformation of chlorinated organic compounds (Ward et al. 1997). Particularly, oxidative enzymes (e.g. oxygenases) responsible for the oxidation of phenols, ammonia and methane by various microorganisms have non-specific activities toward non-growth substrates (Kim and Hao 1999). However, some factors such as the inhibitory effects of the initial growth-substrate or co-metabolic substrate on the enzyme as well as the inhibitory effects of products and limitations in NAD(P)H generation may adversely affect the degradation (Alvarez-Cohen and Speitel 2001). As shown in Fig. 9.1, short-lived toxic intermediate products may cause damage on oxygenase enzyme or cell.

In this case, co-metabolic oxidation of the non-growth substrate consumes the reductant NAD(P)H which is then not regenerated (Fig. 9.1). Thus, NAD(P)H, which is a potentially limiting reactant during co-metabolic reactions, must be provided by external or endogenous regenerants. The products of growth-substrate oxidation may undergo further degradation that regenerates NAD(P)H for additional substrate oxidations (Fig. 9.1). Therefore, it is essential that a growth-substrate is provided at least periodically for growth of new cells and induction of enzyme production (Alvarez-Cohen and Speitel 2001). Co-metabolic degradation occurring in the absence of external regenerants is referred to as the resting cells condition. In this case, the reducing energy can only be provided by endogenous energy sources or general biomass that often limits the co-metabolic degradation rate and leads to product toxicity (Chang and Alvarez-Cohen 1995b; Kim and Hao 1999). Competitive inhibition has often been observed between the growth- and co-metabolic substrates. It may lower the co-metabolic degradation rates and vice versa (Chang and Alvarez-Cohen 1995b). However, as reported in a review, non-competitive inhibition is also possible for an ammonia monooxygenase (AMO) utilizing pure culture degrading monohalogenated methanes, ethanes and chloropropane and for a propane-oxidizing mixed culture degrading TCE (Alvarez-Cohen and Speitel 2001).

9.3.2 *Aerobic Co-metabolism Using Phenol, Toluene, Propane and Other Organics As Primary Substrates*

Co-metabolic degradation of various chlorinated organics by phenol, toluene or propane oxidizers is widely reported. For example, TCE was degraded by propane, toluene and phenol oxidizers whereas CF and 1,2-DCA were not degraded by toluene and phenol oxidizing bacteria (Chang and Alvarez-Cohen 1995a, b). Co-metabolic TCE degradation in the presence of toluene was also shown in other studies (Field and Sierra-Alvarez 2004; Yeager et al. 2004). In addition, VC and DCE and in one case PCE co-metabolism was demontrated when toluene was the primary substrate (Field and Sierra-Alvarez 2004).

Speitel and Segar (1995) studied the co-metabolic degradation of various chlorinated aliphatics by a mixed culture of phenol degraders in biofilm reactors. PCE could not be degraded whereas the maximum specific degradation rate of others was as cis-1,2-DCE > TCE > 1,1-DCE > trans-1,2-DCE.

In co-metabolic transformation of chlorinated phenols, phenol serves as an ideal growth-substrate for phenol oxidizers to induce necessary enzymes due to its structural analogy. For example, biodegradation of 2-CP and 4-CP was successfully enhanced in the presence of phenol (Basu and Oleszkiewicz 1995; Li and Loh 2005; Aktaş 2006; Farabegoli et al. 2008). Although 2-CP was not biodegraded when used as the only carbon source (Aktaş and Çeçen 2007), in another study (Aktaş and Çeçen 2009) co-metabolic removal of 2-CP followed the metabolic removal of phenol as shown in Fig. 9.2. As in the case of ALCHs, aerobic transformation leads finally to the release of chloride from which the extent of dechlorination can be assessed.

Co-metabolic transformation of chlorophenols was enhanced in the presence of phenol as the primary substrate when pure and mixed cultures were acclimated (Chiavola et al. 2004; Kim and Hao 1999; Loh and Wu 2006; De Los Cobos-Vasconcelos et al. 2006). Particularly, mixtures of bacterial cultures showed better co-metabolic transformations than single strains (Salmeron-Alcocer et al. 2007). The same type of behavior was also observed in the case of metabolic removal.

Easily biodegradable compounds such as glucose and dextrose can also serve as primary substrates in co-metabolism. 4-CP (Wang and Loh 1999), 2,4 DCP (Ziagova and Liakopoulou-Kyriakides 2007a) and 1,2-DCB (Ziagova and Liakopoulou-Kyriakides 2007b) were co-metabolically degraded in the presence of glucose. Another study demonstrated the aerobic co-metabolism of the chlorobenzoate (2-CBA) and the dichlorobenzoate (2,4-DCBA) by strains growing on glucose-supplemented medium (Corbella et al. 2001).

Some chlorinated compounds themselves may act as a primary substrate for the co-metabolism of another chlorinated compound. For example, chlorobenzene served as a growth-substrate in aerobic co-metabolism of TCE (Kao and Prosser 1999).

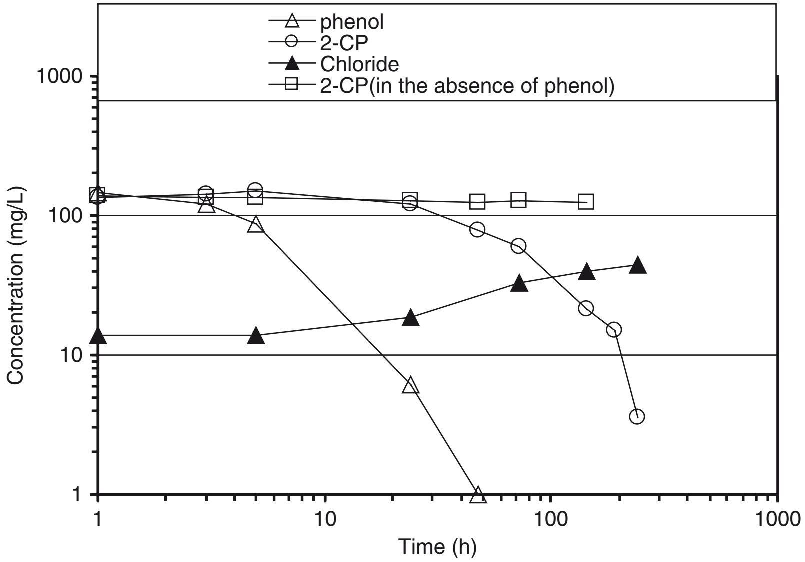

Fig. 9.2 Co-metabolic degradation of 2-CP by an acclimated biomass in the presence of phenol (Adapted from Aktaş 2006)

Higher chlorobenzoates such as 3,4-DCBA were co-metabolized in the presence of a lower chlorinated one, 4-CBA (Adriaens and Focht 1991). Chlorophenols can also serve as growth-substrates for the co-metabolic degradation of another chlorophenol. For instance, 3,5-DCP was biodegraded in the presence of 3-CP whereas the trichlorophenol (3,4,5-TCP) and the tetrachlorophenol (2,3,5,6- TeCP) were degraded in the presence of PCP (Liu et al. 2006).

Polychlorinated biphenyls (PCBs) were shown to be degraded metabolically only under certain conditions by isolated pure cultures (Chaundry and Chapalamadugu 1991; Ahmed and Focht 1973; Takase et al. 1986) and also co-metabolically (Kohler et al. 1988) by biphenyl (Chaundry and Chapalamadugu 1991) and ethylbenzene degraders (Iwasaki et al. 2006). Monochlorobiphenyls can also be degraded only by co-metabolism under aerobic conditions. Also here the position of chlorine plays a role and as an exception 4-chlorobiphenyl may serve as a growth-substrate. Mono- and dichlorodioxins, furans and 2,4,8-dichlorodibenzofuran were also biodegraded only co-metabolically under aerobic conditions (ICSS 2006).

9.3.3 Aerobic Co-metabolism Using Methane As Primary Substrate

Methanotrophs are aerobic micro-organisms using oxygen as the terminal electron acceptor, and require methane or methanol as carbon and energy source. Formation of chlorinated intermediates as a result of incomplete dechlorination was the case for 1,1,1-TCA and 1,1-DCE whereas CT and PCE were not biodegraded at all (Oldenhius et al. 1989). In the study of Chang and Alvarez-Cohen (1995b) measurement of TCE degradation by methane oxidizers in the presence of methane as a growth-substrate and excess NAD(P)H regenerant (formate) showed a decrease in TCE degradation as methane concentration increased, indicating the occurrence of competitive inhibition between methane and TCE.

Mixed or pure cultures of methane oxidizers did not degrade the perchlorinated aliphatics such as PCE and CT (Chang and Alvarez-Cohen 1996). Within similar carbon structure groups (methanes, ethanes and ethenes), the measured transformation capacities generally decreased with the extent of chlorination, whereas similar trends were not observed for degradation rates. A notable exception is 1,1-DCE, which exerted a much higher toxicity than the other dichloroethenes cis-1,2-DCE and trans-1,2-DCE. Another possible exception is VC, which exhibited a transformation capacity equivalent to those for cis-DCE and trans-DCE (Chang and Alvarez-Cohen 1996). In addition to aliphatics, methane oxidizers can also lead to co-metabolic degradation of chlorobenzene (Jechorek et al. 2003).

9.3.4 Aerobic Co-metabolism using Ammonium as Primary Substrate

The majority of studies on ammonium oxidizers has been performed with pure *Nitrosomonas europaea* species and the primary focus was on TCE degradation. Arciero et al. (1989) demonstrated for the first time that ammonia oxidizing bacteria (*Nitrosomonas europaea*) catalyze the degradation of TCE. Ely et al. (1995, 1997), Hyman et al. (1995) and Rasche et al. (1991) also studied co-metabolic degradation of TCE by pure *Nitrosomonas europaea* species. Degradation of chlorinated organic compounds can also take place by the same organisms in the absence of ammonia, although the rates and extent are lower (Vannelli et al. 1990).

In the study of Alpaslan Kocamemi and Çeçen (2005) co-metabolic degradation of TCE was investigated in a batch system using a mixed culture enriched for nitrifiers. TCE inhibited ammonium removal (Fig. 9.3) and analysis showed that TCE was a competitive inhibitor (Alpaslan Kocamemi and Çeçen 2007a). The relative concentrations of ammonium and TCE were crucial and co-metabolic degradation rates generally increased with ammonium, which served as the electron donor (Alpaslan Kocamemi and Çeçen 2007a).

Alpaslan Kocamemi (2005) also investigated the co-metabolic degradability of 1,2-DCA by nitrifiers in a suspended-growth culture. 1,2-DCA had mainly the mixed inhibitor characteristics. Further studies in a continuous-flow nitrifying biofilm reactor showed that the same compound was degraded co-metabolically, but only partial mineralization was observed. 1,2-DCA had an inhibitory effect on ammonium oxidation but not on nitrite oxidation. However, the inhibitory effect of this compound on ammonium oxidation was reversible (Alpaslan Kocamemi and Çeçen 2007b).

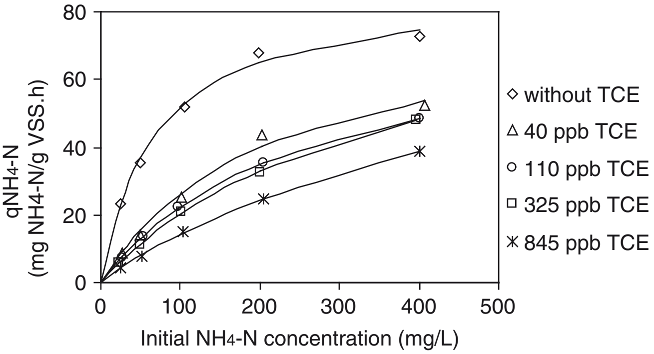

Fig. 9.3 Inhibition of ammonium utilization rate by TCE in a batch suspended growth system containing an enriched nitrifier culture (Alpaslan Kocamemi and Çeçen 2007a)

Chlorinated organics may lead to temporary or full inactivation of ammonia oxidizers. Rasche et al. (1991) investigated the co-metabolic degradation of different types of ALCHs. The first class included CT and PCE, which were not co-metabolized by *Nitrosomonas europaea*. These compounds did not degrade at all, but did also not inactivate the AMO enzyme or cause a toxic effect on cells. The second class of compounds included CM, CA and 1,2-DCA, which did not inactivate oxygen uptake of cells to a great extent, but were co-substrates for the AMO enzyme. They were depleted by co-metabolism, but had minimal inactivation effects. The third class consisted of compounds DCM, CF, 1,1-DCA, 1,1,1-TCA, 1,1-2-TCA, 1,1,2,2,-TeCA, VC, 1,1-DCE, cis-1,2-DCE, trans-1,2-DCE and TCE, which were co-substrates for AMO, as indicated by substrate depletion and chloride production, and produced a turnover-dependent inactivation.

Ely et al. (1997) investigated the co-metabolism of several ALCHs and have shown that an increasing degree of chlorination lowered the transformation rates, especially for chlorinated alkanes. The alkenes showed higher affinity for the AMO enzyme than alkanes.

9.4 Bioremediation of Chlorinated Organic Compounds

9.4.1 Types of Bioremediation

Bioremediation is a general term used to describe the removal of pollutants by micro-organisms (e.g. yeasts, fungi, or bacteria) in contaminated soil, groundwater or other systems. After the release of chlorinated compounds into the subsurface, removal can occur through biological, physical and chemical processes that are known as **natural attenuation**. Biodegradation is the most important destructive natural attenuation mechanism. If the injection rates of the pollutants exceed their natural removal rates, pollutant removal will be inadequate. Therefore, at many polluted sites natural processes are enhanced today. This is termed as **enhanced bioremediation**. Major technologies to accelerate the natural processes involve the addition of microorganisms (bioaugmentation), nutrients, electron donors, or electron acceptors. Some examples are shown in Table 9.2.

9.4.2 Mechanisms of Biological Removal in Natural and Enhanced Bioremediation

In groundwater, soil remediation and at landfill sites, bioremediation depends largely on hydro-chemical and geochemical conditions of the polluted site. The major biological mechanisms for dechlorination and biodegradation of chlorinated organics in groundwater, soil and landfill matrices are anaerobic reductive dechlorination (direct and co-metabolic) and aerobic oxidation (direct and co-metabolic). The redox potential in the matrix provides an indication of the relative dominance of aerobic, anoxic and anaerobic micro-organisms and processes. The electron donors in the subsurface are native organic matter or contaminants. The principal electron acceptors or oxidizing agents in groundwater are oxygen, nitrate, sulfate, manganese (IV), iron (III) and CO_2.

Direct anaerobic reductive dechlorination has often been observed in systems such as aquifers containing ALCHs (e.g. PCE and TCE). The chlorinated compound itself serves as the electron acceptor, and hydrogen serves as the direct electron donor (EPA 2000) which is supplied indirectly through fermentation of substrates such as fuel hydrocarbons, the compounds benzene, toluene, ethylbenzene, xylene abbreviated as BTEX, organic compounds in landfill leachate and natural organic matter. This energy-yielding reaction is referred to as halorespiration or dehalorespiration. The second option is co-metabolic anaerobic reductive dechlorination in the presence of another growth-substrate. However, for ALCHs such as PCE anaerobic reductive dechlorination was often shown to lead to generation of daughter products such as VC having a higher toxicity than parent compounds. The main advantage of aerobic co-metabolism is that usually toxic products are not generated.

At many sites, the anaerobic transformation of PCE and TCE often stops at the intermediate product cis-1,2-DCE. Then, aerobic co-metabolism may play an important role in the transformation of these intermediates into harmless products. Some regions of groundwater are characterized by low concentrations of native and/or anthropogenic carbon and by DO concentrations higher than 1.0 mg/L favoring the conditions for aerobic removal. However, in the aerobic zones of the subsurface, only the less chlorinated ALCHs can be directly used by micro-organisms as electron donors. Groundwaters are largely polluted by TCE which can undergo co-metabolic removal only under aerobic conditions. Besides TCE other ALCHs such as DCE, VC, TCA, DCA, CF, and DCM have been observed to be oxidized co-metabolically under aerobic conditions as shown in detail in a report (EPA 2000).

In enhanced bioremediation the addition of electron donors, electron acceptors, or nutrients can help to provide the proper conditions for removal. If co-metabolic

Table 9.2 Examples of field-scale aerobic bioremediation

System	Pollutants	Mechanism	Conditions for bioremediation	Study type	Place	Reference
Karst aquifer	TCE, cis-1,2-DCE, VC	Aerobic oxidation (co-metabolic and direct)	Presence of ethane, methane, ammonia and dissolved oxygen for co-metabolism	Field	Karst site in Middle Tennessee, USA	Byl and Williams (2000)
Soil	TCE, 1,1,1,-TCA, cis-1,2-DCE	Aerobic oxidation (co-metabolic and direct)	Electron acceptor addition (O_2), electron donor addition (propane)	Field (pilot)	Dover Air Force Base, Dove , Delaware, USA	EPA (2000)
Groundwater	TCE, cis-1,2-DCE, trans-DCE, VC	Aerobic oxidation (co-metabolic and direct)	Electron acceptor addition (O_2 and H_2O_2) Electron donor addition (methane, toluene, and phenol)	Field demonstration	Moffett Naval Air station, CA, USA	EPA (2000)
Groundwater	TCE	Aerobic oxidation (co-metabolic and direct)	Electron acceptor addition (O_2 and H_2O_2) Electron donor addition (toluene)	Field demonstration	Edwards Air Force Base, CA, USA	EPA (2000)
Sediment and Groundwater	TCE, PCE	Aerobic oxidation (co-metabolic and direct)	Nutrient addition, Electron acceptor addition (O_2) Electron donor addition (methane)	Field demonstration	Savannah River Site, Aiken, SC, USA	EPA (2000)

(continued)

Table 9.2 (continued)

System	Pollutants	Mechanism	Conditions for bioremediation	Study type	Place	Reference
Aquifer (experimental wellfield)	ALCHs	In-situ aerobic co-metabolic oxidation	Injection of dissolved propane and O_2	Push-pull test in a noncontaminated aquifer	Oregon State University	Kim et al. (2004)
Groundwater	TCE and chlorobenzene	Aerobic oxidation (co-metabolic and direct)	Phenol added as a growth substrate for TCE co-metabolism	Field and laboratory	Former fire training area at Robins air force base in Georgia, USA	Kao and Prosser (1999)
Aquifer	TCE and cis-1,2-DCE	Aerobic co-metabolic oxidation	Presence of methonotrophs and soluble methane monooxygenase enzyme (sMMO)	Field	Idaho National Laboratory's test area	Wymore et al. (2007)
Groundwater	TCE	Aerobic co-metabolic oxidation	Use of a commercial blend of Pseudomonas sp. (Cl-out microbes) and addition of dextrose	Field	12 sites throughout USA	Saul (2000)
Groundwater	Chlorinated aromatic compounds	Aerobic degradation	On-site circulation	Field	Former pesticide production site	Feidieker et al. (1995)

removal is the aim, usually the addition of growth-substrates such as toluene, methane, or propane or ammonia is necessary which serve as electron donors as outlined in detail in Section 9.3. This mechanism can also operate in soil and landfill matrix provided that a sufficient hydrocarbon source is present or delivered to indigenous micro-organisms. The composition and number of degrading bacteria are also crucial. In many cases, the addition of electron acceptors (O_2 or H_2O_2) and nutrients (nitrogen and phosphorus) is necessary.

9.4.3 Case Studies on Aerobic Bioremediation of Contaminated Sites for Removal of Chlorinated Organics

Table 9.2 lists some of the well-known field-scale applications of in-situ aerobic bioremediation. One of the well-known examples of in-situ aerobic co-metabolic bioremediation is the test at Moffett Field, California. At this hazardous waste site, the simultaneous addition of methane and oxygen was tested for co-metabolic aerobic oxidation of TCE in aquifer material. Intermittent pulses of oxygen and methane were provided to the subsurface, bringing about biodegradation of TCE, cis-1, 2-DCE, and VC in a contaminated aquifer (Semprini et al. 1990). Additional field studies at the test site have shown that toluene and phenol can be more effective electron donors than methane in the stimulation of co-metabolic biodegradation of TCE, cis-1,2-DCE, and VC in groundwater. Then, the full-scale application was carried out at the TCE-contaminated site Edwards AFB that is shown in Fig. 9.4.

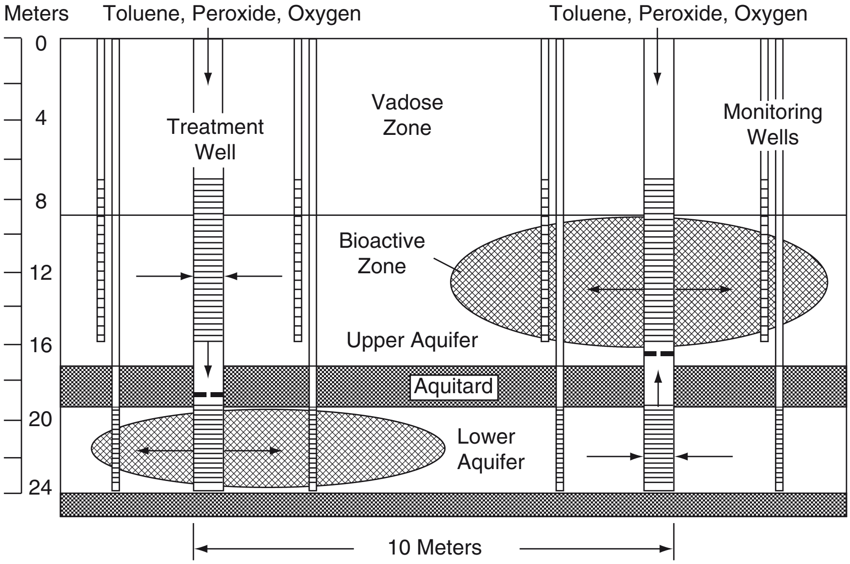

Fig. 9.4 Cross-section of two-well co-metabolic TCE biodegradation treatment system spanning two separate aquifers (McCarty et al. 1998)

Table 9.3 Examples of pilot- or laboratory scale aerobic studies for bioremediation purposes

System	Pollutants	Mechanism	Primary substrate	Study type	Place	Reference
Groundwater (quarternary aquifer)	MCB, 1,4 DCB, 1,2-DCB	Aerobic oxidation (direct)	–	Mobile test unit-semi technical scale	Bitterfeld/Germany	Wünsche et al. (1999)
Groundwater	MCB	Microaerobic oxidation (direct)	–	Lab-scale column	Bitterfeld/Germany	Staps et al. (1999)
Groundwater	MCB	Aerobic BAC filter(direct)	–	Lab-scale column	Bitterfeld/Germany	Lorbeer et al. (2002)
Groundwater	MCB	Aerobic BAC filter (direct)	–	Pilot-scale column	Bitterfeld/Germany	Tiehm et al. (2000)
Groundwater	cis-1,2-DCE, VC	Aerobic oxidation (direct)	–	Batch	Frankenthal/Germany	Schmidt and Tiehm (2008)
Groundwater	MCB	Aerobic co-metabolic oxidation	Methane	Mobile test unit	Bitterfeld/Germany	Jechorek et al. (2003)
Source-zone soil	MCB and 1,4-DCB	Aerobic oxidation (direct)	–	Lab-scale aquifer column	Midwestern USA	Dominguez et al. (2008)
Groundwater	MCB, 1,2-DCB, 1,3-DCB, 1,4-DCB,1,2,4-TCB	Aerobic oxidation(direct)	–	Lab-scale and on-site mobile test unit	Bitterfeld/Germany	Dermietzel and Vieth (2002)
Groundwater	Phenol and 2-CP	Aerobic oxidation (co-metabolic and direct)	Phenol	Lab-scale SBBR	–	Farabegoli et al. (2008)
Subsurface microorganisms grown on butane	CF, 1,1,1-TCA	Aerobic co-metabolic oxidation	Butane	Batch microcosms	–	Kim et al. (1997)

The indigenous bacteria were induced to oxidize TCE co-metabolically when toluene (primary substrate) and oxygen were injected into treatment wells.

Besides field-scale tests, a number of laboratory and pilot-scale studies have been performed mimicking the conditions at a contaminated site. Some examples to these studies are shown in Table 9.3. The Bitterfeld area in Germany is a good example to an aquifer contaminated with a mixture of chlorinated ethenes and benzenes due to industrial activities. The remediation of groundwater was tested via stimulated natural attenuation. The chloroethenes were degraded in the first anaerobic stage, whereas chlorobenzenes were degraded directly under microaerobic conditions (Table 9.3).

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Chapter 10
Photochemical Transformation of Pharmaceuticals in the Aquatic Environment: Reaction Pathways and Intermediates

Ioannis K. Konstantinou, Dimitra A. Lambropoulou, and Triantafyllos A. Albanis

Abstract In recognition of the growing concern regarding the photochemical transformation of pharmaceuticals in the aquatic environment, the focus of this chapter is on current knowledge on the photochemical transformation of selected pharmaceutical compounds in aquatic systems in order to reveal the key areas and perspectives of this research field. Some of the most important groups of pharmaceuticals known to occur in the environment, such as non-steroidal anti-inflammatory drugs, analgesics, antidepressants and estrogens, are discussed in this chapter. Processes considered include environmental photolysis and photochemical advanced oxidation processes (PAOPs) in homogeneous (UV/H_2O_2, Photo-Fenton and Photoelectron-Fenton) and heterogeneous (TiO_2/UV) media. The phototransformation of pharmaceuticals proceeds usually through the formation of long-lived intermediate species. Thus, we have attempted to provide an overview of the nature of principal organic intermediates, the degradation pathways followed and the evolution of the mineralization in the photochemical process considered. Major degradation pathways usually include hydroxylation, isomerization, dehalogenation, dealkylation, cyclization, decarboxylation, dimerization and ring opening (for aromatic compounds), leading to corresponding derivatives as well as carboxylic acids.

10.1 Introduction

In spite of the fact that nowadays pharmaceuticals are viewed as environmental contaminants (Daughton and Ternes 1999) and substantial progress has been made towards environmental monitoring (Heberer et al. 2001; Kolpin et al. 2002;

I.K. Konstantinou
Department of Environmental and Natural Resources Management,
University of Ioannina, 30100 Agrinio, Greece

D.A. Lambropoulou (✉)
Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
e-mail: dlambro@chem.auth.gr

T.A. Albanis
Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece

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Roberts and Thomas 2006; Selimi et al. 2006), limited information is available on the degradation mechanisms, the identity of the transformation products (TPs) and their origin, fate and impact on the environment. Consequently, concerns regarding pharmaceuticals and their TPs in view of risk assessments for natural ecosystems have recently increased (Barceló and Petrovic 2007; Ellis 2006; Khetan and Collins 2007).

Once released into the environment via the discharge of treated or untreated wastewater, pharmaceuticals are subjected to the same potential transport and degradation processes as other organic contaminants. The predominant elimination processes can be of biotic or abiotic nature. Following the current state of knowledge for the microbial degradation of pharmaceuticals and taking into account the fact that in general pharmaceuticals have a designed resistance to biodegradation, it is considered that microbial degradation is not an important loss process in aquatic environment (Dbska et al. 2004; Kümmerer 2004). However, many pharmaceuticals are expected to be eliminated from the environment by abiotic degradation processes (e.g. hydrolysis, photolysis, redox reactions, etc.). Among them, direct photolysis and indirect photodegradation processes including reaction with photo-excited dissolved organic matter (DOM), and transient reactive species such as singlet oxygen ($^1O_2$), hydroxyl radical ($HO^•$), peroxy radicals (•OOR), solvated electrons (e_{aq}^-), generated by irradiation of various aquatic components (DOM, NO_3^-, Fe^{3+}), may be an important removal process for these compounds, since usually their structure contains aromatic rings, heteroatoms and other functional groups that can either directly absorb solar radiation or react with the above-mentioned photogenerated transient species in natural waters (Arnold and McNeill 2007; Boreen et al. 2003; Doll and Frimmel 2003). The effect of light in the destruction of organic chemicals has also proven to be useful in water treatment technology. In the last decade, many works have demonstrated that Photochemical Advanced Oxidation Processes (PAOPs), which are generally defined as processes involving generation of powerful transitory species, principally the hydroxyl radical ($HO^•$) by photochemical means (including solar light), may be interesting and promising processes in water treatment technology (Ikehata et al. 2006; Litter 2005). PAOPs involving oxido-reductive reactions can be also useful as techniques for studying the formation of TPs in environmental media mainly by abiotic processes. It has to be noted that the assessment of the reliability of a degradation treatment for a pollutant relies also on the nature of the TPs generated, which can be a great concern as they can be even more toxic than the precursor itself. This emphasizes the importance of monitoring the evolution of degradation intermediates and ensuring the complete destruction of by-products during the treatment, especially when other wastewater constituents that may compete for oxidants are present.

A relatively sufficient number of studies have been reported in the literature regarding the photolysis and the degradation of pharmaceuticals by PAOPs in the last decade (Hernando et al. 2007; Ikehata et al. 2006; Klavarioti et al. 2008). However, most of them are focused on the degradation and mineralisation rates in different aquatic media and the comparison of the performance of different photocatalytic and photochemical systems while few data is available on the reaction mechanisms involved in the photolytic and photocatalytic degradation of pharmaceuticals under simulated or natural solar light. Thus, our attention has been mainly focused on the reaction types and mechanisms of selected pharmaceutical families, based on the identification of the phototransformation products (photo-TPs). However, the purpose of this chapter is not to provide a complete literature review on the topic of the photochemical transformation, but rather to provide specific examples of research documenting the importance of elucidation of photolysis and photocatalysis reaction pathways and identification of TPs in order to gain additional information and insight about the fate of frequently detected pharmaceuticals in the aquatic environment.

10.2 Transformations of Pharmaceuticals in Water by Photolysis and Photocatalysis

10.2.1 Direct and Indirect Photolysis

10.2.1.1 Nonsteroidal Anti-inflammatory Drugs (NSAIDs)

Diclofenac (DCF). DCF has been extensively studied for its photodegradation in natural waters. Previous studies (Andreozzi et al. 2003a; Buser et al. 1998; Moore et al. 1990; Packer et al. 2003; Poiger et al. 2001) indicate that direct photolysis is the dominant transformation pathway for DCF elimination under environmental conditions. Rapid photodegradation (sunlight) was observed with a half-life of less than 1 h in lake water (Greifensee, Switzerland), while three TPs have been detected (Buser et al. 1998). Two photo-TPs have been identified as the methyl esters of carbazole-1-acetic acid and its 8-chloro derivative, respectively, and were produced by a light-enhanced esterification. They were previously identified as photo-TPs of DCF in aqueous buffer or methanol solutions irradiated with UVA light (Moore et al. 1990). The structure of a third photo-TP was not identified.

A more detailed study on the photo-TPs of DCF in water under direct solar irradiation has been performed by Agüera et al. (2005) by the combinatory use of gas chromatography-mass spectrometry (GC/MS) and liquid chromatography coupled with time-of-flight mass spectrometry (LC/TOF-MS). Thirteen photo-TPs were identified demonstrating that photolysis of DCF occurs through two main routes. The first one proceeds via photocyclisation of DCF into the corresponding 8-chloro-9H-carbazole-1yl-acetic acid, which was the main photo-TP detected, followed mainly by the degradation of the alkyl chain and to a lesser extent by hydroxyl substitution of chlorine to form the 8-hydroxy-9,9a-dihydro-4 aH-carbazol-1-yl) acetic acid, a highly reactive product that can be the precursor of dimers. The photocyclization process has been reported also elsewhere (Encinas et al. 1998; Moore 1998; Poiger et al. 2001). The other route goes through an initial decarboxylation of DCF followed by further oxidation of the alkyl-chain, and partial (one chlorine atom) dechlorination (Agüera et al. 2005). Photochemical dehalogenation of aromatics has been reported frequently in the literature.

Naproxen (NPR). Another compound of the NSAIDs family that has been sufficiently studied for its photodegradation in natural waters is NPR. NPR is subject mainly to direct photolysis (half-life of 42 min) while oxidation by $^1O_2$ is unimportant in the photochemical fate of naproxen in natural waters (Packer et al. 2003). Direct photolysis products of NPR were identified in the presence and absence of molecular oxygen (Boscá et al. 1990; Jimenez et al. 1997; Moore and Chappuis 1988). Under anaerobic conditions, 1-ethyl-6-methoxynaphthalene (NPR1) and 1-(6-methoxy- 2-napthyl) ethanol (NPR2) has been observed. Under aerobic conditions, 1-(6-methoxy-2-napthyl) ethanol (NPR2) was initially formed and was subsequently oxidized to 2-acetyl-6-methoxynaphthalene (NPR3) (Jimenez et al. 1997; Moore and Chappuis 1988). The detection of the above principal TPs was also ascertained in recent studies (DellaGreca et al. 2004) of NPR photodegradation in distilled water. Their formation could be explained by the conversion of the carboxylate (RC(=O)O–) group to a carboxyl radical (RC(=O)O) by photoionization into a first step, followed by decarboxylation to produce the corresponding benzylic radical which can abstract a hydrogen atom from a suitable donor present in the reaction media resulting in the ethyl derivative (pathway a, Fig. 10.1), or can react with molecular oxygen (pathway b, Fig. 10.1), leading to the formation of an alcohol or ketone group in the place of the carboxylate group (DellaGreca et al. 2004; Packer et al. 2003). Carbinol and ketone TPs were generated through an unstable hydroperoxide that was isolated in early irradiation times (DellaGreca et al. 2004). Furthermore, olefin (NPR4) and ethoxy (NPR5) derivatives were generated in distilled water whereas two dimer derivatives (NPR6 and NPR7) were identified in the presence of inorganic salts. The unstable hydroperoxide intermediate could be also taken into account to explain the formation of these dimers.

Ketoprofen (KETO). Keto was also rapidly transformed in environmental waters (Lin and Reinhard 2005; Matamoros et al. 2009) via direct photolysis. The photodegradation

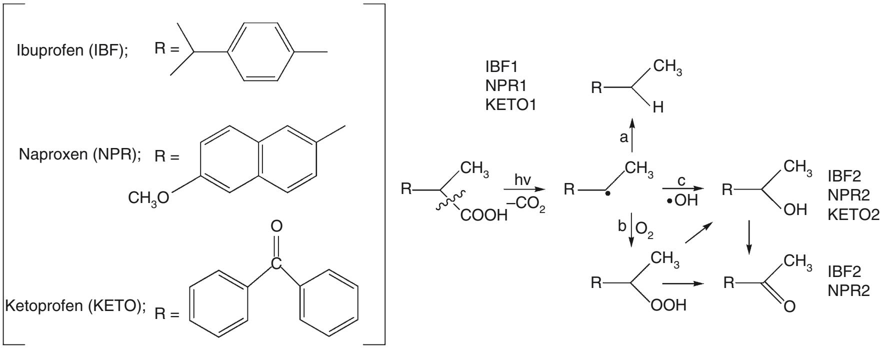

Fig. 10.1 Common photodegradation pathways and major photoproducts for α-aryl propionic acids family of NSAIDs in the aquatic environment (Based on Agüera et al. 2005; Buser et al. 1998; Castell et al. 1987; DellaGreca et al. 2004; Isidori et al. 2005; Matamoros et al. 2009)

pathway of KETO involves also an initial decarboxylation step as observed for NPR and DCF (Martinez and Scaiano 1997; Matamoros et al. 2009; Nakajima et al. 2005) followed by hydrogen abstraction to form 3-ethylphenyl (phenyl) methanone (pathway a; KETO1) and reaction with O_2 or $HO^•$ (pathway b and c) to produce derivatives such as (3-(1-hydroxyethyl)phenyl)(phenyl) methanone (KETO2). Then, side chain dealkylation and subsequent cleavage of the aromatic rings take place leading to the formation of benzophenone and 1-phenylethanone, respectively. It should be noted that, the latter photo-TPs and KETO2 were found more persistent than the parent KETO, hence it can be found more frequently in surface waters.

Ibuprofen (IBF). Contrary to the previously discussed NSAIDs, IBF was transformed only minimally via direct irradiation using an Hg-vapour lamp and indirect photolysis mediated by radicals (other than $HO^•$) was considered as the primary photolysis process for IBF in surface waters (Castell et al. 1987). IBF undergoing the same photochemical decarboxylation route via intermediate benzylic radicals and the generation of TPs through hydrogen abstraction (pathway a; IBF1), reaction with O_2 or $HO^•$ (pathways b or c; IBF2 or IBF3, respectively) and dimerization was reported (Castell et al. 1987). According to the previous pathways and products, some common photodegradation pathways (Fig. 10.1) could be proposed for α-aryl propionic acid group (NPR, KETO and IBF) of NSAIDs.

Mefenamic Acid (MFAC). The photolysis of MFAC in sunlit natural waters is much slower compared to diclofenac and both direct and indirect photodegradation processes were assigned for its dissipation. Significant photosensitization was observed in solutions of Suwanee River fulvic acid and Mississippi River water and a direct reaction of MFAC with excited triplet state of dissolved organic matter was proposed as the major photosensitization process. However, its photo-TPs have not been identified (Werner et al. 2005).

10.2.1.2 Anti-depressants/Anti-epileptics and Anti-anxiety Agents

Carbamazepine (CBZ). Much work has been completed on the photochemical behaviour of CBZ (Andreozzi et al. 2002; 2003a; Chiron et al. 2006; Doll and Frimmel 2003; Lam and Mabury 2005). The aquatic persistence of CBZ has been suggested to be limited by photochemical reactions in surface waters and faster degradation of CBZ in the presence of NOM or Fe(III) and Cl^- was documented (Andreozzi et al. 2002; Chiron et al. 2006; Doll and Frimmel 2003; Lam et al. 2004). The 10,11-epoxy-CBZ was reported as a major photo-TP in pure water by Andreozzi et al. (2002) and Lam and Mabury (2005); using GC-MS methods.

More recently, Chiron and co-workers described that direct photolysis of CBZ proceeds through two routes (Chiron et al. 2006). A first minor pathway proceeds via hydration of the C10–C11 double bond to form a hydroxy-derivative (CBZ1; 10-hydroxy-CBZ). The other main photodegradation pathway involves possibly a ring contraction process through the formation of CBZ-9-carboxaldehyde resulting from 10-hydroxy-CBZ (Chiron et al. 2006; Vogna et al. 2004a). Then, the CBZ-9-carboxaldehyde intermediate might be transformed with three different ways: (a) further hydroxylation with loss of the –$CONH_2$ group leading to hydroxyacridine-9-carboxaldehyde (CBZ2) and acridone (CBZ3) to a lesser extent; (b) simultaneous loss of the carboxyaldehyde and the –$CONH_2$ groups yielding acridine (CBZ4), a toxic, mutagenic and carcinogenic product and (c) the formation of two dimers; the first was generated by coupling after the loss of the carboxyaldehyde group (CBZ5) and the second dimer after the simultaneous reduction of the –$CONH_2$ groups (CBZ6). In the presence of Fe(III) at pH 2.0, additionally to the previous photoproducts, hydroxyl-CBZ (CBZ7) and a quinonid CBZ analogue (CBZ8) were formed via two-step $HO^•$ attack on phenyl ring, respectively. Afterwards, an intramolecular loss of H_2O from CBZ8 could be assumed for the cyclization and the production of a second quinonid CBZ derivative (CBZ 9). Both quinonid TPs were not detected upon CBZ photodegradation in the presence of nitrate (•OH mediated process), suggesting an electron transfer mechanism by Fe(III) that might also take place in natural waters in the presence of other species (e.g. Mn) (Chiron et al. 2006).

At pH 2.0 with Fe(III) + Cl^-, two chlorinated compounds were also detected, chloro-10-hydroxy-CBZ (CBZ10) and chloro-dihydroxy-CBZ (CBZ11) by the attack of Cl_2 •- radicals formed upon chloride oxidation by $HO^•$. At pH 7.5 in the presence of Fe(III) and no chloride, dihydroxy-CBZ (CBZ 12, 4 isomers) was formed. At pH 7.5 in the presence of Fe(III) + Cl^-, in addition to CBZ 1, 2, 4, 5, 7, 8, and 12, the chlorinated compounds CBZ 10 and 11were also detected (Chiron et al. 2006). The marked differences on the structure of the TPs depending on the water matrix components highlight once more the importance of conducting photochemical studies using natural water samples.

10.2.1.3 Oestrogen Hormones

17β-Estradiol (E2) and 17α-EthinylEstradiol (EE2). E2 and EE2, a natural and synthetic oestrogen respectively, known to contribute to a large extent to the estrogenicity of various effluents have been recently studied for their photodegradation and their TPs were identified with GC/MS and LC/MS techniques (Mazellier et al. 2008). Photodegradation pathways for E2 implying: (a) the oxidation of the –OH groups to form estrone (E1) and the quinone methide derivative; (b) the loss of –OH group attached to the five-membered ring by a dehydration process leading to derivatives with a cyclopentene moiety or a new three-membered ring; (c) the monohydroxylation of the aromatic ring or the six-membered saturated ring linked to the aromatic one and (d) further oxidation of the –OH groups added in the previous step to form keto or 1,2-quinone or hydroquinone derivatives. Similarly, photo-TPs of EE2 corresponded to quinone methide and 1,2-quinone and ring monohydroxylation derivatives (Mazellier et al. 2008).

A summary of photodegradation intermediates and mechanisms for the pharmaceuticals discussed herein is presented in Table 10.1.

10.2.2 Homogeneous and Heterogeneous Photocatalysis

10.2.2.1 NSAIDs and Analgestics

Diclofenac (DCF). DCF is the most widely studied compound of this class. The available data show that DCF degradation follows similar, but not identical reaction pathways, depending on the applied treatment (UV/H_2O_2, Photo-Fenton, or TiO_2 photocatalysis). In the heterogeneous photocatalysis by TiO_2 (Calza et al. 2006), hydroxylation and cleavage of the NH-bridge are the initial reactions followed by dehalogenation and stepwise aromatic ring opening. By the Photo-Fenton treatment (Pérez-Estrada et al. 2005), two tentative degradation routes were observed. The main one, similar to TiO_2 photocatalysis, was based on the initial hydroxylation of the phenylacetic acid moiety in the C-4 position and subsequent formation of a quinone imine derivative that was the starting point for further multistep degradation involving oxidation and decarboxylation reactions. An alternative route was based on the direct $HO^{\bullet}$ attack on the aliphatic chain of DCF leading to the formation of TPs containing the biphenyl amino moiety which successively follow an oxidative process forming C–N cleavage products. In the case of H_2O_2/UV (Vogna et al. 2004b), the decomposition of DCF proceeds also through the hydroxylation and the breaking of the C–N bond but generation of quinone imine derivatives was not observed. Most of the above mentioned intermediates were identified by using different analytical instruments including LC-TOF-MS, LC-MS(IT) and GC-MS (Table 10.2). It is worth to point out that carbazole derivatives which formed via photocyclisation in the photolysis process have not been detected in any of the photocatalytic processes discussed here.

Ibuprofen (IBF). A comparative study for the TiO_2 photocatalytic treatment of three NSAIDs drugs, IBF, DCF and NPX under different operational conditions (catalyst load, temperature and dissolved oxygen concentration) has been reported by Méndez-Arriaga et al. (2008). Based on the TPs identified with LC-MS/TOF system together with the complementary results obtained from the degradation of IBF by means of the photo-Fenton reagent (not yet published by the same research group) the authors suggested that oxidant attack of the $HO^{\bullet}$ on the isobutyl chain or/and on the propanoic moiety is the first step of the degradation process, followed by a second, less predominant step of demethylation or decarboxylation giving rise to other different organic acids such as propionic, formic or hydroxypropionic acid. Hydroxy derivatives were the most important residual compounds, while decarboxylated derivatives which have been reported as major TPs in direct or indirect photolysis of NSAIDs (see Fig. 10.1) were observed only in the presence of O_2 (40 mg/L).

Table 10.1 Summary of photochemical studies, analytical methods, reaction pathways and major TPs of selected PPCPs chemical families

PPCPs	Process	Water matrix	Analytical methods	Reaction pathways	Major transformation products	References
Nonsteroidal anti-inflammatory drugs (NSAIDs)						
Diclofenac	Natural sunlight	Demineralised water and reconstructed freshwater Lake water	GC-EI-MS (Q), LC/MS (ToF) GC-EI-MS (Q)	Photocyclisation Decarboxylation, Alkyl-chain oxidation, Dechlorination Esterification	8-chloro 9H-carbazole-1yl-acetic acid and corresponding hydroxylated (hydroxy- and di-hydroxy 9H-carbazole-1yl-acetic acid), dealkylated (3-Chloro-carbazole) derivatives Decarboxylated, alkyl- oxidized (8-chlorocarbazole-1-formic acid) and dechlorinated derivatives Methyl esters of carbazole-1-acetic acid and its 8-chloro derivative	Agüera et al. (2005) Buser et al. 1998
Ibuprofen	UV-VIS	Methanol	IR-, ^{1}H-NMR,^{13}C-NMR	Decarboxylation Dimerization	p-ethylisobutylbenzene, 1-(4-isobutylphenyl)ethanol4-isobutylacetophenone 2,3-bis-(isobutylpheny1)butane	Castell et al. 1987
Naproxen	Simulated sunlight	Distilled water Drinking water	EI-MS,^{1}H NMR, MALDI-TOF	Decarboxylation, Alkyl-chain oxidation, Dimerization	1-ethyl-6-methoxynaphthalene, 1-(6-methoxy-2-napthyl) ethanol, 2-acetyl-6-methoxynaphthalene Dimers bis [1,1′-oxydiethylidene]	DellaGreca et al. 2004 Isidori et al. 2005
Ketoprofen	Simulated sunlight	Freshwater and Seawater	GC-EI-MS (Q)	Decarboxylation Hydroxylation Dealkylation Phenyl-keto bond scission	(3-ethylphenyl)(phenyl)methanone, (3-(1-hydroxyethyl)phenyl)(phenyl) methanone, Benzophenone 1-phenylethanone	Matamoros et al. 2009

Anti-depressants/anti-epileptics and anti-anxiety agents						
Carbamazepine	Simul-ated sunlight	Milli-Q water, River and estuarine water Synthetic field water	LC/APCI-MS/MS (IT), LC/ESI-MSn(IT)LC-ESCI-MS/MS	Hydroxylation Ring contraction and subsequent loss of the carboxyaldehyde and the -$CONH_2$ groups Hydroxylation Chlorine addition Cyclization Oxygenation	10-hydroxycarbamazepine Carbamazepine-9-carboxaldehyde, hydroxyacridine-9-carboxaldehyde, acridone, acridine, dimer derivatives Hydroxy and dihydroxy-carbamazepine Quinonid carbamazepine derivative Chloro-10-hydroxycarbamazepine Chloro-dihydroxycarbamazepine 10,11-epoxycarbamazepine	Chiron et al. 2006 Lam and Mabury 2005
Estrogens						
17β-estradiol 17α-ethinylestradiol	Simul-ated sunlight	Distilled water	LC-APCI-MS(IT) GC-EI-MS	Hydroxylation OH group oxidation–Dehydration	Hydroxy derivativesCarbonyl group-containing oxidation products as estrone, quinone methide and 1,2-quinone derivatives Cyclization or saturated derivatives	Mazellier et al. 2008

Table 10.2 Summary of photocatalytic studies, analytical methods, reaction pathways and major TPs of selected PPCPs chemical families

PPCPs	Photocatalytic process	Water matrix	Identification methods	Reaction pathways	Major TPs identified	References
Nonsteroidal anti-inflammatory drugs (NSAIDs) and analgestics						
Diclofenac	Photo-Fenton Solar light	Demineralized water	GC-EI-MS (Q) GC-PCI-MS (Q) LC-ESI-MS (ToF)	Hydroxylation- OH group oxidation Dechlorination Cyclization – dehydration Decarboxylation – aliphatic chain oxidation Cleavage of C-N bond Opening of the non-chlorinated ring	Hydroxy and quinone imine derivatives Hydroxy-dechlorinated quinone imine derivatives 1-(2,6-dichlorophenyl)-5-hydroxyindolin-2-one Decarboxylated, alkyl- oxidized derivatives (i.e. (E)-6-(2,6-dichlorophenylimino)-3-oxocyclohexa-1,4-dienecarbaldehyde, 2-(2,6-dichlorophenylamino)benzaldehyde) C-N cleavage products (i.e. 4-amino-3,5-dichlorophenol, 2,6-dichloroaniline, N-(2,6-dichlorophenyl)acetamide) Small organic acids (acetic, maleic, oxalic, formic)	Pérez-Estrada et al. 2005
	H_2O_2/UV(λ 254nm)	Distilled water	GC-EI-MS (IT)^{1}H-, ^{13}C-NMR authentic standards	Hydroxylation Dechlorination Cleavage of C-N bond	Hydroxy-derivatives2-(2-(2-chloro-6-hydroxyphenylamino)phenyl)acetic acid C-N cleavage products (i.e. 2,5-dihydroxyphenylacetic acid, 2,6-dichloroaniline, 2-hydroxyphenylacetic acid)	Vogna et al. (2004b)
	TiO_2/Simulated sunlight	Milli-Q water	LC-ESI-MSn(IT)	Hydroxylation- OH group oxidation Decarboxylation – aliphatic chain oxidation Cleavage of C-N bond Opening of the aromatic ring	Hydroxy, bihydroxy and quinone imine derivatives Decarboxylated and oxidized derivatives Chloro or hydroxyl-phenol derivatives Carboxylic acids (formic acid)	Calza et al. 2006
Ibuprofen	TiO_2/Simulated sunlight	Milli-Q water	LC-ESI-MS(ToF)	Hydroxylation in the isobutyl chain or/and on the propanoic moiety Demethylation or decarboxylation	Hydroxy derivatives Propionic acid, formic acid and hydroxypropionic acid or sodium salts	Méndez-Arriaga et al. 2008

Paracetamol	H_2O_2/UV (254 nm) H_2O_2/UV (254 nm) TiO_2/Simulated sunlight ($\lambda \geq 365$ nm) TiO_2/UV (UVA and UVC)	Distilled water Distilled water Distilled water Milli-Q water	GC/EI-MS (IT) GC/MS (IT) GC-EI-MS(Q) GC-EI-MS(Q)	Hydroxylation Hydroxylation – '*ipso*' addition mechanism Detachment of the acetamide group Oxidation	Acetamides (2-hydroxy-4-(N-acetyl)-aminophenol and 3-hydroxy-4-(N-acetyl)-aminophenol) Hydroxy-nitrogenous TPs Hydroquinone, 1,4-benzoquinone Hydroxy/keto dicarboxylic acids	Vogna et al. 2002 Andreozzi et al. 2003b Zhang et al. 2008 Yang et al. 2008
Anti-depressants/anti-epileptics and anti-anxiety agents						
Carbamazepine	TiO_2/Simulated sunlight	Milli-Q water	LC-ESI-MS/MS (QqQ)	Hydroxylation Oxygenation Ring contraction and subsequent loss of the carboxaldehyde and the -$CONH_2$ groups	Hydroxy and dihydroxy – carbamazepine10,11-Dihydrocarbamazepine-10,11-epoxide, Acridine,acridine-9-carboxaldehyde,hydroxyacridine-9-carboxaldehyde, hydroxyacridine-9-carboxyalcohol	Doll and Frimmel 2005
	H_2O_2/UV(254 nm)	Distilled water	GC-EI-MS(IT)	Opening of the dibenzoxazepine moiety and cleavage of the C-N bond Decarboxylation	2-aminobenzoic, 2-hydroxybenzoic acid, 2-hydroxyphenol Aliphatic acids	Vogna et al. 2004a
Estrogens						
17*β*-Estradiol	TiO_2/Simulated sunlight	Aqueous solution	GC-EI-MS(Q)	Hydroxylation OH group oxidation	Hydroxy-E2 Keto-E2 derivatives	Ohko et al. 2002
	$FeCl_3$/$NaNO_2$ Simulated sunlight	Distilled water	GC-EI-MS(Q)	Hydroxylation/OH group oxidation Nitro group addition Decarboxylation	Nitro estrogen derivatives (i.e. 2-nitroestradiol and 4-nitroestadiol) Small organic acids	Wang et al. 2007
Estrone	Photo-Fenton	Distilled water	HPLC-UV	Hydroxylation/OH group oxidation Benzene ring cleavage Decarboxylation	Non identified structures	Feng et al. 2005

Paracetamol (PCM). In recent studies, similar degradation pathway was proposed for the decomposition of PCM by both processes, H_2O_2/UV degradation (Vogna et al. 2002) and TiO_2 photocatalysis (Yang et al. 2008; Zhang et al. 2008), which is primarily based on the attack of $HO^•$ radicals to the aromatic ring by both normal and '*ipso*' addition mechanism, with the latter to be the most predominant. Main reaction intermediates and products were identified by GC/MS analysis including aromatic compounds (hydroquinone or 1,4-benzoquinone), acetamide derivatives and carboxylic acids. To get insight into the transformation process of PCM by the H_2O_2/UV treatment, Vogna and co-workers used integrated GC-MS/NMR methodologies based on ^{15}N-labelling. The findings clearly highlighted the high potential of the combined methodologies into the identification process of the TPs (Vogna et al. 2002).

10.2.2.2 Anti-depressants/Anti-epileptics and Anti-anxiety Agents

Carbamazepine (CBZ). Different authors have shown that CBZ can be efficiently eliminated by both UV/H_2O_2 (Vogna et al. 2004a), and TiO_2 (Doll and Frimmel 2005) treatments, through a series of acridine intermediates (highly toxic TPs). Degradation is predominantly initiated, in both cases, by hydroxylation at the position 10 of the CBZ molecule to give a radical intermediate that can evolve into CBZ-10,11-epoxide that has been reported as major TP in pure water photolysis (Andreozzi et al. 2002; Lam and Mabury 2005). The remainder comprises hydroxylation by forming hydroxyacridine isomers. Subsequent opening of epoxide ring would give a labile intermediate that suffers facile ring contraction to give 9-acridine-9-carboxaldehyde. This latter would decompose to yield acridine. Oxidant attack of •OH radicals to the aromatic ring moieties of the parent molecule leading to mono and dihydroxylated derivatives is considered an alternative transformation route, which has been previously reported by photolytic processes (Chiron et al. 2006). Despite the detection of TPs, which comes from the early oxidation steps, Vogna and co-workers (2004a) have also identified, by GC-MS and HPLC, as main detectable species, phenol-type derivatives such as anthranilic acid (2-aminobenzoic acid), salicylic acid (2-hydroxybenzoic acid) and catechol (2-hydroxyphenol) as well as small organic acids (hydroxyacetic, oxalic, malonic, oxaloacetic, maleic, fumaric, succinic, tartronic, malic and tartaric acids) yielding from the subsequent oxidation of the initial hydroxy-CBZ derivatives. Both LC and GC proved to be useful in the structural elucidation process. However, the observed degradation of CBZ in the GC, forming acridone and iminostilbene, and the missing of the TPs formed in the initial degradation steps have been underlined as drawbacks for the GC-MS method (Vogna et al. 2004a).

10.2.2.3 Oestrogen Hormones

17β-estradiol (E2) and Estrone (E1). Several groups of investigators reported the effective decomposition of estrogens and the removal of associated estrogenicity by different PAOPs. However, only few of them are focused on the identification of the intermediates (Feng et al. 2005; Ohko et al. 2002; Wang et al. 2007). Ohko et al. (2002) investigated the degradation of E2 in water by TiO_2 photocatalysis. Based on the experimental results as well as on theoretical calculations of the frontier electron densities of the E2 molecule, the authors concluded that the phenol moiety of the E2 molecule should be the starting point of the photocatalytic oxidation of E2. Afterwards, sequential oxidations took place by $HO^{\bullet}$ attack on the hydroxylated aromatic ring of E2, initiating its degradation and forming keto-derivatives which finally mineralized to CO_2 after ring opening and successive oxidation – decarboxylation steps. In addition to the TiO_2 photocatalysis, the catalytic removal of E2 was studied by Wang et al. (2007) using a combination of a nitrite and a ferric salt ($FeCl_3/NaNO_2$) as a photocatalyst in water under mimicked natural environmental conditions. Nitroestrogens (i.e. 2-nitroestradiol and 4-nitroestradiol) and low molecular weight organic acids (e.g. malonic acid) were identified as major intermediate products by GC-MS for E2.

E1 is another compound of this family, the photocatalytic degradation of which was studied in UV-VIS/Fe(III)/H_2O_2 system (Feng et al. 2005). Six TPs, which are more polar than the parent compound, were detected by HPLC with a UV detector during the treatment and a tentative degradation mechanism, similar to that of other oestrogen compounds such as E2, was proposed. However, elucidation of their structures has not been performed and further work is necessary to reveal the photocatalytic mechanism of E1.

Details of the intermediates and mechanisms of the photocatalytic treatment of pharmaceuticals discussed herein are presented in Table 10.2.

10.3 Conclusions

Over the past few years a growing number of studies have been published that have investigated the photochemical transformation of pharmaceuticals in aqueous media, including photolysis as well as homogeneous and heterogeneous photocatalysis. In this chapter we have presented some illustrative examples on the phototransformation of pharmaceuticals. Several significant issues have been raised from these studies. The most important of them from our point of view can be concluded as follows:

- Most of the pharmaceuticals covered in this chapter, with few exceptions, are considerably reactive towards PAOPs. Photolysis itself can also be a predominant fate process in the aquatic environment for a number of pharmaceuticals that have survived biological treatments in WWTPs.
- UV/H_2O_2 and TiO_2 photocatalysis are the light oxidation processes most widely used to destroy pharmaceuticals. Even though Fenton and Photo-Fenton are important oxidation treatments for industrial wastewaters, up to now there are only few publications dealing with the removal of pharmaceuticals.
- Advanced analytical instrumental methods such as GC (EI or CI)-MS (Q or IT) (and modern LC (ESI or APCI)-MS/MS have been widely used for identifying

TPs and elucidation of reaction pathways, with the latter to be the method of choice in many cases. Despite several problems accounting from the nature of some TPs such as the high polarity, low concentrations, short lifetimes, etc. most of the TPs can be identified in a straightforward manner.

- Hydroxylation, isomerization, dehalogenation, dealkylation, cyclization, decarboxylation, dimerization and ring opening (in aromatic compounds) are among the most frequently observed mechanisms of Pharmaceutical photochemical transformation.

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Chapter 11
The Challenge of the Identification and Quantification of Transformation Products in the Aquatic Environment Using High Resolution Mass Spectrometry

Juliane Hollender, Heinz Singer, Dolores Hernando, Tina Kosjek, and Ester Heath

Abstract The environment is contaminated by a number of micropollutants and their degradation products, many of which still remain undetected. Nowadays, several European regulations require the inclusion of transformation products in environmental risk assessment and monitoring. In the last decade, intense efforts have been taken to recognize the identity, quantity, and toxicity of unknown transformation products. Liquid chromatography combined with mass spectrometry has become a key technique for environmental analysis, now allowing the development of screening, identification, confirmatory and quantitative methods for the trace analysis of polar compounds in complex environmental matrices. The combination of modern technologies comprising high resolution, high mass accuracy and mass fragmentation enables the identification of compounds without having the authentic standards or even the detection of unknown analytes. However, a reliable confirmation of proposed structures using NMR spectroscopy or available standards is still desirable. This chapter presents new analytical strategies to identify and quantify transformation products generated by human metabolism, microbial degradation, or other environmental breakdown processes. Various hyphenated mass spectrometric techniques used for structure elucidation, such as liquid chromatography

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J. Hollender (✉) and H. Singer
Eawag, Swiss Federal Institute of Aquatic Science and Technology,
8600 Dübendorf, Switzerland
e-mail: juliane.hollender@eawag.ch; heinz.singer@eawag.ch

D. Hernando
National Reference Centre for Persistent Organic Pollutants and Spanish REACH Reference Centre – University of Alcalá, 28871-Alcalá de Henares, Madrid, Spain
University of Almeria, Spain
e-mail: dhernan@ual.es

T. Kosjek and E. Heath
Jožef Stefan Institute, Ljubljana, Slovenia
e-mail: tina.kosjek@ijs.si; ester.heath@ijs.si

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coupled to time-of-flight mass spectrometry, quadrupole-time-of-flight and linear ion trap-Orbitrap hybrid mass spectrometry are presented on three case studies of pharmaceutical and pesticide transformation products in environmental matrices, such as wastewater and groundwater.

11.1 Introduction

The environment is contaminated by a number of organic micropollutants released from urban, industrial, and agricultural activities, many of which still remain undetected. Although environmental monitoring includes more and more organic compounds, such as biocides, pesticides and pharmaceuticals, the analyses still mainly focus on parent compounds. However, the environmental exposure to their transformation products can be relevant as shown for pesticides in groundwater in the USA (Kolpin et al. 1997, 2004; Boxall et al. 2004) as well as in Switzerland (Hanke et al. 2007). In both studies, several pesticide transformation products (such as metolachlor-ESA or -OXA from the parent pesticide metolachlor) were found in higher concentrations in groundwater than the parent compounds. In the case of pharmaceuticals, human metabolites are excreted from the human body instead of or along with the parent compounds, often in considerable amounts. There is very limited knowledge on the environmental behaviour of those human metabolites. Some metabolites, such as conjugates of sulfamethoxazole and ethinylestradiol are cleaved back to the parent compound already in the sewer or in wastewater treatment plants (WWTP) (D'Ascenzo et al. 2003; Göbel et al. 2005). Few recent studies include the fate of persistent human metabolites of pharmaceuticals in the aquatic environment. Bendz et al. (2005) detected human ibuprofen metabolites not only in the WWTP as Buser et al. (1999), but also in the receiving river, while carbamazepine metabolites were found in WWTP effluent and even in drinking water (Miao et al. 2005; Hummel et al. 2006). In contrast to human metabolism of pharmaceuticals, which is studied in detail before pharmaceuticals are approved, their fate in the environment, including transformation pathways and formation of stable transformation products, has gained attention only recently. Only sparse information is currently available on transformation products of pharmaceuticals and their human metabolites formed in the environment or wastewater treatment plants (Kosjek et al. 2007).

As a consequence to findings of transformation products in the environment, the current European directive on drinking water as well as the guideline for groundwater quality with respect to pesticide contamination includes transformation products (Drinking Water Directive 1998; European Guidance Document 2003). Regarding chemical risk assessment, the need to identify and characterize relevant metabolites or transformation products is mentioned in several European directives and guidelines, for instance, in the EMEA guideline on the environmental risk assessment of medical products for human use (European Medicines Agency 2006) and the Council directive concerning the placing of plant protection products on the market (European Directive 1991). However, little concrete guidance on how to identify relevant transformation products is given.

Apart from the difficult selection of relevant transformation products for monitoring purposes, there are several challenges in analyzing transformation products in environmental samples such as surface and ground water. The first is, that the generally low but nevertheless potentially toxicologically relevant concentrations in the ng L^{-1} range require enrichment, separation from the matrix, and sensitive detection. The second challenge is the clear identification of transformation products without reference standards, which are often not available. An additional challenge is the identification of previously unidentified transformation products, which have never been described in the literature.

If the elemental composition is known to unequivocally identify the molecular structure of a transformation product without a reference standard, nuclear magnetic resonance (NMR) analysis coupled with liquid chromatography (LC) would be the method of choice. Although LC-NMR was successfully applied to environmental samples in a few cases (Levsen et al. 2000; Reineke et al. 2008), it requires costly equipment and is not yet sensitive enough for the low concentrations typically found in environmental samples. In contrast, GC-MS-(MS) and LC-MS-(MS) allow quantification in the concentration level down to a few ng L^{-1}. Without reference standards, a complicated interpretation of the fragmentation pattern in MS/MS or MS^n spectra is indispensable, which may give decisive hints for the identification of unknown transformation products. In modern GC-MS instruments, an electron impact (EI) ionization source is normally employed to provide a wealth of structural information in the mass spectra. EI is performed at 70 eV, thus yielding mass spectra which are identical over time and between instruments for a given compound. The resulting spectra can then be matched against spectra of authentic compounds which may be found in extensive GC-MS libraries. This ability to match analytical data to known spectra can significantly facilitate the structural elucidation of unknowns (Chiron et al. 1997). On the other hand, many transformation products are polar compounds containing hydroxy-, carboxy-, or amino-functional groups which enable GC-MS analysis only after derivatization. Derivatization can be avoided by employing LC separation, followed by electrospray or atmospheric pressure chemical ionization and tandem mass spectrometry, which is therefore the preferred identification technique for polar transformation products (Eichhorn et al. 2005). Ionization under different conditions results in a number of possible fragmentation patterns for a given compound, and consequently no large LC-MS libraries are commercially available which complicates the identification procedure.

A new approach to overcome the limitations discussed for GC-MS and LC-MS is to employ high-resolution mass spectrometry detection technology. Table 11.1 provides an overview of existing commercially available mass spectrometric techniques with respect to resolution, mass accuracy and sensitivity. The most common mass spectrometer in organic trace analytics is the triple quadrupole mass spectrometer,

Table 11.1 Comparison of current mass spectrometers concerning resolving power, mass accuracy, and sensitivity

Mass spectrometer	Resolving power[a] (FWHM)	Mass accuracy[a] (ppm)	Sensitivity[a] (absolute)
Quadrupole (Q)	Unit resolution[b]	100	fg-pg
Quadrupole ion trap (QIT; linear, 3D)	20,000	50	fg-pg
Time-of-flight (TOF)	20,000	3	pg
Sector field (magnetic/electric)	80,000	2	fg-pg
Orbitrap	100,000	2	fg-pg
Fourier transform ion cyclotron resonance (FT-ICR)	1,000,000	1	fg-pg

[a] Common values for low mass range (about *m/z of* 400); mass resolution is dependent on different parameters like scan speed, mass, instrument design, etc.; special instruments can reach better values.

[b] Unit mass resolution is the resolution for standard quadrupole instruments; with special hyperbolic quadrupole instruments a resolving power of 5,000 and a mass accuracy of 5 ppm can be achieved.

which selectively filters ions based on their mass-to-charge ratio (*m/z*) in two consecutive quadrupoles combined by a collision cell. It uses oscillating electrical fields to selectively stabilize or destabilize the paths of ions passing through a radio frequency (RF) quadrupole field. The quadrupole ion trap and linear quadrupole ion trap work on the same physical principles as the quadrupole mass analyzer, but the ions are trapped and sequentially ejected. In contrast, in time-of-flight mass spectrometry, ions are accelerated by an electrical field to the same kinetic energy with the velocity of the ion depending on its *m/z*. Thus, the time ions need to reach the detector can be used to determine the *m/z*. Sector field mass analyzers, which are nowadays rarely utilized in organic trace analytics, use an electric and/or magnetic field to affect the path and/or velocity of the ions. According to their *m/z* the ions are differently deflected. In the relatively new Orbitrap mass spectrometer ions are electrostatically trapped in an orbit and the mass is measured by detecting the image current produced by the ions oscillating in the presence of an electric field. The frequencies of these image currents depend on the *m/z* of the ions. Mass spectra are obtained by Fourier transformation of the recorded image currents. In very costly Fourier transform ion cyclotron resonance mass spectrometer the image current is produced in a magnetic field which enables superior resolution and mass accuracy.

Combination of two or more *m/z* separation devices of different types, the so-called hybrid mass spectrometer, can combine the advantages of two techniques. A triple quadrupole mass spectrometer with the final quadrupole replaced by a time-of-flight tandem mass spectrometry (QTOF) or linear ion trap combined with an orbitrap mass spectrometry (LTQ-Orbitrap) have especially been shown to enable fast, sensitive and reliable detection and identification of low molecular weight substances thanks to their high mass accuracy and mass resolution (Van Bocxlaer et al. 2005; Lacorte and Fernandez-Alba 2006; Bueno et al 2007; Krauss and Hollender 2008). Full-scan mass spectra acquired with high mass accuracy and resolution allow selective searching for the molecular ions of transformation products based on their exact mass, while MS/MS technology provides structural information based on compound fragmentation.

Several studies report the use of high-resolution mass spectrometry to screen for transformation products in biodegradation experiments or photolysis studies carried out in the laboratory (Ibanez et al. 2004; Durand et al. 2006; Gomez et al. 2008; Ruan et al. 2008). In these studies, transformation of the parent compounds is studied at high initial concentrations in controlled matrix. In that case, classical techniques such as UV-VIS spectrometry can help characterizing the products as shown in Längin et al. (2009). Screening and identification of pesticides and their transformation products in environmental samples by the combination of LC-ion trap with LC-TOF instruments have also been described (Hernández et al. 2004, 2005; Thurman et al. 2005). A systematic procedure to screen for large numbers of transformation products in environmental samples containing a variety of organic compounds at low concentrations in the ng L^{-1} range using an LTQ-Orbitrap has only recently been reported (Kern et al. 2009).

The scope of this chapter is to present the potential of new hybrid tandem mass spectrometers to identify and quantify transformation products generated by human metabolism, microbial degradation, or other environmental breakdown processes. The strategies to identify transformation products by different hyphenated mass spectrometric techniques are presented in case studies where the advantages and the limitations of the structure elucidation procedure are also discussed. The first case study deals with the identification of a transformation product which is produced from a pharmaceutical during microbial degradation in the wastewater treatment process. The QTOF technology may enable identification of degradation products that are not yet described in the literature. In contrast, human metabolites are studied in detail in drug development procedure and are stated in pharmaceutical dossiers. Reference standards are sometimes not available and therefore clear identification must be carried out using, for instance, LC-TOF as presented in the second case study for a human metabolite in wastewater. The compound structure was confirmed by a QTRAP. Finally, we present the identification of a pesticide transformation product from groundwater samples. In this case study, Orbitrap technology enabled the identification of the transformation product in low environmental concentrations concurrently with a targeted screening. The case studies presented herein not only include the application of three different hybrid LC-MS techniques, but at the same time we show the identification of transformation products in very different matrices from relatively pure groundwater to highly contaminated wastewater.

11.2 Case Studies for Identification of Transformation Products by Different High Resolution Mass Spectrometric Techniques

11.2.1 Case Study 1: Identification of a Biotransformation Product of the Pharmaceutical Diclofenac in Wastewater by Ultra Performance Liquid Chromatography Hyphenated with Quadrupole-Time-of-Flight Mass Spectrometry

Among the most powerful instruments for the identification of unknown analytes is the quadrupole – time-of-flight mass spectrometer (QTOF), a hybrid mass spectrometric system that combines the advantages of ion separation and the detection principle of time-of-flight (TOF) systems and the fragmentation obtained with MS^2 experiments. TOF instruments provide full-scan sensitivity, high mass resolution (10,000–20,000**,** full width at half maximum), good mass – accuracy (<3 ppm), and theoretically limitless scan range (Campbell et al. 1998). However, structural elucidation with the stand-alone TOF is primarily feasible for compounds with easy in-source fragmentation or those having a characteristic isotopic pattern (Petrović and Barceló 2007). As an alternative, the hybrid QTOF, in which the final resolving mass filter of a triple quadrupole is replaced by a TOF analyzer, also enables the acquisition of high resolution mass spectra with accurate masses for the product ions. This gives the analyst a much higher degree of certainty when identifying compounds in non-target analyses, by positively and unequivocally confirming target compounds (Van Bocxlaer et al. 2005; Petrović and Barceló 2006). While this instrument is already a well established tool for the confirmation of target micropollutants in environmental matrices, its use for the identification of complete unknowns or transformation products is still growing. So far only a few studies have reported the application of QTOF in this field (Eichhorn et al. 2005; Pérez et al. 2007; Kosjek et al. 2008).

As an example of use of QTOF-MS, in this paper we describe the separation, detection, and successful identification of a nitro-analogue of diclofenac, a biotransformation product produced in a pilot wastewater treatment plant. At the outset of the study, emphasis was placed on quality chromatographic separation, which is of great importance in a complex environmental matrix, such as wastewater. Thus, ultra performance liquid chromatography (UPLC) was employed and enabled elution of the analytes in narrow, concentrated bands resulting in improved resolution, increased peak capacity, and increased speed of chromatographic separation (Petrović et al. 2006). This was performed with a Waters Acquity UPLC system (Waters Corp. Milford, MA, USA), equipped with a C-18 column with a 1.7 μm particle size (Waters Acquity 50 × 2.1 mm) using water / methanol gradient elution at a flow rate of 0.3 mL min^{-1}. The UPLC system was hyphenated to a hybrid quadrupole orthogonal acceleration time-of-flight mass spectrometer (QTOF Premier, Waters, Milford, Massachusetts, USA). To aid in the detection of biotransformation products, post-acquisition data processing was employed using the MetaboLynx™ software package. The algorithm, a part of MassLynx v4.1 software (Waters), searches extracted mass chromatograms for expected transformation products based on predicted or unpredicted molecular changes relative to the parent compound and thus aids in the detection and identification of unknowns, particularly those buried in spectral noise. The software compares mass spectral chromatograms between a control and a sample (Freed et al. 2004). Thus, the use of MetaboLynx™ software for comparison of treated and untreated wastewater samples spiked with diclofenac resulted in detection of diclofenac biotransformation product, eluted at 5.0 min. Accordingly, the isotopic cluster analysis was performed in order to determine the isotope ratio between cluster ion fragments and yielded the same results. Figure 11.1 illustrates a segment from the MetaboLynx report file with the extracted mass chromatogram of the biotransformation product (top right), its mass spectrum (top left), and the absence in the control sample chromatogram (bottom).

The high resolution and accurate mass measurements provided by the TOF mass analyser identified the deprotonated molecular mass [M – H]$^-$ 338.9945. Using the "Elemental composition calculator" tool (±10 ppm mass error, C: 0–15, H: 0–20, N: 0–3, O: 0–10, Cl: 0–2) we were able to assign a highly probable elemental formula of the diclofenac biotransformation product ($C_{14}H_{10}N_2O_4Cl_2$). Comparing to the elemental formula of diclofenac ($C_{14}H_{11}NO_2Cl_2$), the biotransformation product shows a substitution of a hydrogen atom for a NO_2 group. The structure of the biotransformation product was studied based on its TOF-MS-(ESI$^{(-)}$) and TOF-MSMS-(ESI$^{(-)}$) fragmentation (Fig. 11.2). Besides the deprotonated molecule

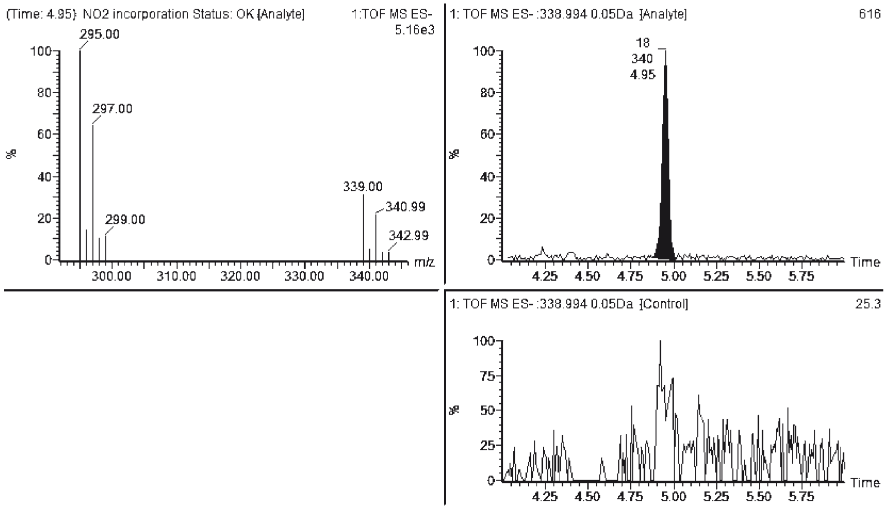


Fig. 11.1 Extracted from the MetaboLynx report file: analyte (*top*) and control (*bottom*) sample mass chromatograms and TOF-ESI(–) spectrum (*left*) of a peak eluting at t_R 4.95 min

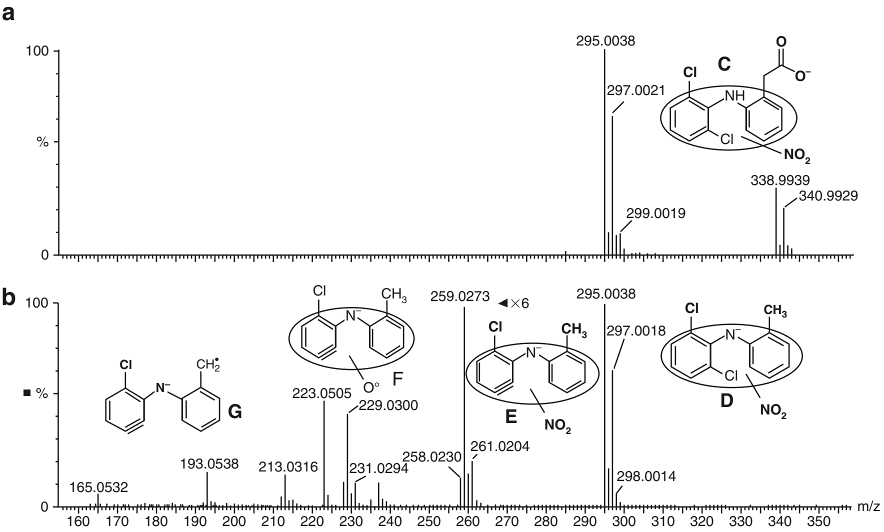


Fig. 11.2 *Top*: TOF-ESI(−) mass spectrum of biotransformation product (**a**); *bottom*: MS/MS spectrum of m/z 339 (**b**); proposed chemical structures of deprotonated molecule (m/z 339, **c**) and principal product ions 295 (**d**), 259 (**e**), 229 (**f**) and 213 (**g**) (Reproduced from Kosjek et al. (2008). With permission of Elsevier)

$[M - H]^-$ (*m/z* 339), the elimination of CO_2 to form *m/z* 295 also occurred under MS conditions due to in source fragmentation. The TOF-ESI(−) mass spectrum in Fig. 11.2a illustrates a dichloro isotopic pattern in both, *m/z* 339 and 295. The collision induced dissociation of *m/z* 339 (Fig. 11.2b) resulted in further losses of HCl with *m/z* 259 and homolytic cleavages of $NO^\cdot$ with m/z 229 or $NO_2^\cdot$ with *m/z* 213. The product ion with *m/z* 223 is indicative of the loss of HCl from *m/z* 259, while *m/z* 193 corresponds to the loss of HCl from the product ion with *m/z* 229. The ion fragments proposed in Fig. 11.2 were compared with fragmentation pattern of parent compound and confirmed by accurate mass measurements in which the mass error did not exceed 0.7 mmu. The identification procedure is described in detail in Kosjek et al. (2008). In conclusion, the results indicate that the biotransformation yields a nitro-analogue of diclofenac. However, the exact position of the nitro group within the molecule could not be derived from the MS/MS data, and further investigations applying nuclear magnetic resonance (NMR) are necessary for complete structure elucidation. The incorporation of the NO_2 group into the aromatic ring is a rather unusual transformation process, which does not occur during human metabolism. However, this transformation has previously been reported to occur on pesticides in the environment (Hernández et al. 2008) and is reasoned by the presence of nitrate in aquatic media (Hogenboom et al. 1999; Kosjek et al. 2008).

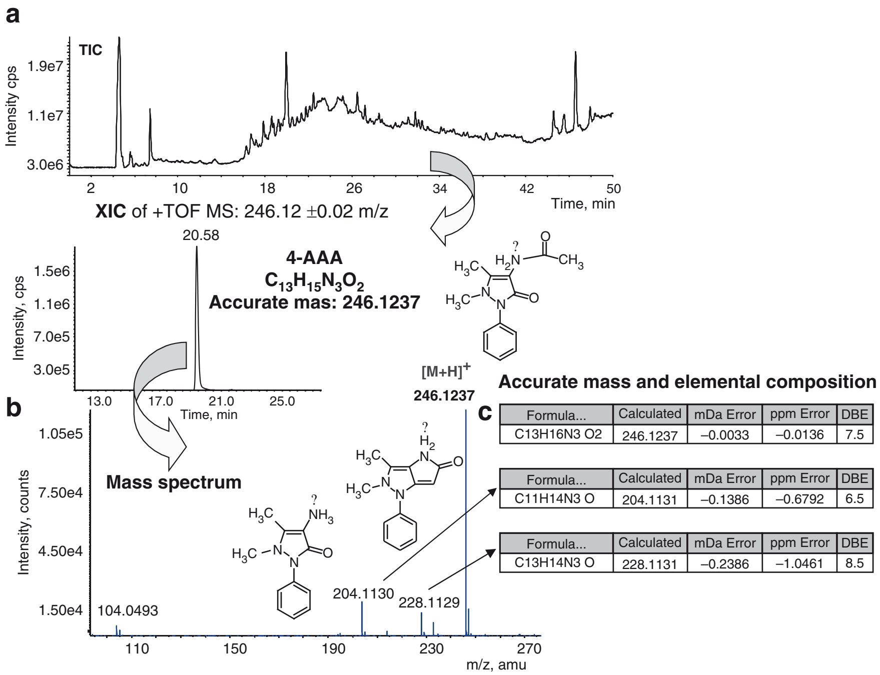
With this study the key attributes of the QTOF instrument were confirmed: MS/MS fragmentation, high resolution, good mass accuracy, high sensitivity, and the ability to record a complete mass spectrum for each pulse of ions injected into the device. Further, this study implies that environmental and wastewater treatment processes yield different transformation products than human metabolism does.

11.2.2 Case Study 2: Identification of the Human Pharmaceutical Metabolite N-Acetyl-4-Aminoantipyrine by Liquid Chromatography Combined with Time-of-Flight Mass Spectrometry and Quantification by Quadrupole/Linear Iontrap Mass Spectrometry

Structural elucidation with a self-standing TOF is only feasible for compounds with easy in-source fragmentation or a characteristic isotopic pattern. If a hybrid system such as a QTOF is not available, additional measurements on a low resolution tandem mass spectrometer can be acquired to confirm the structure suggested based on the molecular ion obtained by TOF. As an additional benefit, target analysis based on MS/MS fragmentation by an triple quadrupole or ion trap provides excellent performance for quantitative analysis because of its inherent selectivity and sensitivity (Barceló and Petrović 2007; Hernando et al. 2007a, b). Ion traps (IT) are particularly powerful for unequivocal confirmation or elucidation of molecular structures, since very fast and sensitive full scan modes (including MS^2 and MS^n) can be applied. The latest generation of linear ion trap (LIT) mass spectrometers enables the use of selected reaction monitoring (SRM) dwell times as low as 2 ms without loss of sensitivity enabling multi-target methods. QqLIT systems offer hybrid triple quadrupole/linear ion trap capabilities. Working in LIT mode, the QTRAP systems provide improved performance and enhanced sensitivity in full scan MS (EMS) and product ion scan (enhanced product ion (EPI)) modes. An extra operational mode of this hybrid system is the possibility of combining in the same run, SRM and EPI scans, by the built-in information-dependent acquisition (IDA) software, thus obtaining at the same time quantification and additional structural information.

This case study describes an analytical protocol that combines the use of QTRAP and TOF instruments to achieve both accurate and reliable target compound monitoring and identification of one of the major known metabolites of the antipyretic drug dipyrone (Bueno et al. 2007). The analytical strategy proposed in this work provides a comprehensive approach to increase the scope of a monitoring program for the identification of emerging contaminants (including transformation products and metabolites) in wastewater.

The chromatographic separations in both QTRAP and TOF systems were performed using an HPLC (series 1100, Agilent Technologies, Palo Alto, CA) equipped with a reversed-phase C-18 analytical column (Zorbax SB, Agilent Technologies) of 5-µm particle size, 250-mm length, and 3.0-mm i.d. Gradient LC elution was performed with 0.1% formic acid and 5% MilliQ water in acetonitrile as mobile phase A, and 0.1% formic acid in water (pH 3.5) as mobile phase B (for details see Bueno et al. 2007)



Formula...	Calculated	mDa Error	ppm Error	DBE
C13H16N3 O2	246.1237	−0.0033	−0.0136	7.5

Formula...	Calculated	mDa Error	ppm Error	DBE
C11H14N3 O	204.1131	−0.1386	−0.6792	6.5

Formula...	Calculated	mDa Error	ppm Error	DBE
C13H14N3 O	228.1131	−0.2386	−1.0461	8.5

Fig. 11.3 Identification of *N*-acetyl-4-aminoantipyrine (4-AAA), a major metabolite of the antipyretic drug dipyrone, by TOF system

As an example, the identification of N-acetyl-4-aminoantipyrine (4-AAA) by a TOF system is shown in Fig. 11.3. This major human metabolite of the antipyretic drug dypirone was identified for the first time in wastewater and surface water by Zuehlke et al. (2004). The strategy for identifying non-target analytes in the samples was based on three steps: (a) selection of the extracted ion chromatogram (XIC) for the target m/z, (20 mmu); (b) background-subtracted mass spectrum; (c) verification of accurate mass and elemental composition of the molecule and fragment ions. The agreement between the measured and calculated masses within a <5 ppm error level, along with matching retention times and mass spectra if reference standards are available, provided an unequivocal confirmation of the compounds in the samples. Analysis of spiked wastewater extracts resulted in errors lower than 2 ppm for the target compounds. Applying this strategy, other metabolites were also identified (4-dimethylaminoantipyrine; N-formyl-4-aminoantipyrine; 4-amino-antipyrine; antipyrine), confirmed with the acquisition of the appropriate standards, and finally included in the monitoring program.

Identification of transformation products by QTRAP systems in wastewater samples was reinforced by the acquisition of three transitions. Additionally, confirmation by ratio of SRM transitions was also used as an identification criterion and as a way to detect possible contributions of matrix interferences to the transition intensities, thus avoiding overestimations or false positive findings in quantitative analysis. For instance, the metabolite of carbamazepine, carbamazepine 10,11-epoxide was confirmed by the acquisition of three SRM transitions (253.2 → 180.2; 253.2 → 236.2 and 253.2 → 210.2). By IDA software, QTRAP systems enable the application of survey scans in SRM mode and EPI mode in a single run. This alternative is useful for compounds for which the second transition is not detected or is present at low intensity and additional structural information is required for a suitable confirmation.

In summary, target analysis of contaminants by QTRAP provided quantitative results for a large group of selected compounds. The analyses by TOF-MS enabled the identification of non-target compounds in wastewater samples.

11.2.3 Case Study 3: Identification of A Transformation Product of the Pesticide Chloridazon in Groundwater by Liquid Chromatography Combined with Linear Iontrap-Orbitrap Mass Spectrometry

Orbitrap technology was introduced to the market in 2005. The hybrid system of linear ion trap combined with the new orbitrap technology (LTQ-Orbitrap) combines high sensitivity with high mass resolution (R > 100,000) and high mass accuracy (<2 ppm) (Hu et al. 2005; Makarov et al. 2006). In recent years several studies reported the use of this new technology to identify unknown micropollutants, metabolites, and transformation products in laboratory studies or environmental samples including surface and groundwater (Peterman et al. 2006; Ruan et al. 2008; Reineke et al. 2008; Kern et al. 2009).

As an example of the use of LTQ-Orbitrap, we describe the separation, detection, and successful identification of a transformation product of chloridazon in groundwater parallel to a multi-targeted screening. As part of a Swiss national survey in 2008, we screened approximately 20 groundwater samples from various catchments within both agricultural and urban areas for the occurrence of more than 200 pharmaceuticals, pesticides, biocides, and their transformation products. Additionally, the samples were analysed for non-target compounds using accurate mass screening. For this purpose, all samples were enriched using solid phase extraction (SPE). Subsequently, 20 μL of the SPE extract were injected into the LC system. Chromatographic separation of the extracts was achieved on a C-18 column (XBridge, Waters, 50 × 2.1 mm, particle size of 3.5 μm) using gradient elution with methanol and water (0.1% formic acid) at a flow rate of 200 μL min^{-1}. After electrospray ionisation in the positive and negative mode, ions were detected by a LTQ-Orbitrap XL mass spectrometer (Thermo Fisher Scientific Corporation). High-resolution mass spectra (HR-MS) with a resolution of 60,000 were recorded to extract the chromatograms of target and non-target analytes. To confirm peak findings, data-dependent high-resolution product ion spectra (HR-MSMS) at a resolution of 7,500 were also produced. In order to receive more than ten HR-MS scans for each peak and simultaneously enough HR-MSMS within one chromatographic measurement, the resolution had to be set to this relatively low value. Mass calibration was carried out with external standard calibration compounds and a typical mass accuracy of <3 ppm was achieved.

For the identification of more than 200 compounds, the accurate masses were extracted from the HR-MS-TIC with a mass filter of 5 ppm and confirmed by matching the HR-MSMS and the retention time with the related reference standards. To find unknowns, non-target compound detection was performed by filtering the total acquired mass range (115–1,000 m/z) of the HR-MS-TIC (Fig. 11.4a) with a 5 ppm mass extraction window using the Formulator software (Thermo Fisher, USA). As a result, up to 5,000 extracted ion chromatograms containing peaks with a signal-to-noise ratio greater than 5 were collected per sample. After sorting the data set by retention time and peak intensity, compound peaks with high signal intensity and distinct isotopic patterns were processed further.

As an example, the protonated molecule $[M+H]^+$ with an accurate mass of 160.0272 occurred in nearly all groundwater samples with an intense peak at 2.2 min (see Fig. 11.4b). By taking the accurate mass and the isotope pattern into account, the elemental composition $C_5H_6Cl_1N_3O_1$ could be unequivocally assigned to this peak by constraining the atoms to C, H, N, O, S, Cl, and Br for the elemental formula fit. The excellent match of the measured and theoretical isotope pattern is depicted in Fig. 11.4d and e. Searches in the Scifinder and Pubchem data base for $C_5H_6Cl_1N_3O_1$ resulted in approximately 100 possible chemical structures. By comparing the measured HR-MSMS with predicted mass spectra proposed by the software Massfrontier (Thermo Fisher, USA) along with estimated retention times for all possible structures from the data base search, the best match for the identified elemental composition was determined to be chloridazon-methyl-desphenyl. Because a reference standard was available for this compound, the retention time and the HR-MSMS were matched between the sample (Fig. 11.4f) and the reference standard (Fig. 11.4g). Due to this comparison it could be unequivocally confirmed that the unknown compound is indeed chloridazon-methyl-desphenyl.

Chloridazon is a systemic herbicide which is widely used for sugarbeet and beet crops. The biological formation of chloridazon-methyl-desphenyl from chloridazon takes place in soil (Roberts and Hutson 2002; EU DG 2006). Chloridazon (5-amino-4-chloro-2-phenylpyridazin-3(2H)-one) is first degraded to chloridazon-desphenyl which is further transformed to chloridazon-methyl-desphenyl (Fig. 11.5). Both transformation products were detected in many of the investigated groundwater samples in concentrations up to several 100 ng L^{-1}. This is in agreement with findings of Weber et al. (2007), who described the occurrence of these compounds in surface, ground, and drinking water in Germany. The transformation products were most often found in higher concentrations than the parent compound which reinforces the need to include transformation products in environmental quality monitoring.

In summary, the LTQ-Orbitrap instrument concurrently enables a multi-targeted screening (with sensitivity comparable to a tandem mass spectrometer) and an identification of unknowns based on high mass resolution and mass accuracy for molecular ions and fragments.

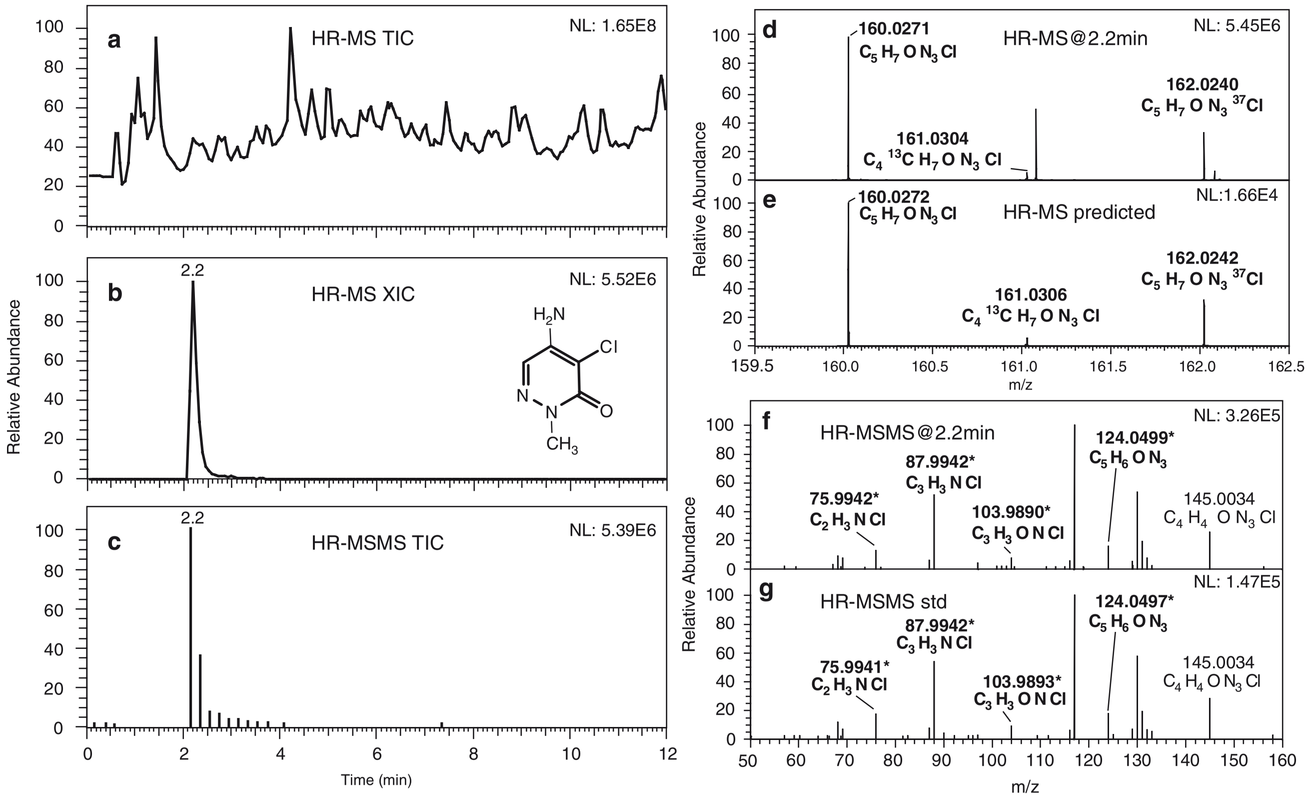


Fig. 11.4 Chromatograms and spectra of an enriched ground water sample for the identification of chloridazon-methyl-desphenyl as a mobile and persistent transformation product of the herbicide chloridazon (**a**): Total ion chromatogram of HR-MS scans (R 60'000, 115–2,000 m/z) (**b**): Extracted ion chromatogram (5 ppm) of $[M + H]^+$ 160.0272 m/z (**c**): Data dependent HR-MSMS scan of 160.0272 (R 7'500, 50–175 m/z) (**d**): Measured HR-MS at 2.2 min (R 60'000, 115–2,000 m/z) (**e**): Theoretical HR-MS of the elemental composition $C_5H_6ClN_3O$ ($[M + H]^+$=160.0272) (**f**): Measured HR-MSMS of 160.0272 at 2.2 min, marked fragments (*) were predicted by Massfrontier G: Measured HR-MSMS of a standard solution of chloridazon-methyl-desphenyl

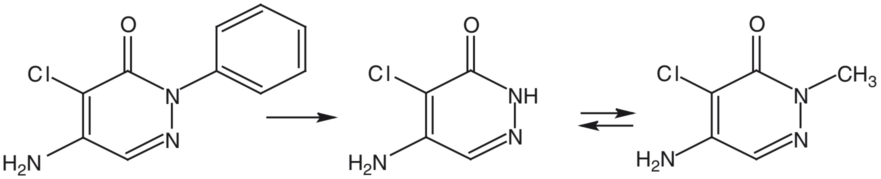


Fig. 11.5 Proposed formation of the transformation product methyl-desphenyl-chloridazon from chloridazon in soil (Weber et al. 2007)

11.3 Conclusions

The three case studies demonstrate that hybrid tandem mass spectrometry, which combines two mass spectrometric technologies including high resolution technique, opens possibilities for identification of polar transformation products without reference standards and even gives decisive hints for the identification of previously unknown transformation products. The hybrid mass spectrometry technology can be applied to different environmental matrices from relatively pure groundwater to highly contaminated wastewater. The new generation of instruments allows the detection of concentrations down to the low ng per liter range. Since the software tools for an automatic non-targeted screening mostly do not provide sufficient support and are demanding to work with, the detection of unknown transformation products is still time consuming and requires analysis by those with a high level of chemical expertise. The examples presented herein and described in the literature on the elucidation of transformation products are still scarce and more studies are needed to improve the knowledge about the occurrence of transformation products in the environment. Along with the identification and quantification of these compounds, the toxicity assessment is another important task, which may help to clarify the burden that the transformation products pose to human health and the environment.

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Chapter 12
Transport and Fate of Xenobiotics in the Urban Water Cycle: Studies in Halle/Saale and Leipzig (Germany)

Mario Schirmer, Frido Reinstorf, Sebastian Leschik, Andreas Musolff, Ronald Krieg, Karsten Osenbrück, Marion Martien, Kristin Schirmer, and Gerhard Strauch

Abstract This chapter on urban water in large population centres like Halle/Saale and Leipzig (Germany) focuses on the source, distribution and transport behaviour of xenobiotics as indicator substances for anthropogenic impacts on urban water systems.

M. Schirmer (✉)
Department of Water Resources and Drinking Water, Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstr. 133, 8600 Dübendorf, Switzerland
Phone: ++41 44 823 5382, Fax: ++41 44 823 5210, e-mail: mario.schirmer@eawag.ch

F. Reinstorf
Department of Water and Waste Management, University of Applied Sciences Magdeburg-Stendal, Breitscheidstr. 2, 39114 Magdeburg, Germany
e-mail: frido.reinstorf@hs-magdeburg.de

S. Leschik, A. Musolff and G. Strauch
Department of Hydrogeology, UFZ – Helmholtz Centre for Environmental Research, Permoserstraβe 15, 04318 Leipzig, Germany
e-mail: sebastian.leschik@ufz.de; andreas.musolff@ufz.de; gerhard.strauch@ufz.de

R. Krieg
Department of Hydrogeology, UFZ – Helmholtz Centre for Environmental Research, Theodor-Lieser-Str. 40, 6120, Halle (Saale), Germany
e-mail: ronald.krieg@ufz.de

K. Osenbrück
Department of Isotope Hydrology, UFZ – Helmholtz Centre for Environmental Research, Theodor-Lieser-Str. 40, 6120, Halle (Saale), Germany
e-mail: karsten.osenbrueck@ufz.de

M. Martien
Chair Biotechnology of Water Treatment, Brandenburg University of Technology Cottbus, Institute for Environmental Technology, Siemens-Halske-Ring 8, 03046, Cottbus, Germany
e-mail: marion.martienssen@tu-cottbus.de

K. Schirmer
Department of Environmental Toxicology, Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstr. 133, 8600, Dübendorf, Switzerland
e-mail: kristin.schirmer@eawag.ch

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The xenobiotics reported here are micropollutants including pharmaceuticals, personal care products (collectively known as PPCPs) and industrial chemicals, which show low concentrations in urban waters. Such chemicals can be endocrine disrupters or are otherwise eco-toxic. The concepts presented herein required a new methodology for assessing the impact of human activities on the urban water system and processes in urban watersheds. To this end, we used different approaches in relation to the hydrogeological and hydrodynamic settings of the cities of Halle and Leipzig. For the Halle urban area, a conceptual flow and transport model was developed based on interaction between the river Saale and groundwater, and mass fluxes were computed, based on water balance calculations. For Leipzig, as a first approach, we established a monitoring program that involved various urban land use types and investigated their influence on the urban water system. Multivariate statistics and integral pumping tests were applied to account for the spatially highly heterogeneous conditions and time-varying concentrations. At both sites, we demonstrated the use of indicators consisting of physico-chemical parameters, ions, isotopes and compound-specific patterns of xenobiotics. The chosen indicators of pH, temperature, electrical conductivity, redox conditions, nitrate, sulphate, chloride, boron, the isotopes of hydrogen, nitrogen, oxygen, sulphur and boron, as well as bisphenol A, carbamazepine, technical 4-nonylphenol (t-nonylphenol), galaxolide, tonalide, and gadolinium, helped to balance urban substance fluxes and assess urban effects on surface water quality. From our current quantification, it is clear that predicting contaminant behaviour in urban areas demands a detailed process understanding which cannot be derived from laboratory experiments or phenomenological analyses at the catchment scale. Through an installation of measuring equipment at the interfaces between the unsaturated and saturated zone as well as between ground- and surface water, in situ contaminant transport and fate can be quantified from the cm- up to the m-range.

12.1 Introduction

Urban water systems are commonly polluted by diffusive and direct contribution of anthropogenic activities (Ternes 1998; Ricking et al. 2003). Besides industrial contaminants like aromatic and chlorinated hydrocarbons and other persistent organic compounds, the urban aquatic environment is also polluted by potentially eco-toxic compounds such as pharmaceuticals, fragrances and industrial chemicals (Heemcken et al. 2001; Heberer 2002a,b; Stachel et al. 2003; Peck and Hornbuckle 2006; Reinstorf et al. 2008), and trace elements (Möller et al. 2002; 2003) carried in by surface and sub-surface wastewater and seepage processes. Surface and groundwater in urban catchments are currently in focus due to the increasing human activities including industrial production, transportation and housing.

Due to their polarity, some of the xenobiotics including pharmaceuticals as well as sludge, are not significantly retained in sludge and sediments (Clara et al. 2002; Ricking et al. 2003; Peck and Hornbuckle 2004; Peck et al. 2006) and may contaminate groundwater.

Other substances, including endocrine active contaminants are more lipophilic and can accumulate in organic (biofilms) and sediment material (Ahel et al. 2000). It is therefore clear that urban wastewater represents the most important pathway for these anthropogenic micropollutants, particularly when the condition of the sewer system can strongly influence the urban surface water and groundwater. Moreover, the contamination of urban water could have a long-term impact on the urban ecosystem, as shown for example, by carbamazepine (Andreozzi et al. 2002). In order to protect drinking water resources, the German Environmental Agency has initiated a proposal to set a current maximum limit for a variety of pharmaceuticals of 0.1 μg L^{-1} until the data base has been improved (Geiler 2006). This calls for improving our knowledge of sources, distribution, migration, sorption and reaction processes, and eco-toxicological properties of these new emerging substances, and assessing their effects on urban water systems (Schwarzenbach et al. 2006; Schirmer and Schirmer 2008; Musolff 2009). It is therefore necessary to find and use suitable indicators for studying the fate of these water bound micropollutants in surface and groundwater within the urban environment (Schirmer et al. 2007).

To achieve this goal, we tested a variety of physical and hydrochemical parameters which are related to anthropogenic activities and which have tracing properties in different urban environments. Selected indicators were evaluated for their applicability to reflect the various impacts on the urban water cycle under the given hydrogeological conditions and urban infrastructure. Several of the indicators are xenobiotics which are considered representatives for a larger number or classes of micropollutants.

12.2 Investigations in the Cities Halle/Saale and Leipzig (Germany)

Our research on urban water resources in large cities like Halle/Saale and Leipzig has focused on the source, distribution and transport behaviour of xenobiotics as indicator substances for the anthropogenic impact on urban surface water and groundwater (Strauch et al. 2008).

These indicators were evaluated for their applicability to reflect the various impacts on the urban water cycle under the given hydrogeological conditions and urban infrastructure. The most important criteria we chose were: (1) they should be typical for anthropogenic emissions, for example from hospitals or housing; (2) some should be persistent to better reflect their spread in the environment; (3) some should be non-persistent to assess their potential for biodegradation; (4) some should be mobile (conservative tracers) to allow measuring fluxes between the hydrological compartments; (5) some should be important in terms of the health of the population or the ecosystem; and (6) they should reflect the path of other chemicals that are important for humans or ecosystem health. Finally, we chose indicators for which concentration measurements are not too labour-intensive and for which sampling efforts are moderate.

In view of these selection criteria, the selected indicators and their physico-chemical properties, including their original use, are shown in Table 12.1. The presented concepts required new methodologies for assessing the impact of human activities on the urban water system and processes within urban watersheds. To this end, we used different approaches and measurement scales in relation to the hydrogeological and hydrodynamic setting of the cities of Halle and Leipzig.

12.2.1 Case Study: City of Halle/Saale

The city of Halle/Saale is part of a semi-arid region in Germany with a mean annual precipitation of 450.8 mm (1961–1990) and an annual mean air temperature of about 9°C. The city is situated 96 m above sea level downstream of Leipzig and has an area of approximately 135 km^2 with about 240,000 inhabitants (Fig. 12.1). The rivers Saale and Weiße Elster merge south of the city and flow northwards through Halle with a mean discharge MQ = 98.6 $m^3\ s^{-1}$ (Gauge Halle-Trotha). The nearest gauging station for the river Weiße Elster, Gauge Oberthau, is located downstream (north west) of Leipzig, a city of about 500,000 inhabitants. The mean discharge there is about MQ = 24.8 $m^3\ s^{-1}$. The city of Halle/Saale is located above a very heterogeneous geological formation with more than 16 aquifers identified within the city limits. In addition to the Quaternary and Tertiary sediments, the layers of the Muschelkalk, Buntsandstein, Zechstein and the Rotliegendes are also of great importance. A valley aquifer comprising gravels and sands of the Niederterasse and Holocene fluvial gravels is found in the flood plain areas and underlays the upper aquifer.

Over a period of 5 years we made detailed measurements of xenobiotic concentrations in the surface and groundwaters within the city of Halle/Saale (Reinstorf et al. 2008). The water sampling at the river Saale was carried out at a total of eight sites along the river Saale. The sampling results presented here occurred during six sampling events between the years 2002 and 2005. The groundwater sampling was carried out at eight monitoring points. Here the results are shown from four sampling sites for the sampling date March 24, 2004.

Pharmaceutical analysis was carried out as follows: solid phase extraction (SPE), clean-up for sample preparation and GC-MS analysis. Details of sampling and chemical analysis are described in Reinstorf et al. (2008).

On the basis of these concentrations alone, however, a significant influence on the city's water resources could not be shown. A more representative measure of urban impact uses a combination of concentrations and water fluxes, i.e. measuring impact on the basis of mass flux. Therefore, for the urban area of Halle/Saale, a mass flux balance model for the river system within the city was created considering the interaction between the surface water of the river Saale and the groundwater beneath the city. The elements of the model are inflow (rivers Saale and Weiße Elster) and outflow (river Saale) of the domain, the outlet of the wastewater treatment plant into the river Saale, retardation as a sum of adsorption and biodegradation

Table 12.1 Range of indicators in the urban water cycle, their occurrence, use and selected physico-chemical properties

Indicator compound	Application/occurrence/effect	Physico-chemical properties
Bisphenol A (BPA)	Component in plastics (resins, poly-carbonate) Endocrine disruptor (estrogene)	Degradable aerobically (Ying et al. 2008)
Carbamazepine (CBZ)	Antiepileptic drug	Persistent, high mobility (Fenz et al. 2005)
t-Nonylphenol (NP)	Constituent of detergents, anti-oxidants Endocrine disruptor Interaction with estrogenic receptor	Linear NP degradable, complex compounds more persistent
Galaxolide (HHCB)	Fragrance, chemo sensitizer (Luckenbach and Epel 2005)	Persistent
Tonalide (AHTN)	Fragrance, chemo sensitizer (Luckenbach and Epel 2005)	Persistent
Gadolinium (Gd); Gd-DTPA	Contrast component in human medicine Geogene occurred as Rare Earth Element	Persistent
Nitrate (NO_3^-)	Fertilizers, component of wastewater; Carcinogenic	Denitrification, oxidizing, high mobility
Sulphate (SO_4^{2-})	Geogenic: mineral and drinking water, salt water, brines Anthropogenic: wastewater, landfill drainage	Reducible
Chloride (Cl^-)	Geogenic: mineral and drinking water, salt water, Brines; anthropogenic: wastewater, landfill drainage	Persistent
Boron (B)	Ingredient in detergents	High mobility
Hydrogen isotopes	Water and water-related compounds	Isotope fractionation at transfer processes
$^2H/H$	Sources, origin, transport, mixing processes	
Nitrogen isotopes	Air, N-bearing compounds (bound, dissolved)	Isotope fractionation at transfer processes
$^{15}N/^{14}N$	Origin, degradation, mixing processes	
Oxygen isotopes	Water, air, rocks/sediments	Isotope fractionation at transfer processes
$^{18}O/^{16}O$	Origin, transport, mixing processes	
Sulphur isotopes	Minerals, S-bearing compounds: origin, degradation, acidification	Isotope fractionation at transfer processes
$^{34}S/^{32}S$		
Boron isotopes	Borates, detergents	Isotope fractionation at transfer processes
$^{11}B/^{10}B$	Origin, transport	

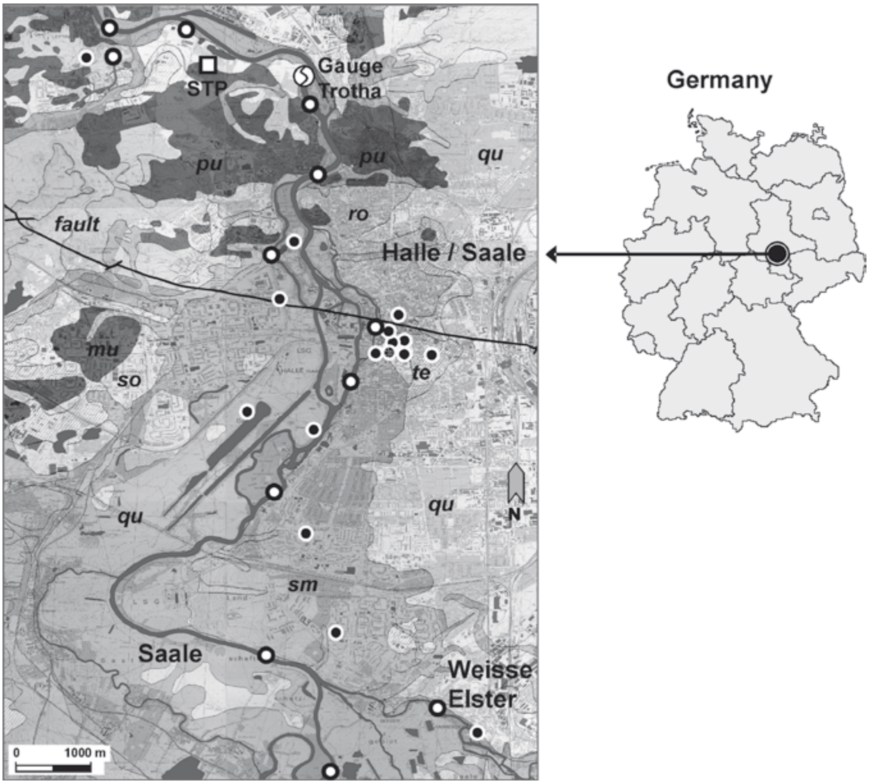

Fig. 12.1 Study area and location of sampling sites within the city of Halle (● groundwater, ○ surface water). STP indicates the location of the wastewater treatment plant. Shaded areas roughly represent the main geological units, qu: Quaternary (sand, gravel, clay), te: Tertiary (sand, silt), sm/so: Buntsandstein (sandstone), mu: Muschelkalk (limestone), ro: Pre-Quaternary (fractured sandstones and shists), pu: Pre-Quaternary (Permian porphyrs)

of pollutants in the river sediments and a diffuse component due to groundwater inflow into the river Saale. Since the concentrations often changed considerably over time, it was decided to calculate average mass fluxes and thus we derived a complete mass balance (Table 12.2). A detailed discussion and in depth evaluation of the different contributions can be found in Reinstorf et al. (2008).

The results show that the loads of galaxolide (fragrance; +182%), tonalide (fragrance; +364%), t-nonylphenol (+26%) and carbamazepine (antiepilepticum; +21%) increased significantly within the city. It can be concluded that the city indeed influences the amount of these micropollutants in the surface water and groundwater. In contrast, the bisphenol A (industrial chemical, endocrine disrupting substance; +2%) load stagnates. Since bisphenol A can be degraded biologically, degradation along a river reach of about 20 km is possible. It can thus be assumed that, at least for bisphenol A, degradation processes within the river are masking the influence of the city as a contaminant source.

Table 12.2 Balance of the mass flux rates of the entire city area of Halle/Saale

Substance	Input (Saale, Weiße Elster & WWTP) (kg yr^{-1})	Output (Saale) (kg yr^{-1})	Trend of the mass fluxes during the city passage	Corresponding concentration in the diffuse groundwater inflow (μg L^{-1})
Bisphenol A	657.1	668.0	Stable	0.4
Carbamazepine	469	569.6	Increasing	3.7
t-Nonylphenol	419.9	529.7	Increasing	4.0
Galaxolide	149	420.8	Increasing	10.0
Tonalide	33.6	156.2	Increasing	4.5

WWTP: wastewater treatment plant.

The calculated value for "corresponding concentrations in the diffuse groundwater inflow" (Table 12.2) represents the residual of the mass balance equation. The calculated values are similar in magnitude to the maximum measured concentrations in the groundwater. However, a comprehensive explanation and assessment of the sources and transport processes leading to this magnitude of concentrations is not yet possible.

Underlying the conclusion of increasing load in urban waters as they pass through the city is the concept of using mass fluxes to indicate the impact of the city rather than using measured concentrations alone. A computation of the water balance components was therefore necessary, which produced additional information but also increased uncertainty. The uncertainty results from the input variables which are determined for the hydrological water balance model. In fact, the increased uncertainty may also influence the reliability of the mass flux calculation. The robustness of the model was proven by means of an error assessment which considered the total uncertainty resulting from the model itself and its input parameters. A detailed discussion of the model uncertainty can be found in Reinstorf et al. (2008).

To investigate the uncertainties, further investigations were performed in groundwater underlying the city of Halle/Saale using isotopic ($\delta^{18}O$, $\delta^{2}H$ of water, $\delta^{34}S$-SO_4) and chemical tracers (major hydrochemistry, boron) (Osenbrück et al. 2007). Because of their widespread occurrence and their recalcitrance against biodegradation, the investigations focused on the antiepileptic drug carbamazepine (CBZ) and the polycyclic musk fragrance galaxolide (HHCB).

The results indicate that the presence of CBZ and HHCB in urban surface and groundwater is not restricted to wastewater effluents and receiving surface waters but also severely affects urban groundwater. Concentrations of CBZ and HHCB in groundwater ranged from <0.002 to 0.68 and 0.003 to 0.085 $\mu g\ L^{-1}$, respectively, while the given maximum values are comparable to the concentration range of the river Saale. Please note that the calculated values in Table 12.2 are the "corresponding concentrations in the diffuse groundwater inflow" which represents the residual of the mass balance equation. These are not actually measured concentrations.

According to stable isotope and hydrochemistry data, local infiltration of river water into groundwater as well as diffuse wastewater exfiltration from leaky sewer systems are the relevant sources of CBZ and HHCB in urban groundwater. The importance of river bank filtration at wells close to the river Saale is indicated by hydrochemical compositions close to that of river water, by similar temporal variations of $\delta^{18}O$ and $\delta^{2}H$ in groundwater and the river Saale, and consistent $\delta^{34}S$ values of dissolved sulphate in groundwater and river water. In particular, $\delta^{34}S$ provided a sensitive indicator for river water infiltration into groundwater due to different sources of sulphate in the Saale catchment (Triassic evaporites) and in urban groundwater (sulphide oxidation). Because boron mainly originates from wastewater in the investigated part of the city, boron concentrations reflect the admixture of wastewater containing PPCPs to urban groundwater.

Attenuation of PPCPs during transport with river infiltrate and with wastewater seepage have been estimated using known concentrations of PPCPs in river water and raw wastewater and the fractions of river water and wastewater in groundwater derived from stable isotopes and boron content, respectively. Within this context, we are talking about attenuation which might include biodegradation. However, since from our data, we cannot distinguish between biotic and abiotic processes, we refer to attenuation in general.

Attenuation during river bank filtration ranged from 0% to 60% for CBZ and from 60% to 80% for HHCB, in accordance with increasing sorption affinities. Much higher attenuation of 85–100% for CBZ and 95–100% for HHCB was found in the case of wastewater exfiltration. This is most likely related to higher organic matter content and higher transit times along the respective flowpaths.

Residence times also affect PPCP attenuation during river water infiltration into the Quaternary aquifer. At one well, which is influenced by quasi-continuous river infiltration, the residence time was determined by fitting different analytical lumped parameter models to the measured time series of $\delta^{18}O$ in groundwater. During slow infiltration of river water through the colmation layer of the river (timescale of 150 days), the time series of CBZ in river and groundwater revealed an attenuation of about 20–40% similar to the other wells. By contrast, a distinct leap in CBZ attenuation to nearly 100% was observed during a flood event with fast infiltration of river water into the aquifer (timescale of 5 days). This surprising difference in transport behaviour is attributed to the increased suspended load as well as to different flow paths during the flood event.

12.2.2 *Case Study: City of Leipzig*

About 500,000 people inhabit the city of Leipzig which lies at 118 m above sea level in the northwestern part of Saxony. It has an area of about 298 km² and a mean annual precipitation of 512 mm (1951–2003). The mean annual temperature is 9.1°C (Schmidt et al. 2005). The hydrological setting is characterized by the river system of the Weiße Elster which flows through Leipzig from the south to northwest, and its tributaries Pleisse, Luppe, Parthe and connecting channels along the river flood plains (Jordan and Weder 1995).

Quaternary and Tertiary sediments form the main aquifers of the upper groundwater system. Up to ten Quaternary and up to seven Tertiary aquifers can be distinguished. The Quaternary aquifers consist of Elster and Saale glacial-fluvial sediments whereas the underlying Tertiary sediments form inter-bedded layers of clay, gravel, sand and lignite (Jordan and Weder 1995). The latter were mined for lignite around Leipzig until the early 1990s.

As a first approach, we established a monitoring program in Leipzig that involved various urban land use types and investigated their influence on the urban water system. Multivariate statistics and integral pumping tests were applied to resolve the temporally variable and spatially highly heterogeneous conditions.

We first established a hydrogeological monitoring program that involved various urban land use types and investigated their influence on the urban water system in Leipzig (Strauch et al. 2008). Based on these findings, we concentrated on an integral

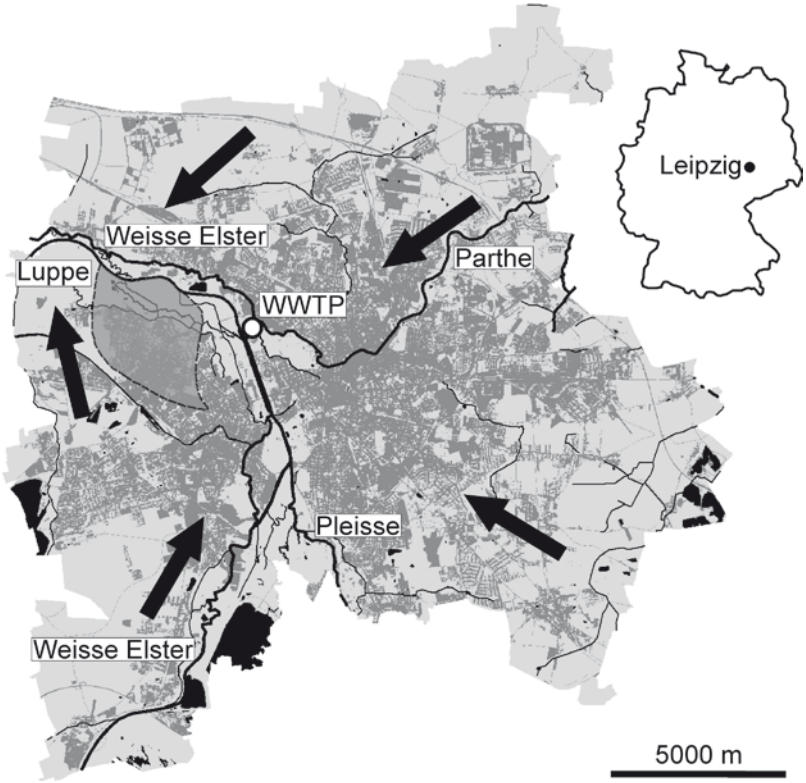

Fig. 12.2 City of Leipzig (Germany) and surface water system (black). WWTP – municipal wastewater treatment plant; black arrows indicate mean groundwater flow direction; shaded area in the northwest marks the position of the watershed-sewershed-study site

study in the northwestern part of the city. Within the study site, the groundwater catchment and wastewater catchment (sewershed) were identical (Fig. 12.2). Thus, an integral quantification of water and contaminant fluxes between surface water, groundwater and wastewater was possible. A 13-month monitoring program of xenobiotic concentrations in all urban water compartments revealed that these indicators were ubiquitous (Musolff et al. 2007). On the basis of descriptive and multivariate statistics of the measured concentration, for surface water, the main pathways were found to be wastewater treatment plant effluent as well as the input of raw wastewater from sewer overflow and other sources. Xenobiotic contamination of the groundwater was caused by leaky sewers and the infiltration of wastewater-bearing surface water (Musolff et al. 2007). Spatial and temporal variability of xenobiotic concentrations was found to be high in wastewater as the primary source and in the receiving ground- and surface water. With the help of multivariate statistics, the complex spatiotemporal patterns of xenobiotic concentrations were partially resolved (Musolff et al. 2009). For instance, daily loads of caffeine, galaxolide and tonalide were characterized by a pronounced seasonality in surface water due to their likely temperature-dependent attenuation. Other substances such as bisphenol A and carbamazepine did not show seasonal patterns. Thus, time and place of sampling as well as the choice of xenobiotic indicators has a substantial influence on the results. Heterogeneity and seasonal effects should therefore be considered in studies on xenobiotics in urban waters.

In a further study, a new methodology to estimate mass flow rates M_{sewer} from leaky sewers was developed. The problem of heterogeneous concentration patterns in the vicinity of leaky sewers as a result of different leaks and fluctuating household wastewater input was overcome with the Integral Pumping Test method (IPT; Bayer-Raich 2004). Large volume sampling up- and downstream of a leaky sewer section yielded reliable average concentrations of target wastewater indicators along control planes (CP) perpendicular to the natural groundwater flow direction (Fig. 12.3). Mass flow rates M_{CP} were calculated from these average concentrations. The difference between M_{CP} up- and downstream of the leaky sewer yielded the mass flow rate M_{sewer} per length of the sewer. For chloride as a wastewater indicator, a M_{sewer} value of 7.8 g m_{sewer}^{-1} d^{-1} was obtained (Leschik et al. 2008; 2009).

The new IPT methodology can be used to estimate average mass flow rates M_{sewer} from leaky sewers into groundwater for desired indicator substances under field conditions. The M_{sewer} values can be used to assess the impact of leaky sewers on the groundwater. Due to the significant effort required for pumping well operations and laboratory sample analyses, a complete survey of the sewer network was not possible. The successful application of the new methodology also depends on background concentrations in the groundwater. Dilution of exfiltrating wastewater with groundwater and dilution during pumping limits the applicability of this method to field sites with strong sewer exfiltration. The transfer of M_{sewer} values to

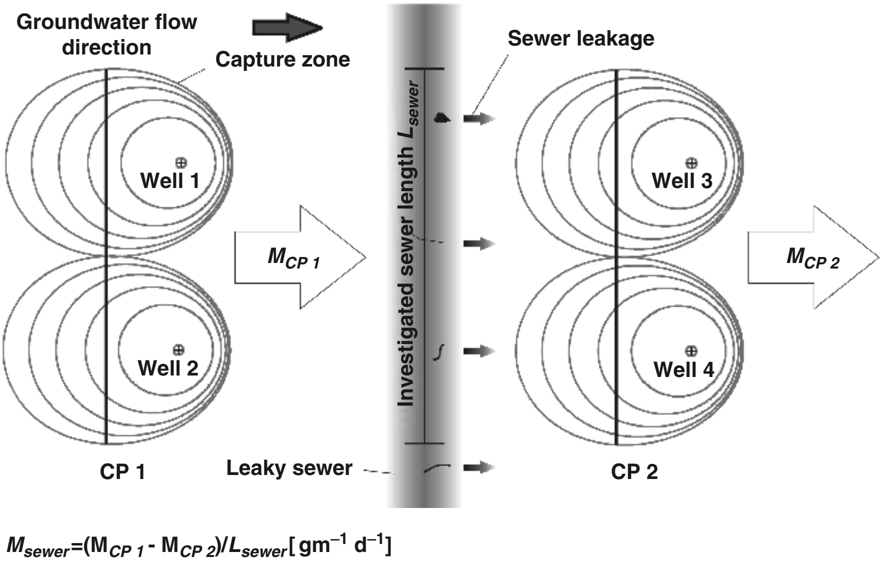

Fig. 12.3 Schematic diagram of M_{sewer} estimation by the operation of IPT's up- and downstream of a leaky sewer section. The length of the control planes (CP) is given by the size of the capture zone

other sewer networks needs to account for different field conditions which influence wastewater exfiltration (e.g. leak size or sediments in the vicinity of the sewer).

12.3 Summary and Conclusions

Identification of anthropogenic impacts on urban waters is often problematic by means of concentration measurements alone. In many cases, the input concentration is too low and retardation, degradation processes as well as dilution can mask this influence. Only mass balances taking into account all compartments, soil water, groundwater, surface water and the effluent of wastewater treatment plants, can give an overall picture, show mass fluxes and exclude dilution influences. However, the challenge to meaningfully estimate contaminant fluxes and their effects on urban water systems requires an understanding of the input, transport and attenuation processes at the local scale with a simultaneous perspective on the catchment scale. Due to often considerable aquifer heterogeneity combined with extensive subsurface infrastructure and a wide range of contaminants in urban areas, new and efficient investigation, monitoring and evaluation strategies are required. In most cases, approaches and technologies which have been developed over the past few decades for industrially contaminated areas form a good basis; however, they have to be further developed for the special requirements of the urban environment. From current preliminary quantification, it is clear that predicting contaminant behaviour in urban areas demands a detailed process understanding which cannot be derived from laboratory experiments or phenomenological analyses at the catchment scale. Through an installation of measuring equipment at the interfaces between the unsaturated and saturated zone as well as between ground- and surface water, in situ contaminant transport and fate can be quantified from the cm- up to the m-range.

New projects to investigate the water cycle in urban areas should include strategies to minimise contaminant input as well as development of sustainable remediation technologies for urban contamination of surface and groundwater which are also applicable for megacities. On one hand, urban areas are often a potential contaminant source for downgradient communities and ecosystems, and on the other hand, urban aquifers are often sources for drinking water production, especially in megacities. Thus, we have to invest considerable effort into the protection of urban aquifer resources. This is especially important due to the fact that megacities have developed in many parts of the world. As we move more towards a precautionary water protection, close collaboration between researchers and practitioners is essential.

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Chapter 13
Pharmaceutical Contaminants in Urban Water Cycles: A Discussion of Novel Concepts for Environmental Risk Assessment

Stefan Scholz, Kristin Schirmer, and Rolf Altenburger

Abstract Urban water cycles are threatened in many ways by human activities, including the discharge of chemicals by industrial and household effluents. Since more than a decade it has been recognised that the active ingredients of human pharmaceuticals contribute to the chemical contamination of urban surface waters and may pose a serious risk to the environment. Pharmaceuticals reach the aquatic environment due to their everyday use, excretion by humans and incomplete degradation in sewage treatment works. Their environmental concentrations are generally low. Due to their biologic activity, however, pharmaceuticals are considered as candidate compounds for low-level and chronic effects. Indeed, some pharmaceuticals, such as compounds interfering with reproductive hormones, provoke long-term effects on aquatic vertebrates in the ng/L range. Therefore, appropriate regulations for the environmental risk assessment as part of the approval of new medicines have been established. It was criticised, however, that these guidelines would not have been able to detect or predict the effects of some compounds with already known environmental impact. Thus, approaches for amending existing guidelines have been suggested. In this review, we give a brief overview on current and novel approaches for the prospective environmental risk assessment of human pharmaceuticals in the aquatic environment. In particular, we compare different strategies to identify potential ecotoxic effects and the possible applications within a regulatory framework. We indicate a number of tools that could improve

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S. Scholz (✉) and R. Altenburger
Department of Bioanalytical Ecotoxicology, UFZ – Helmholtz Centre for Environmental Research, Permoserstraβe 15, 04318 Leipzig, Germany Phone +49 341 235 1080, Fax +49 341 235 1787, e-mail: stefan.scholz@ufz.de; rolf.altenburger@ufz.de

K. Schirmer
Department of Environmental Toxicology, Eawag, Swiss Federal Institute of Aquatic Science and Technology, Ueberlandstr. 133, 8600 Dübendorf, Switzerland
ETH Zürich, Institute of Biogeochemistry and Pollutant Dynamics, 8092 Zürich, Switzerland
e-mail: kristin.schirmer@eawag.ch

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the detection of compounds with potential low-level effects or hitherto unknown but relevant alternative mode of actions with implications for long-term effects.

13.1 Introduction

Urban water cycles are threatened in many ways by human activities. River regulations, transportation, and withdrawal of water for households and industry, have impacts on surface and ground water ecosystems in multiple ways. Furthermore, the discharge of chemicals through industrial and household effluents poses a serious risk to human and environmental health. Traditionally, the determination of chemicals in surface waters has focussed on industrial chemicals or pesticides, with a particular focus on persistent organic pollutants. However, for more than a decade it is evident that human lifestyle and disease treatment significantly contribute to the presence of xenobiotics in the aquatic environment (Daughton and Ternes 1999; Ternes et al. 2004). Personal care products and human pharmaceuticals are detectable in surface and ground waters and in some cases in drinking water as well. Typically, concentrations range from ng/L to μg/L levels (e.g. Alder et al. 2006; Fent 2008; Heberer 2002a). Among the detected contaminants are many widely used active components of human pharmaceuticals such as antiphlogistics, antibiotics, antidiabetics, antiepileptics, beta blockers, antihistamines, calcium antagonists, psychotropics, muscle relaxants, diuretics, decongestants, antigouts, contrast media and hormones. The relatively high – with respect to surface waters – concentrations of human pharmaceuticals in raw wastewaters, the increase of concentrations in receiving rivers downstream of sewage treatment plants and mass flux analyses indicate that municipal discharge, particularly the sewage treatment effluents, represent the major route of introduction (Alder et al. 2006; Ellis 2006; Reinstorf et al. 2008; Schirmer et al. 2007; Strauch et al. 2008). Environmental concentrations of human pharmaceuticals are related to their prescription rates and their persistence (Jones et al. 2002; Zwiener et al. 2000). Some pharmaceuticals are detected in the aquatic environment even though they are relatively readily degradable (e.g. ibuprofen, diclofenac) (Bartels and von Tümpling 2007; Zwiener et al. 2000). Due to their high prescription rate they are, however, continuously supplied to the aquatic environment so that their rate of transformation and removal is lower than or equal to their rate of introduction. Therefore, these types of contaminants have also been termed pseudo-persistent (Ellis 2006).

The widespread distribution and continued discharge of pharmaceuticals in the aquatic environment call for an appropriate environmental risk assessment. The risk assessment of existing pharmaceutical contaminants is, however, hampered by a limited availability of appropriate data. Until a few years ago, environmentally relevant physico-chemical or toxicological data have not been requested for the registration of new pharmaceuticals (Koschorreck and Apel 2006). Currently, available data indicate a generally very low acute ecotoxicity. LC_{50} values in different organisms are reported in most cases well above 1 mg/L (Fent 2008).

However, exceptions have been demonstrated as well. For example, the concentration that caused 50% of Daphnids to die within 48 h of exposure was found to be as low as 5.7 ng/L for the parasiticide ivermectin (Garric et al. 2007). Even fewer data are reported for chronic toxicity, which on average occurs at concentrations 1,000 times below the concentrations for acute toxicity (Fent 2008). The comparison of maximum concentrations in wastewater treatment effluents and chronic toxicity indicate that effluent concentrations are usually 1–2 orders of magnitude below the concentrations causing chronic toxicity (with the exception of the contraceptive ethinylestradiol, Fent 2008). Given that the wastewater effluents are usually diluted at least by a factor of 10 (based on the average national level, Alder et al. 2006; in individual cases, however, such as for instance in brooks in Berlin sewage proportions of about 90% have been reported, Heberer 2002b) when discharged into the receiving waters, the risk of triggering adverse effects can be considered low. However, this conclusion must be drawn with care since (1) chronic toxicity data, particularly for fish, are missing and (2) a number of studies demonstrate potential serious long-term environmental effects of pharmaceutical contamination. Prominent examples are the decline of vulture populations due to diclofenac contaminated carcasses (Oaks et al. 2004) or interference with reproduction of fish by estrogenic contaminants (Tyler et al. 1998). Furthermore, histopathologic, cytologic and immunohistochemic analysis of fish exposed to low levels of diclofenac indicated subtle effects with potential long-term implications (Hoeger et al. 2005; Schwaiger et al. 2004). (3) Usually complex mixtures of pharmaceuticals are present in the environment and hence additive or synergistic low level effects may occur that cannot be predicted from the effect levels of individual compounds (4) All pharmaceuticals are biologically active and may have further unknown or unwanted side effects. By limiting the estimation of chronic toxicity to a few known testing schemes, such as the fish early life stage test, potential long-term effects may not be detected and accounted for.

In this review, we will give a brief overview on current (January 2009) and novel approaches for the prospective environmental risk assessment of human pharmaceuticals contamination in the aquatic environment. Particularly, we compare different strategies to identify potential ecotoxic effects and their possible application within a regulatory framework.

13.2 The Current Approach: ERA Based on PECs and Acute/Chronic Toxicity PNECS

The environmental risk assessment (ERA) for the registration of human pharmaceuticals follows the principles that have been established for the regulation of pesticides, biocides and chemicals (EMEA/CHMP 2006; FDA 1998). Thus, the initial step is to verify if the compound, theoretically, could reach the environment and thereby provoke adverse effects. This step is followed by the calculation of “predicted environmental concentrations” (PECs) in order to estimate the potential exposure concentrations for the environment. A subsequent effect assessment leads to the generation of "predicted no-effect concentration" (PNEC). PNECs are derived from experimentally generated effect concentrations multiplied by an assessment factor, which shall compensate for uncertainties based on interspecies and interlaboratory variance and the extrapolation from acute to chronic toxicity. PECs and PNECs are then used for the calculation of a "risk quotient" (RQ). In case of RQs >1 (PNECs are lower than PECs, thus indicating a considerable likelihood of an adverse effect) appropriate mitigation measures are considered. In contrast to the regulation of veterinary pharmaceuticals, a risk benefit analysis including the possibility to deny approval is not foreseen for human pharmaceuticals.

The currently established ERA of human pharmaceuticals is focussed on active ingredients of products and is carried out in a tiered approach with trigger values for each step. Only if these trigger values are exceeded subsequent steps for risk assessment have to be performed. The most elaborate procedures are implemented in the European Union and the USA (EMEA/CHMP 2006; FDA 1998). Some of the major differences between the appropriate guidelines are (Fig. 13.1) (see Bound and Voulvoulis 2004, for a detailed description and comparison):

- The FDA guideline uses the environmental introduction concentrations (EIC, i.e. the concentration in effluents from treatment works) as an initial trigger. In the EU a simplified, worst-case PEC is used. This initial PEC-calculation assumes that the pharmaceutical is not degraded during the passage from sewage treatment plants and that the total amount of the excreted drug is entering surface waters. Further assessment is only considered if a threshold concentration of 1 μg/L (EIC) or 10 ng/L (PEC) is exceeded. If a tenfold dilution of wastewater by receiving waters is assumed, this results in a tenfold higher trigger value by the FDA guideline. To reach the EIC trigger an annual production of 40–50 t of an active ingredient of a pharmaceutical in the US would be necessary, quantities not often exceeded in the US market (Bound and Voulvoulis 2004). However, the trigger value is not considered for compounds interfering with reproduction of vertebrates or lower animals below 0.01 μg/L. For these compounds a subsequent analysis including a tailored risk assessment based on the specific mode of action has to be performed independent of the threshold. No appropriate measures to identify such compounds are proposed.
- The EMEA guideline for the ERA of human pharmaceuticals considers chronic toxicity as a relevant biological effect only. Short-term tests such as those included in the FDA tiered approach are regarded as generally not applicable for human pharmaceuticals, since continuous exposure of the aquatic environment via sewage treatment effluents is assumed. Three specific tests are proposed in the EMEA guideline, the algae growth inhibition test (OECD 201 1984), the *Daphnia sp.* reproduction test (OECD 211 1998) and the fish early life stage test (OECD 210 1992). According to the above mentioned request for a "tailored risk assessment" for compounds interfering with reproduction at low concentrations, additional tests may be requested.
- In the FDA guidelines the estimation of toxicity using quantitative structure activity relationships (QSAR) is principally possible. A testing approach, however, is generally preferred.

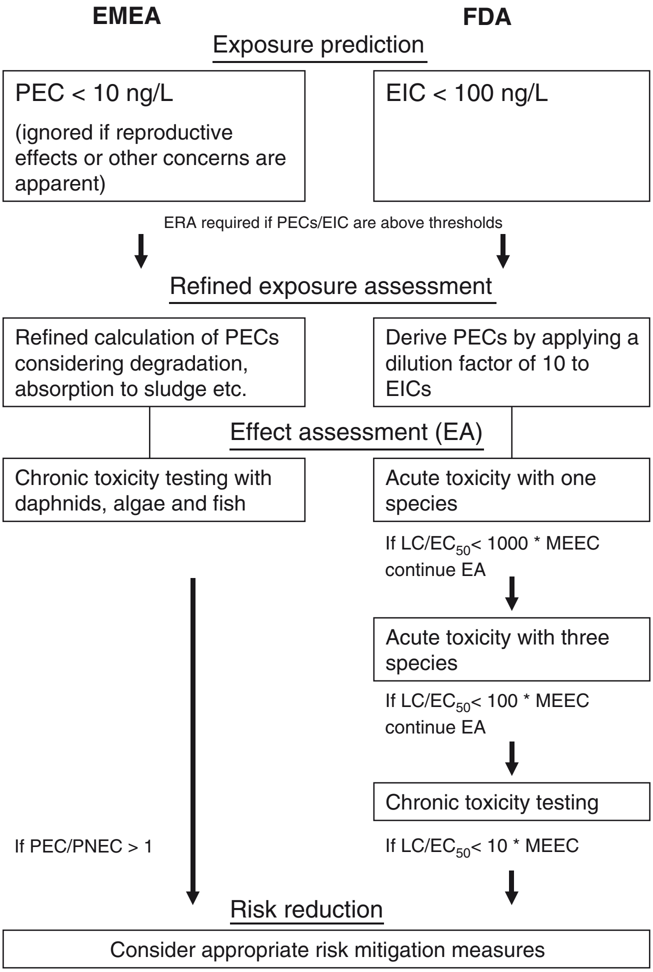

Fig. 13.1 The basic principles of environmental risk assessment within the registration of new pharmaceuticals in the EMEA and FDA guidelines (EMEA/CHMP 2006; FDA 1998). Please note that PNECs are calculated from effect concentrations using assessment factors. Abbreviations: PEC = predicted environmental concentration (surface waters), EIC = expected introductory concentration (at the point of sewage discharge), EA = effect assessment, LC/EC_{50} = concentration at which have of the test organisms dye or show an appropriate effect, MEEC = maximum expected environmental concentration (EIC or PEC whatever is greater), PNEC = predicted no-effect concentration

A retrospective analysis using the traditional approach based solely on acute toxicity of the most sensitive species and assessment factors does not indicate a high ecotoxicity of pharmaceuticals (Cunningham et al. 2006; Knacker et al. 2006). However, some of the compounds are clearly known to pose a serious risk to the environment, such as ethinylestradiol. They affect organisms at the ng/L exposure level, but these effects are only observed on a long-term scale (Kidd et al. 2007). The commonly used assessment factors of 100–1,000 to extrapolate from acute to chronic toxicity are unable to cover the chronic effect levels. Compounds such as ethinylestradiol or the beta-blocker propranol show acute-chronic-ratios of about 150,000 and 49,000, respectively, in fish (Ankley et al. 2005).

13.3 Novel Approaches for a Tailored Risk Assessment of Pharmaceuticals

The guidelines cited above aim at implementing an effective ERA while keeping the costs to a minimum. Therefore, worst-case scenarios, relatively simple estimations for the PECs and standard tests for acute and chronic toxicity are considered. The appropriate regulations such as those implemented by EMEA are appreciated by many ecotoxicologists as a step in the right direction. It was criticised, however, that these guidelines would not have detected or predicted the effects of ethinylestradiol on fish or of diclofenac on vultures (Sumpter 2007) calling for an amendment of existing ERA guidelines. Concerning the recent revision of the guideline for the regulation of veterinary pharmaceuticals a number of critical aspects that also apply to the regulation of human pharmaceuticals were raised (EMEA 2007). For instance, it was noted that for many products the decision on whether there is an environmental risk is based exclusively on the exposure assessment. Only compounds that may interfere with reproduction may require testing if their predicted exposure falls below the threshold level of 10 ng/L. However, pharmaceuticals may have other modes of action (MoAs) of potential concern and indicating these MoAs as well as reproductive effects would be very valuable. Furthermore, dealing with potentially mobile and/or harmful metabolites and environmental transformation products, the assessment of mixtures and the specification of assessment factors were seen as critical items within the effect estimation. Therefore, a number of approaches have been developed that may help to improve biological effect analysis of the current risk assessment procedure and these are described in the following paragraphs.

13.3.1 Using Mammalian Effect Data to Generate Alerts for Potential Effects in Fish

For the approval of new pharmaceuticals their pharmacological and toxicological properties are already intensively studied with respect to effective therapeutic levels and doses with potential adverse effects on human health. These data are obtained with laboratory model species such as rats or mice and comprise at least pharmacokinetic information such as the active ingredients, absorption, clearance, volume of distribution, and maximal blood concentration. Given the fundamental similarity of the biochemical inventory and physiological functions of vertebrates, data from mammalian studies may be used for the prediction of potentially adverse effects in organisms serving as sentinels in environmental risk assessment (Lange and Dietrich 2002; Seiler 2002). As proposed by Huggett et al. (2003, 2005) and Owen et al. (2007), in particular the human blood plasma concentration at steady state (BPC_{ss}) for the intended therapeutical effect could be of value for such an enterprise. Arguing that pharmaceuticals are selected for their highly specific biological activity this internal concentration would indicate the lowest concentration of an active ingredient that elicits any observable biological effects. Given that in non-target organisms this effect could be regarded as equally possible due to structural and functional similarity it should be considered as adverse, that is there is no therapeutical objective. The major task therefore would be to reasonably estimate an internal blood plasma concentration for the sentinel organism used for environmental assessment. To this end Huggett et al. (2003) suggested to estimate the blood-water partitioning of a given pharmaceutical from the octanol-water partitioning coefficient ($\log K_{ow}$) of the compound. The amount of a compound available for partitioning derives from its predicted or measured environmental concentration. Eventually, therapeutic blood plasma levels ($BPC_{mammals}$) of laboratory models such as mice, rats or even human data from clinical studies are compared with the expected blood plasma concentration in the sentinel organism, say fish BPC_{fish}. Now, if the BPC_{fish} is above the $BPC_{mammals}$, a risk for the organism could be assessed asking for further detailed assessment (Fig. 13.2). The model for calculating internal blood plasma concentrations critically depends on the use of reasonable K_{ow} values, which is non-trivial as many pharmaceuticals dissociate within the physiological and environmental pH-range and may therefore give rise to different apparent K_{ow} values.

The Huggett-model is particularly useful for the identification of adverse effects on fish, for comparing different compounds and their prioritisation for further testing. The model anticipates that long-term, subacute effects on fish, such as interference with reproduction, may be provoked by the same mode of action responsible for the pharmacologic effect. It is based on the assumption that structurally and physiologically conserved drug targets are present within vertebrates (see below). This is evidently an oversimplification as for example binding affinities between target molecules in different animals may vary and lead to an over- or under-estimation of the risk based on therapeutic effect concentrations. Therefore, Huggett et al. proposed as a first modification the use of a "functional equivalence ratio" (FER) to account for differences in the binding to target molecules (Huggett et al. 2005). The FER might be derived from binding affinity studies or in vitro target gene regulation comparisons. In case that no data on the FER are available a factor of 1 could be assigned to fall back to the default model. This amendment, however, ignores that theoretically a drug could also have a higher efficacy in a non-target organism.

The approach of Huggett et al. is interesting because it exploits the already generated wealth of data of preclinical and clinical safety evaluations of drugs. In order to confirm the usefulness of mammalian data for an ERA, a comparison of pharmacologic effective doses with chronic ecotoxicity data is required – which has

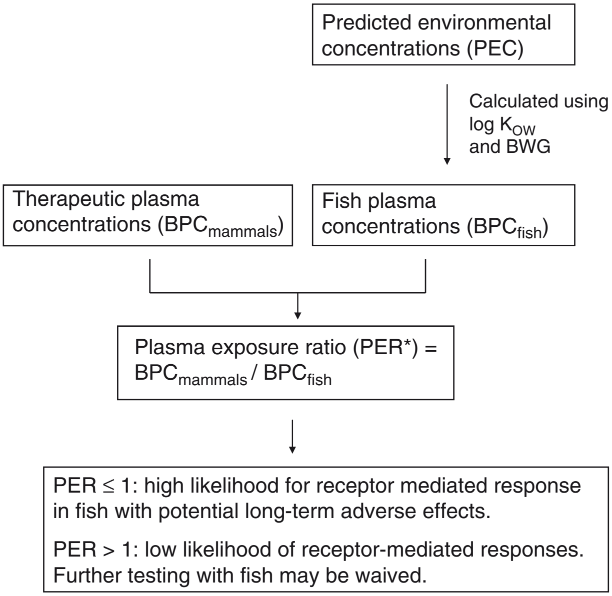

Fig. 13.2 The use of mammalian data for the environmental risk assessment of pharmaceuticals (modified from Huggett et al. 2003, 2005). * The plasma exposure ratio (PER) can be modified by dividing with a functional equivalence ratio considering differences in receptor binding affinities between mammals and fish (default value = 1). Abbreviations: BWG = blood water partitioning variable, K_{ow} = octanol-water-partition coefficient

as of yet been performed exemplarily for a few compounds only, for example for beta-blockers (Owen et al. 2007). Furthermore, it has to be investigated, whether the mammalian data can also be used for predicting effects on invertebrate and algal species. This ability should depend on the presence of the particular pharmacological targets in these species. With respect to the societal demands for reducing animal testing as well as the need for the development of cost-effective testing strategies, the use of mammalian data may address at least the potential to waive fish tests. Moreover, the use of mammalian data could support the development of appropriate testing methods tailored to the anticipated MoA.

13.3.2 Exploring Molecular Target Information for Effect Assessment

Environmental effects of pharmaceuticals such as those reported for ethinylestradiol or diclofenac can be associated with high affinity interactions with conserved drug targets in wild life species (Gunnarsson et al. 2008). These interactions can be indicated by comparison of evolutionary conservation of the drug targets in classes of organisms. If appropriate human drug orthologs (genes that are similar because they have originated from a common ancestor) are present in the aquatic species of concern, this points to possible unwanted effects in non-target species through presence of homolog receptive structures similar to the therapeutic MoA of the pharmaceutical in humans. Thus, Gunnarsson et al. (2008) proposed that aquatic environmental risk assessments for human drugs should include comprehensive studies on conserved drug targets. They analysed about 1,300 known human drug targets and were able to identify about 1,100 orthologs in aquatic vertebrates. Even in less related species such as the fruitfly *Drosophila melanogaster* or the green algae *Chlamydomonas rheinhardii*, for about 50% and 30%, respectively, of the human drug targets orthologs could be identified. The approach of Gunnarson et al. may be particularly useful in combination with the use of mammalian toxicology and pharmacology data. For instance, orthologs of the estrogen receptor are not present in various invertebrate species, yeast, algae and bacteria. Thus, it can be considered as unlikely that effects on these species will occur at levels related to the pharmacological dose. If appropriate orthologs are present, existing pharmacologic data might be used to extrapolate for ecotoxic effects or appropriate tests considering the mode of action of the compound have to be initiated.

13.3.3 Prediction of Adverse Long-Term Effects from Alternative Short-Term Tests

Given the continuous exposure of aquatic organisms to subacute level of pharmaceutical contaminants, the most relevant effects are those caused by a long-term exposure. However, within the ERA, chronic effect assessment of aquatic vertebrates is one of the most expensive and resource demanding procedures. Moreover, ethical concerns regarding the increased demand for animal testing emerge (van der Jagt et al. 2004). In particular, the identification of effects on reproduction and population development using multiple-generation-tests, such as those proposed for the assessment of potential endocrine disrupting compounds at higher tier levels, are highly resource-intensive (EPA 2003). However, a long-term effect may be closely linked to an initial molecular interference causing alterations at the molecular level. These molecular changes could lead to the development of biomarkers for the prediction of long-term effects. A prominent example is the analysis of estrogen-responsive genes or proteins (Hutchinson et al. 2006). If long-term reproductive effects are compared to the estrogen-responsive gene/protein induction of vitellogenin in fish, a clear correlation can be established. Deviations from the correlation appear relatively small – considering that data comprise analyses from different species, stages, compounds, protein or gene expression and the use of different exposure scenarios (Fig. 13.3). With more stringent experimental conditions this correlation would probably further improve. The potential of molecular screening approaches for the prediction of long-term effects has already been recognised as a valuable tool in regulatory applications, and has led to the development of fish

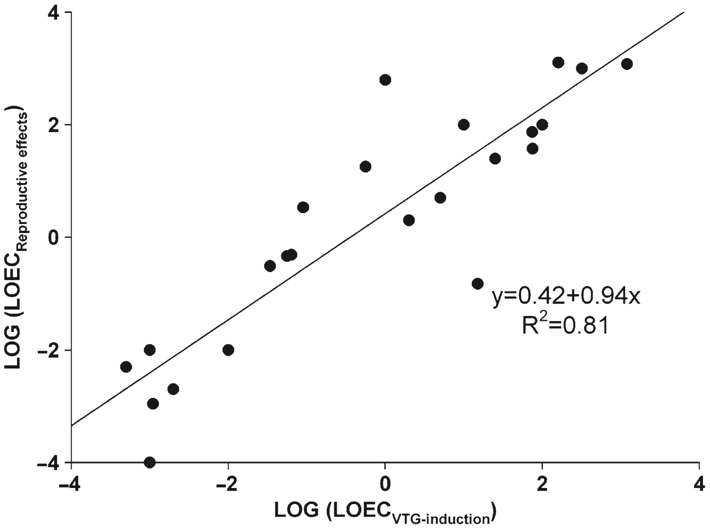

Fig. 13.3 Correlation of vitellogenin gene/protein induction and reproductive effects in fish. Data were extracted from Scholz and Mayer (2008) and comprise studies with four model species (zebrafish – *Danio rerio*, medaka – *Oryzias latipes*, fathead minnow – *Pimephales promelas* and three-spined stickleback – *Gasterosteus aculeatus*). Each data point represents a study in which the vitellogenin induction as well as adverse effects on reproduction (reduced fecundity or fertility) have been analysed for the same species and within the same experiment (LOEC = lowest observed effect concentrations, μg/L). The figure represents data from experiments with 14 different compounds (ethinylestradiol, 17-β-estradiol, estrone, 4-nonylphenol, nonylphenol polyethoxylate, 4-pentylphenol, buzyl bentyl phthalate, fadrozole, methoxychlor, bisphenol A, 3-benzyledene camphor, benzophenone-2 and letrozole). An analysis of ethinylestradiol only has revealed a very weak correlation of exposure time and VTG-induction levels. Therefore, the figure comprises data from experiments with a wide range of exposure periods from 1 to 144 days in juvenile and adult fish

screening assays for the identification of compounds interfering with reproductive hormones (OECD 2006; USEPA 2007). Thus, if the long-term reproductive effects of potential estrogenic or anti-estrogenic pharmaceuticals are considered in higher tier studies they might be predicted from simpler biomarker-based test systems and used as alternatives for animal-demanding and expensive long-term studies.

In order to identify potential chronic effects on fish the EMEA guideline for the ERA of human pharmaceuticals requests data obtained by the fish early life stage test (OECD 210 1992). These effects may also be predicted from alternative short-term experimental set-ups, such as exposure to fish embryos. Therefore, various research groups have recently aimed at the identification of subacute biomarkers in the fish embryo, particularly genes or proteins of which the expression was changed by the exposure to chemicals (see Scholz et al. 2008, for an overview on these studies). A comparison of effect levels of the expression of several marker genes have indeed indicated a high sensitivity of molecular changes in exposed embryos. These changes were observed at concentrations close to those for which chronic effects in the fish early life stage test have been reported (Weil et al. 2009).

Fish embryos are considered as alternatives to the testing of adult or juvenile fish (Fleming 2007) and testing can be performed at a small scale and thus at high-throughput. Provided that additional data are generated and a clear mechanistic and/or statistical link can be established the analysis of subacute markers in fish embryos might represent a valuable approach for the refinement and reduction of animal experiments within the ERA of pharmaceuticals.

13.3.4 Identification of the Mode of Action for ERA

Pharmaceuticals are targeted to specific receptors in humans and many of them are conserved among a wide range of organisms. The knowledge on the specific mode of action can be explored to predict potential adverse effects from pharmacodynamic and pharmacokinetic data. However, human pharmaceuticals may also provoke other specific effects (secondary MoAs or side effects) not predictable from the therapeutic mode of action (Seiler 2002). Particularly, if no orthologs for a therapeutic target are present or if only a weak homology can be established non-target-related effects with alternative MoAs might become important. Two approaches have been applied for the identification of such specific effects: (1) The analysis of selected potentially relevant MoA using a test battery or (2) the identification of MoAs without a-priory hypothesis using a toxicogenomic approach.

An example for the use of a test battery is given by Escher et al. (2006). Various β-blockers that have been reported to occur in aquatic surface waters were compared with respect to their predicted baseline toxicity (narcosis) and effect concentrations in test systems targeting specific mode of actions such as interference with photosynthesis, estrogen/androgen receptor binding or genotoxicity. A high toxic ratio ($TR = EC_{50\ \text{baseline toxicity}}/EC_{50\ \text{specific effect level}}$) was recorded for the interference of beta-blockers with photosynthesis indicating a specific mode of action that may be partially relevant for the ERA of algal species.

A disadvantage of the application of test batteries is its focus on a selected numbers of generic MoA that may not cover potentially relevant specific mechanisms or side effects (Escher et al. 2005). However, advances in system biology techniques would allow using non-a-priory techniques to identify alternative MoA or confirm the anticipated cross-organism validity of pharmacologic data from mammalian models. In particular, techniques for the analysis of whole transcriptome, proteome and metabolome profiles are useful for a non-hypothesis driven approach (Ankley et al. 2006). The majority of ecotoxicogenomic studies with pharmaceuticals have focussed on the already well-characterised estrogenic or androgenic compounds but a few examples using transcriptome analysis are available for other pharmaceuticals (summarised in Table 13.1). For instance, ibuprofen exposure to *Daphnia* has particularly induced altered expression pattern of genes involved in the eicosanoid pathway (Heckmann et al. 2008). The eicosanoid, eicosapentaenoic acid, is a precursor of prostaglandin. Since ibuprofen is an inhibitor of the prostaglandin synthesising enzyme cyclooxygenase, it appears that even in this evolutionary

Table 13.1 Examples of recent (eco)toxicogenomic studies of pharmaceuticals using non-mammalian species. Studies using estrogens or androgens or derivatives of these compounds were excluded. Ibuprofen is a cyclooxygenase inhibitor and used as antianalgesic drug. The therapeutic action of mianserin is based on its serotonin receptor and a_2-adrenoreceptor antagonism. Valproic acid is used for the treatment of epilepsy and is know to inhibit the GABA transaminase

Compound	Species	Result	Reference
Ibuprofen	*Daphnia magna*	Microarray analysis revealed interruption of crustacean eicosanoid metabolism indicating intriguing similarities of ibuprofen effects in vertebrates and invertebrates.	(Heckmann et al. 2008)
Mianserin	*Danio rerio*	A differential regulation of neuro-endocrine-related genes was observed supporting the therapeutic mode of action in humans.	(van der Ven et al. 2006)
Valproic acid	*Danio rerio*	Distinct differences in expression patterns in embryos exposed to 11 different compounds were observed. The down-regulation of the GABA transporter SCL6 is speculated to be related to the therapeutic mode of action.	(Yang et al. 2007)

relatively distant invertebrate similar pathways as in mammals are activated. Similar conclusions can be drawn from the two other examples highlighted in Table 13.1, that is zebrafish (embryos) exposed to valproic acid and mianserin. Thus, microarray analysis have revealed that indeed a MoA similar to the therapeutic action might be of primary concern and that, for instance, mammalian data might be used to predict potential adverse effects or to indicate the need for potential further effect assessment. However, due to the limited number of available studies this conclusion must be drawn with care.

Identification of potential alternative MoAs by systems biology approaches requires expensive, advanced technologies, appropriate technical skills as well as time-consuming experimental and statistical analysis. It is therefore unlikely that such methodology could be implemented in routine analysis at this point. However, with further advances in technologies and research, system-wide analysis may provide markers that will allow for a quick screening of potential MoA relevant for the identification of adverse effects within the ERA.

13.3.5 Prediction of Effects by QSARs

The use of computational models or QSARs (qualitative/quantitative structure activity relationships) has been suggested for the prediction of effects as part of the ERA of pharmaceuticals (Bound and Voulvoulis 2004; Sanderson et al. 2003).

However, QSARs are of limited value if they are based solely on acute toxicity and generic physico-chemical properties such as the log K_{OW}. Of particular environmental relevance would be the development of QSAR for chronic effects, for instance via the prediction of acute-chronic ratios (ACR) using structural alerts (Ahlers et al. 2006). However, in order to predict subtle, pharmacodynamic effects, QSARs would probably need to be linked to the specific MoA(s) of a pharmaceutical (Sanderson and Thomsen 2007). Such a mechanistic link would also be in compliance with OECD guidelines on the validation of QSARs (OECD 2007). Given the wide range of specific MoAs for pharmaceuticals this is, however, a complex task. Therefore, QSAR focussed on the identification of selected MoA such as binding to certain receptors appear to be more promising (Vedani et al. 2008). In this respect QSAR and the identification of the mode of action (see above) can be regarded as complementary approaches that would mutually support the development of tools for the prediction of adverse effects of pharmaceuticals in environmental risk assessment.

13.4 Conclusion

Human pharmaceuticals represent an important source for low-level xenobiotic contamination introduced in urban water cycles primarily due to human consumption and discharge of municipal wastewaters. The ERA of human pharmaceuticals is a complex task due to the multiple possibilities of specific interactions via pathways related to their therapeutic activity and potential secondary MoAs or side effects. For practical, economic and ethical reasons it will be impossible to consider all existing possibilities of interaction within environmental organisms for the environmental risk assessment of pharmaceuticals. However, a variety of tools indicated in this chapter could be already applied to improve the current ERA and for example prioritize compounds that will need additional testing. (1) Mammalian pharmacodynamic data could be used to identify potential compounds acting at very low concentrations and for which effect assessment is required even in case where PECs are below 10 ng/L. (2) Testing may not be focussed solely on unspecific chronic toxicity but consider the MoA of the pharmaceutical – provided that the appropriate targets are present in the test organism. The presence of potential targets can relatively easily be demonstrated by exploitation of sequence data bases. (3) Using a targeted testing approach and/or QSAR analysis, compounds with MoAs of concern such as endocrine disrupting compounds may be identified and prioritized for further testing. (4) Future research may indicate other MoA with potential long-term effect for the environmental organisms. There should be provisions to account for those in future testing guidelines, as our knowledge is rapidly expanding. (5) Predictive tools for chronic fish toxicity and impairment of fish reproduction should be – in case they are successfully validated – deployed in order to refine and reduce the number of animal experiments.

The above suggested tools are particularly aiming to detect compounds with low-level effects or hitherto unknown but relevant alternative mode of actions.

Some of these tools do not require any additional laboratory testing. Since they could be implemented with rather minor additional effort they could be considered for the amendment of existing guidelines of the environmental risk assessment of human pharmaceuticals.

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Chapter 14
Hydroxy Benzoate Preservatives (Parabens) in the Environment: Data for Environmental Toxicity Assessment

Ingrid Bazin, Aurelie Gadal, Eveline Touraud, and Benoit Roig

Abstract Parabens are alkyl esters of p-hydroxybenzoic acid that could be encountered in various environmental waters; and there is little available information about the adverse effects of these compounds on aquatic organisms. Moreover, information concerning their levels and potential environmental long-term effects are currently missing.

This paper aims at increasing the knowledge on the potential hazard of parabens. Four microorganism model systems (*Vibrio fischeri*, *Photobacterium leiognathi*, *Daphnia magna* and *Tetrahymena thermophila*) have been used for this purpose. In addition, estrogenicity has been studied for parabens and binary mixtures of estrogenic compounds and parabens by using a recombinant yeast estrogen screen assay (YES). Following the EU EMEA Environmental Risk Assessment guideline for classification of dangerous substances and considering the results obtained with *Daphnia magna*, methyl, ethyl and n-propyl parabens should be classified as harmful substances for aquatic organisms, whereas n-butyl and benzyl parabens as toxic substances. Concerning the biological activity, parabens are 8,000–900,000-fold less estrogenic than estradiol, the most estrogenic one being the aromatic compound benzylparaben. Higher estrogenic effect has been observed when estrogenic compounds have been added to parabens.

14.1 Introduction

Parabens (and/or their salts), alkyl esters of *p*-hydroxybenzoic acid, are widely used as preservatives and bactericides in cosmetics, toiletries, and personal care products (deodorants, bath gels, shampoos, lotions, etc.). Studies indicated that they are also used as anti-microbial agents in food and beverages (Doron et al. 2001; Soni et al. 2001, 2002). Cashman and Warshaw (2005) estimated that exposure to parabens in the United States was about 75 mg day^{-1} (1.3 mg kg^{-1}day^{-1} for a person weighing 70 Kg).

I. Bazin (✉), A. Gadal, E. Touraud, and B. Roig
Ecole des Mines d'Alès, LGEI center, 6 avenue de Clavieres, 30319 Alès Cedex, France
e-mail: Ingrid.Bazin@mines-ales.fr; Phone: 33 44 66782724, Fax: 33 46 6782701

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Currently, there is a trend to reduce their use because of the growing evidence that they are endocrine disrupters. Estrogenic activity in human has been reported (Soni et al. 2005) and studies in vivo and in vitro showed that parabens can mimic estrogen-like activity. Industries are even more averse to use parabens in their formulations since they were found in breast cancer tissue (Darbre et al. 2004) although their involvement remains unknown.

Various in vitro assays have shown that parabens can bind to estrogen receptor (Routledge et al. 1998; Darbre et al. 2002) and that individual parabens may have a weak estrogenic activity (Routledge et al. 1998). A correlation between the length of the paraben ester chain and the estrogenicity has been demonstrated (Routledge et al. 1998; Lemini et al. 2003). On the other hand, parabens have been reported to stimulate the proliferation of MCF-7 breast cancer cells (Okubo et al. 2001; Byford et al. 2002; Darbre 2006), increase uterine weight and have male reproductive tract effects (Darbre et al. 2004). Several studies concluded that paraben's effects on endocrine function are similar to those of endogenous estrogens and they may affect the development and sexual maturation of a number of wildlife species (Oishi 2001, 2002a, 2002b; Kang et al. 2002; Lemini et al. 2004; Tavares et al. 2009).

Moreover, exposure to parabens (after application or oral ingestion) can cause other effects such as skin irritation and eczematous eruption (Elder 1984; Cashman and Warshaw 2005; Soni et al. 2002, 2005).

Parabens are continuously released in the aquatic environment mainly through domestic wastewater. Although they are removed in a considerable proportion during conventional sewage water treatments (Lee et al. 2005), methyl, ethyl, propyl and butylparabens have been detected in water samples at the ng L^{-1} level (Canosa et al. 2006) and more recently in soils and sediments at the ng kg^{-1} range (Núñez et al. 2008).

However, few data are available concerning the acute and chronic toxicity of parabens towards aquatic organisms. Yamamoto et al. (2007) have shown that the measured toxicity (EC_{50}, LC_{50}, LOEC) using medaka (*Oryzias latipes*), daphnia (*Daphnia magna*) and green algae (*Pseudokirchneriella subcapitata*) ranged from 0.52 to 9.5 mg L^{-1} for butyl and benzyl parabens, with benzylparaben found to be more toxic than butylparaben.

Quantitative structure–activity relationship (QSARs) has also been used to predict chemical properties, environmental fate and (eco) toxicology of these compounds. Predicted values (using ECOSAR^{TM} computer programme USEPA 2000) have been found very close to measured values (ratio between predicted and measured values is not higher than ten).

In this study, we used commercial tests (Daphtoxkit F^{TM}, Microtox^{R}, Protoxkit F^{TM}, Toxscreen) to explore the acute toxicity of single solutions of methylparaben, ethylparaben, n-propylparaben, n-butylparaben, and benzylparaben.

Furthermore, estrogenicity of those five parabens has been assessed using the Yeast Estrogen Screen assay and compared with estrogenicity of reference estrogenic compounds (17-β estradiol, ethinylestradiol, and estriol). Finally, the estrogenic potential of binary mixtures (paraben/paraben or paraben/estrogenic compound) have also been investigated and predictions of concentration-response curves have been proposed.

14.2 Materials and Methods

14.2.1 Chemicals

Methylparaben (MP), ethylparaben (EP), n-propylparaben (PP), n-butylparaben (BP), benzylparaben (BzP), 17β–estradiol (E2), 17α-ethinylestradiol (EE2), and estriol (E3) were purchased from Sigma-Aldrich. All stock solutions were prepared in methanol and serially diluted in distilled water to obtain the target concentrations. The methanol concentration in the exposure solutions, including controls, was 0.01% (v/v) in distillate water in the tested solutions, which is a non-effect dose as estimated in preliminary tests.

14.2.2 Bioassays for Global Toxicity

Toxicity of parabens was evaluated by using the following commercial bioassays purchased from R-Biopharm (Saint Didier au Mont d'Or, France).

- *Daphtoxkit test*. It is a 24 and 48 h mobility inhibition test, using the cladoceran crustacean, *Daphnia magna*. It was performed in accordance with test procedures prescribed by national and international organizations (e.g. OECD 202, ISO 6341, EEC, USEPA, ASTM). The potassium dichromate, $K_2Cr_2O_7$ was the control substance.

For each chemical, two consecutive assays were performed in two steps:

1. A "range finding test" corresponding to the range of concentration for which daphnids exhibited a tolerance (mortality or immobilization) to the toxicant between 0% and100%
2. A "definitive test" determining the concentration causing the death or immobilization of 50% of the population (EC_{50})
   - *Microtox test*. It uses natural luminescent bacteria *V. fischeri* and measures inhibition of the luminescence after 15 and 30 min of exposure to tested solutions. The experimental procedure is based on the ISO 11348 standard protocol (ISO 11348-2 1994). 2-4-dichlorophenol (DCP) was used as control solution.
   - *Protoxkit test*. It is a multigenerational growth test using the ciliate protozoan, *Tetrahymena thermophila* based on the measurement (440 nm) of the growth inhibition at 24 and 28 h (Protoxkit 1998). The potassium dichromate, $K_2Cr_2O_7$ was the control substance.
   - *Toxscreen*. This test measures the decrease of the luminescence of the naturally luminescent marine bacteria *Photobacterium leiognathi SB strain* (Ulitzur et al. 2002) after 30 min of exposure to tested solutions. 2-4-dichlorophenol (DCP) was used as control solution

For each test, the determination of the concentration causing a decrease of 50% (EC_{50}) of the test response (end-point) allows to asses the toxicity of the solution tested. Death or immobilization, growth inhibition and luminescence inhibition are the respective end-points of *Daphtoxkit test, Protoxkit test, Microtox and Toxscreen*.

The guideline provided in the Directive 93/67/EEC, permits to classify the hazard of parabens as:

- Harmful ($EC_{50} > 100$ mg L^{-1})
- Moderate toxic ($10 < EC_{50} < 100$ mg L^{-1})
- Toxic ($1 < EC_{50} < 10$ mg L^{-1})
- Very toxic ($EC_{50} < 1$ mg L^{-1})

14.2.3 Bioassays for Estrogenicity

Yeast strain BY4741 (García-Reyero et al. 2001) has been used to assess the estrogenicity of parabens alone and/or in mixture. It is a recombinant yeast strain containing β-galactosidase reporter gene under the control of the estrogen responsive element ERE. The test consisted on the measurement of the β-galactosidase activity (fluorescence at 460 nm after excitation at 355 nm) after 6 h of exposure with the tested solutions.

14.2.4 Experimental Approach to Mixture

Two mixtures have been studied: homogenous mixtures with two parabens and heterogeneous mixtures with paraben and estrogenic compounds (estriol or 17β-estradiol or 17α-ethinylestradiol).

Composition of the mixture was determined by the concentration of each compound producing a same estrogenic effect (equieffective).

Estrogenic activity of the mixture expressed in estradiol equivalents (Eqv) named “calculated values” is compared with the theoretical estrogenic activity, named “predicted values” calculated from the concentration addition model (Payne et al. 2000, 2001; Thorpe et al. 2006). In order to avoid variability from the cell culture, the estradiol dose-response curve was established before each experiment.

14.3 Results and Discussion

14.3.1 Toxicity Studies of Individual Paraben

Table 14.1 reports the toxicity (expressed as EC_{50}) and the Lowest Observed Effect Concentration (LOEC, expressed as EC_{20}) of methyl, ethyl, n-propyl, n-butyl and benzylparaben according to the different bioassays.

Table 14.1 Toxicity of the test compounds in four bioassays expressed in mg.L^{-1}

	Daphtoxkit			Protoxkit			ToxScreen			Microtox		
Chemicals	EC_{50}24h	EC_{50}48h	LOEC	EC_{50}24h	EC_{50}28h	LOEC	EC_{50}15min	EC_{50}30min	LOEC	EC_{50}15min	EC_{50}30min	LOEC
Methylparaben	32 ± 3	21 ± 10	15 ± 7	54 ± 19	58 ± 15	11.5	31 ± 22	35 ± 18	8.5	9.6 ± 0.3	10 ± 0.2	2.9 ± 0.4
Ethylparaben	25 ± 2	23 ± 3	12 ± 3	25 ± 4	30 ± 2	10.7	19 ± 3	24 ± 4	5.5	2.5 ± 0.4	2.7 ± 0.4	0.55 ± 0.01
nPropylparaben	13 ± 2	7 ± 5	6 ± 3	9.7 ± 0.4	12.5 ± 0.2	2.6	21 ± 3	25 ± 4	4.5	2.5 ± 0.5	2.6 ± 0.7	0.9 ± 0.3
nButylparaben	6.2 ± 1.8	6 ± 1.8	3.2 ± 0.7	5.3 ± 2.5	7.3 ± 2.3	2.5	3.7 ± 0.3	4.3 ± 0.7	1.12	2.5 ± 0.3	2.8 ± 0.5	0.7 ± 0.1
Benzylparaben	5.2 ± 1.7	6 ± 0.7	1.2 ± 0.5	4.3 ± 0.4	5.7 ± 0.9	0.48	1.3 ± 0.1	1.6 ± 0.3	0.25	0.11 ± 0.05	0.11 ± 04	0.02 ± 0.01

LOEC values ranging from 1 to 15, 0.4 to 8.5, 0.5 to 11, 0.02 to 2.9 mg L^{-1} respectively for *Daphnia magna*, *Photobacterium leiognathi, Tetrahymena thermophila and Vibrio fischeri* showed that, for these compounds, Microtox is the most sensitive test. These results are in agreement with those observed by Vasseur et al. (1984) who demonstrated in particular that the inhibition of a natural luminescent microorganism exhibited better sensitivity for effluents containing compounds with amines, quinones and phenols substitution compared to the inhibition of the mobility of a crustacean. In more recent studies, Microtox was compared to Daphtoxkit with the same conclusion concerning the better sensitivity of the former (Davoren and Fogarty 2004; Loureiro et al. 2005; Mendonça et al. 2007). Consequently, Microtox® became a reference test as illustrated by the recommendation of its use by US-EPA and the International Standard Organization.

Concerning the global toxicity (EC50), all the tests and therefore the corresponding microorganism (end-point) used, pointed out that benzyl paraben appears to be the most toxic compound. On the other hand, the behaviour of the other alkyl paraben, with 1 (C1 = methylparaben), 2 (C2 = ethyl paraben), 3 (C3 = propylparaben) or 4 (C4 = butylparaben) carbons was different from a test to another. Indeed, if Microtox did not measure a significant difference of toxicity between C2, C3 and C4, Daphtoxkit and Protoxkit showed the influence of the size of the alkyl group in the increase of toxicity. EC_{50} values varied from 5 to 30 mg L^{-1} at 24 h (6–21 mg L^{-1} at 48 h) for *Daphnia magna* and from 4 to 54 mg L^{-1} at 24 h (5.7–58 mg L^{-1} at 28 h) for *Tetrahymena thermophila*.

Regarding all results, a classification of paraben toxicity can be established in different manner according to the test (or the microorganism) considered. With *Daphnia magna*, methyl, ethyl and propylparaben should be classified as moderate toxic for aquatic organisms, whereas butyl and benzylparaben as high toxic substances. With Microtox test, benzylparaben should be classified as "very toxic" for aquatic organisms, methylparaben as "moderate" and the three other chemicals as "high toxic".

Furthermore, it can be noticed that time of exposure seems to be negligible in the extent of the microorganism response. Indeed, two times of exposure were used for each test: 15 and 30 min in ToxScreen and Microtox, 24 and 48 h in Daphtoxkit and 24 and 28 h in Protoxkit. Time of exposure did not have any significant effect on the EC_{50} of all tests, meaning that the mode of action of paraben is very rapid and that the acute toxicity of these compounds can be estimated very rapidly.

On the other hand, toxicity of parabens were compared to the toxicity of other xenobiotics (bisphenol A, phthalates and tamoxifen) that have been described to have similar mode of action (weak estrogenic effect). Literature provides toxicity data obtained with both *Daphnia magna* and Microtox tests. It shows a same range of EC_{50} than those observed with parabens. Indeed, with *Daphnia magna*, EC_{50} for Bisphenol is 10 mg L^{-1} (Chen et al. 2002), 1.53 mg L^{-1} for tamoxifen (DellaGreca et al. 2007), and varies from 4 to 103 mg L^{-1} for phtalates (Jonsson and Baun 2003). Their EC_{50} with *Vibrio fischeri* ranges from 4 to 103 mg L^{-1} (Jonsson and Baun 2003). This comparison raises the question of the survey of parabens. Indeed, bisphenol A, phthalates and tamoxifen are included in the list of household chemicals for

Table 14.2 Predicted values (PBT profiler) of persistence, bioconcentration and chronic toxicity compared to measured values of acute toxicity and environmental concentrations

	Persistence (day)	BCF	Chronic Toxicity in fish ($mg.L^{-1}$)	Toxicity classification	Environmental concentration in wwtp effluent (ng/L) (Lee et al. 2005; Canosa et al. 2006; Núñez et al. 2008)
MP	15 (76% in soil)	6.4	0.18 (toxic)	Moderate	20–30
EtP	15 (81% in soil)	16	0.12 (toxic)	Moderate/toxic	<10
PP	15 (82% in soil)	44	0.078 (high toxic)	Moderate/toxic	10–40
BP	8.7 (80% in soil)	110	0.051 (high toxic)	Toxic	<10
BzP	15 (83% in soil)	110	0.047 (high toxic)	Toxic/very toxic	0.2–16

which environmental levels have to be maintained under surveillance while for parabens, there is no similar procedure.

Finally, acquisition of toxicity data is a precondition for a reliable environmental risk assessment of parabens in addition to values of persistence and bioaccumulation. However, experimental data of persistence and bioaccumulation are not available but they can be predicted by several softwares as for example PBT profiler (http://www.pbtprofiler.net/) (Table 14.2).

According to this predictive model, all parabens are not expected to persist (half-life in all environmental compartment do not exceed 60 days) and they don't have bioconcentration properties (bioconcentration factor [BCF] does not exceed the EPA [Environmental Protection Agency: http://www.epa.gov/] bioconcentration criteria).

Moreover, taking into account the chronic toxicity (predicted for fish by PBT profiler) and acute toxicity (measured for microorganisms in our study), they can be classified as moderate to very toxic for aquatic organisms depending on the compound.

Thus, considering the three factors (P, B, and T) in such a preliminary approach, hazard assessment shows that parabens should not represent a major problem for the environment.

14.3.2 Estrogenicity Studies

14.3.2.1 Individual Parabens

Estrogenicity of parabens has been estimated using the Yeast test and compared to the estrogenicity of 17β-estradiol (E2) as reference compound. Typical dose-response curves for estradiol and parabens have been established and are represented in Fig. 14.1.

All parabens induce a concentration-dependant response of yeast cells. As shown in Table 14.3, the estrogenic potency of parabens is very weak compared to

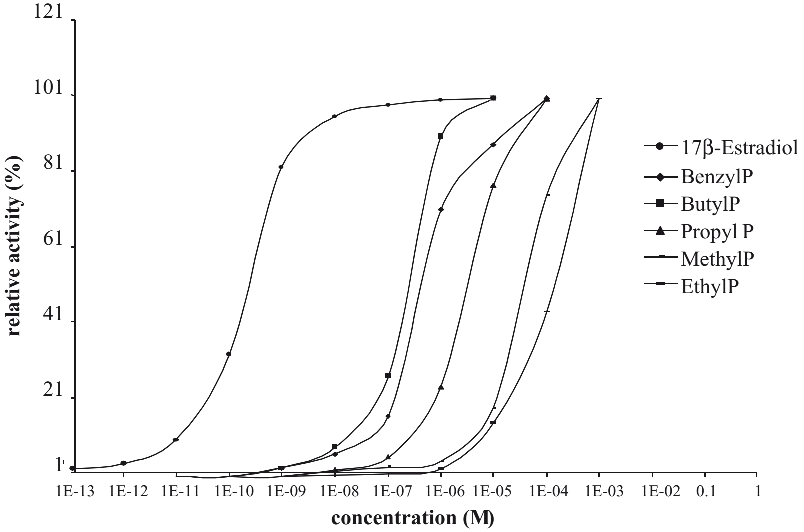

Fig. 14.1 Response of the yeast estrogen screen to a range of parabens of varying alkyl group size (Methylparaben, Ethylparaben, Propylparaben, Butylparaben and Benzylparaben) and 17β-estradiol (E2)

Table 14.3 EC$_{50}$ of 17-β-Estradiol and parabens in distilled water samples obtained in YES test

Methyl Paraben (MP)	Ethyl Paraben (EP)	Propyl Paraben (PP)	Butyl Paraben (BP)	Benzyl Paraben (BzP)	17-β-Estradiol E2
48 +/– 18 mg L^{-1} (3.08 × 10^{-4} M)	7.8 +/– 2 mg L^{-1} (4.73 × 10^{-5} M)	1.32 mg L^{-1} +/– 80 µg L^{-1} (7.21 × 10^{-6} M)	504 +/– 15 µg L^{-1} (2.59 × 10^{-6} M)	351 +/– 28.6 µg L^{-1} (1.54 × 10^{-6} M)	103 +/– 22 ng L^{-1}) (3.77 × 10^{-10} M)

(EC$_{50}$ values, defined as the concentration where transcriptional response reaches 50% of its value at saturating concentration of ligand, were calculated from dose-response assays, using eight concentrations for parabens and ten concentrations for 17β-estradiol).

that of E2: from 8,000 to 900,000-fold less potent (EC$_{50}$ for methyl, ethyl, n-propyl, n-butyl and benzylparaben are 48, 7.8, 1.3, 0.5 and 0.35 mg L^{-1} respectively while it is 103 ng L^{-1} for estradiol). Furthermore, similarly to the global toxicity (described above), estrogenic response increases with alkyl group size (as described previously by Routledge et al. 1998).

14.3.2.2 Binary Mixtures

The estrogenic effect of homogeneous (paraben/paraben) and heterogeneous (paraben/estradiol- like) mixtures has also been investigated. Different binary mixtures are presented in Table 14.4. Estrogenic experimental values measured in

Table 14.4 Composition of tested binary mixtures

	EP	PP	BP	BzP	Estradiol	Estriol	Ethinylestradiol
MP	+	+	+	+	+	+	+
EP		+	+	+	+	+	+
PP			+	+	+	+	+
BP				+	+	+	+
BzP					+	+	+

Concentration ranges tested were chosen such that both a low and high effective estrogenic responses were covered. Thus, E_2, estriol and EE_2 were tested in a concentration range of 10^{-10}–10^{-8} M, parabens were tested in a concentration range of 10^{-4}–10^{-8} M.

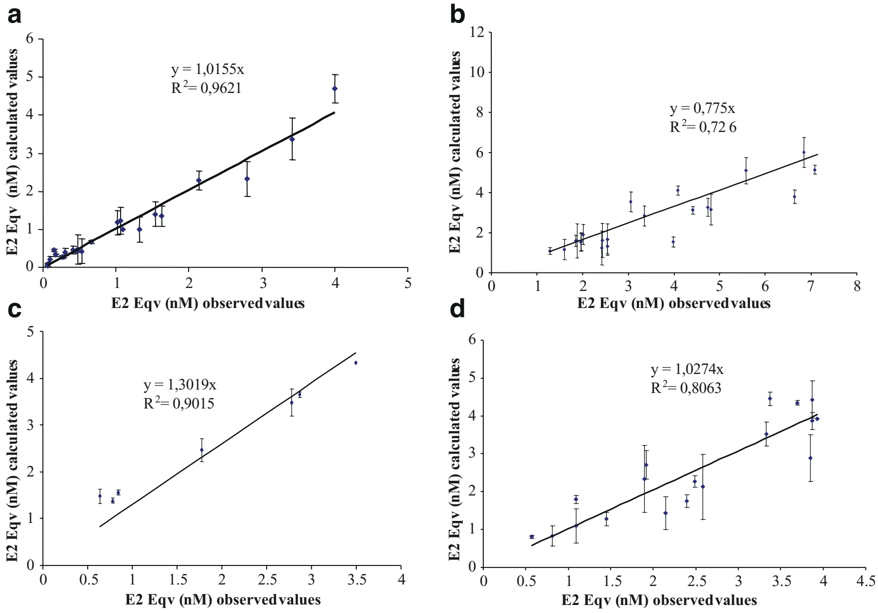

Fig. 14.2 Comparison of calculated and measured estradiol equivalence for homogenous mixture paraben-paraben and heterogeneous mixture paraben-estradiol-like in distilled water: (**a**) homogenous mixture paraben-paraben (**b**) heterogeneous mixture 17β estradiol-Parben (**c**) heterogeneous mixture Estriol-paraben (**d**) heterogeneous mixture 17α Ethinylestradiol-paraben

distilled water have been compared with theoretical calculated estrogenic values obtained with the concentration addition model (Payne et al. 2000, 2001; Thorpe et al. 2006). Results expressed in estradiol equivalent concentrations (E2 Eqv) are reported in Fig. 14.2.

In homogeneous mixtures (Fig. 14.2a), measured E2 Eqv concentrations were generally close to calculated ones. The slope (~1) and the correlation coefficient ($R^2 = 0.96$) comply with the additivity law. Van Meeuwen et al. (2008) showed the same behaviour (concentration addition model) of parabens binary mixtures when there were exposed to MCF-7 cell.

Considering heterogeneous mixtures, in spite of a greater uncertainty, the same trend is observed. The estrogenic effect of paraben-EE2 mixtures (Fig. 14.2d) can be predicted using the concentration addition model. These results are in agreement with works previously described (Rajapakse et al. 2001, 2002; Silva et al. 2002) with binary mixtures of E2 with 8–11 xenobiotics (among which benzyl-4-hydroxyparaben, bisphenol A or genisteine).

In heterogeneous mixtures with estradiol (Fig. 14.2b) and estriol (Fig. 14.2c), the calculated E2 Eqv concentrations are close to the measured ones with a correlation coefficient of 0.7 for estradiol.

In the aquatic environment, some studies proved that the exposure to some alkyl parabens via food and water at the μg L^{-1} level induced a vitellogenic response in juvenile rainbow trout (Bjerregaard et al. 2003; Alslev et al. 2005) or in male medaka (Inui et al. 2003; Yamamoto et al. 2007). Moreover, in mixture with other estrogenic substances (genistein, bisphenol A, etc.), estrogenicity has been expressed at concentrations lower than their individual NOEC (Silva et al. 2002). Our study confirms the general effect of parabens. Nevertheless, results obtained for the mixtures must be cautiously considered as some conclusions from the literature remain contradictory. Indeed, the natural estrogen influence on the global estrogenic effect of a mixture is greatly discussed whatever the biological employed assay was. For example, with the yeast assay, some authors revealed a synergistic effect between estrone and 17β-estradiol (Arnold et al. 1997) whereas others demonstrated only additive effect of mixtures between 17β-estradiol and seven other xenobiotics (Silva et al. 2002; Rajapakse et al. 2002). In MCF-7 assay, some studies described additive effect between parabens and 17β–estradiol (van Meeuwen et al. 2008) while other works indicated a weak antagonistic effect between estradiol and butylbenzylphthalate (Suzuki et al. 2001).

14.4 Conclusions

Due to a wide use in cosmetics, food and pharmaceuticals, parabens are released into the aquatic environment, mainly through domestic wastewater. Then the continual introduction of these benzoates onto sewage treatment systems leads to the question of risk to aquatic organisms.

This preliminary study focused on acute toxicity and estrogenicity of five parabens (methyl, ethyl, n-propyl, n-butyl and benzylparabens). Toxicity and estrogenicity tests have shown that benzylparaben was the most toxic and estrogenic compound. The EC_{50} value (0.1 mg L^{-1} with Microtox) is 1,000-fold higher than environmental concentration reported by Canosa et al. (2006). Benzylparaben is much less estrogenic than hormones for which endrocine disruption has been proved for aquatic organisms. Moreover it can be noticed that acute toxicity of parabens is in the same order of magnitude than some endocrine disruptors ones. Finally, first assays on binary mixtures show that estrogenic effects are additive.

There is a need to collect more data on parabens hazard (ecotoxicity, estrogenicity) and environmental concentrations (surface and groundwater) and to investigate the fate of parabens in environmental compartments in order to discuss their potential risk towards aquatic organisms. Moreover, what we really want to know the chronic effect.

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Part III
Treatment Methods

Chapter 15
Efficiency of Removal of Compounds with Estrogenic Activity During Wastewater Treatment: Effects of Various Removal Techniques

M.H. Lamoree, J.G.M. Derksen, S.C. van der Linden, C.A. Uijterlinde, and P de Voogt

Abstract The effluents from wastewater treatment plants are known to contribute significantly to the total emission of estrogenic compounds, both from natural and anthropogenic sources, into the aquatic environment. As a logical consequence, occurrence of these compounds affects the quality of our surface waters in general, while they may be able to interfere with aquatic wildlife through endocrine disruption.

In a comprehensive monitoring programme, the removal of natural estrogenic hormones, bisphenol A, nonylphenol and nonylphenol ethoxylates was investigated for a number of Dutch wastewater treatment plants. For quantification of these contaminants at very low levels (low ng/L for the hormones and bisphenol A, low μg/L for nonylphenol and its ethoxylates), both GC-MS and LC-MS techniques were applied. In addition, overall estrogenic activity in samples taken from various steps in the treatment cycle was determined by application of the ER-CALUX assay.

M.H. Lamoree (✉)
Department of Chemistry & Biology, Institute for Environmental Studies, VU University,
De Boelelaan 1085, 1081 HV Amsterdam, The Netherlands
e-mail: marja.lamoree@ivm.vu.nl

J.G.M. Derksen
Grontmij | Aquasense, Kruislaan 411a, 1098 SJ Amsterdam, The Netherlands

S.C. van der Linden
BioDetection Systems, Sciencepark 116, 1098 XG Amsterdam, The Netherlands

C.A. Uijterlinde
STOWA – Foundation for Applied Water Research, Arthur van Schendelstraat 816,
3511 ML Utrecht, The Netherlands

P. de Voogt
University of Amsterdam, Institute for Biodiversity and Ecosystem Dynamics,
Nieuwe Achtergracht 166, 1018 VW Amsterdam, The Netherlands
KWR Watercycle Research Institute, Groingenhaven 7, 3433 PE Nieuwegein, The Netherlands

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Apart from a standard approach for wastewater treatment, several additional treatment techniques, that is sand filtration, active coal filtration, membrane bioreactors (in series and stand-alone) were investigated as well.

None of the treatment techniques was able to remove all of the estrogenic activity. In the sewage treatment plant effluents, only estrone, bisphenol A, nonylphenol and nonylphenol ethoxylates were regularly detected, while 17β-estradiol was measured incidentally. In general, implementation of most additional treatment techniques further reduced the estrogenic activity to levels below 1 ng EEQ/L.

15.1 Introduction

In the last 15 years, the discovery of the estrogenic nature of sewage treatment plant (STP) effluents (Purdom et al. 1994) has launched a huge scientific effort to better understand the occurrence and fate of estrogenic compounds and their biological effects on wildlife. In the first pioneering articles that appeared during the nineties (Desbrow et al. 1998; Routledge et al. 1998), the natural estrogenic hormones, that is 17β-estradiol (E2) and estrone (E1), as well as the synthetic analogue ethynylestradiol (EE2) that is the active ingredient in many contraceptive pills were identified as the main contributors to estrogenicity of effluents. During later years, more and more chemicals could be classified as endocrine disrupting compounds (EDCs) having estrogenic activity as measured by an array of in vivo and in vitro bioassays. Compounds or compound classes that were shown to be estrogenic were for example, bisphenol A (BPA), phthalates (used in the production of various plastics) and alkylphenols and their ethoxylates (Jobling et al. 1995; Blair et al. 2000).

In order to accurately measure trace levels of (natural) estrogenic hormones, a variety of analytical methods for their determination in aqueous and solid matrices have been developed, including both gas chromatography (GC) and liquid chromatography (LC) based separation techniques in combination with mass spectrometric (MS) detection (Belfroid et al. 1999; Ternes et al. 2002; Rodriguez-Mozaz et al. 2004; Noppe et al. 2007). For the analysis of chemicals possessing estrogenic activities that originate from industrial sources, for example the alkylphenols and ethoxylates, LC-MS techniques were favoured to analyse the bulk chemicals (De Voogt et al. 2000; Jonkers et al. 2001)

Complementary to the chemical method development for quantitative analysis of natural estrogens as well as chemicals acting as (weak) estrogens, a lot of research was devoted to the in vivo reproductive health effects on fish that occurred after exposure to EDCs. The egg yolk protein vitellogenin, under normal circumstances only produced in mature female fish, was established as a sensitive and specific biomarker for the assessment of estrogenic activity in male fish (Sumpter and Jobling 1995). Obviously, fish are among the first species exposed to effluents that possibly contain chemicals capable of an estrogenic effect. The numerous fish studies focusing on (lack of) reproductive success have been extensively reviewed (Mills and Chichester 2005), supporting the hypothesis that EDCs in the aquatic environment indeed have the capacity to adversely influence reproduction of a number of fish species, at least under laboratory conditions

Evidence that an environmentally relevant concentration of estrogens in surface waters can impact the sustainability of wild fish populations was presented in the study by Kidd et al. (2007). Their findings showed that chronic exposure – the study lasted 7 years during which a whole lake was dosed at regular intervals – of fathead minnows to low concentrations of EE2, that is in the range of 5–6 ng/L, led to feminization of males as measured by a number of markers including vitellogenin mRNA production and intersex as well as altered oogenesis in females. Ultimately, this resulted in the near extinction of fathead minnows from the studied lake.

An important, practical factor to take into account when evaluating environmental risks is the realistic scenario that exposure is always to a multicomponent mixture, possibly leading to combined effects. For fish, this has been described both for the freshwater species fathead minnow in terms of estrogenic response as well as reproductive performance (Brian et al. 2005; Brian et al. 2007) and for the vitellogenic response in marine sea bass (Correia et al. 2007).

From an environmental perspective, the development and implementation of in vitro bioassays for the determination of total estrogenic activity enables the integrated assessment of estrogenic contamination (Vethaak et al. 2005). Although the estrogenic – or anti-estrogenic – response is measured at a lower biological level, that is cell vs. whole organism, in vitro assays such as the ER-CALUX and YES assays or the E-screen have proven their use as reliable, fast screening tools for the integrated measurement of combined estrogenic activity in various matrices (Murk et al. 2002; Legler et al. 2002; Shappell 2006). On a broader scale, they can be used for prioritization purposes for eventual chemical analysis or to direct the fractionation and identification of samples in Effect Directed Analysis (EDA) (also sometimes referred to as Toxicity Identification Evaluation, or shortly, TIE), when tracing the causes of the observed estrogenic effects (Houtman et al. 2006a, 2007; Thomas et al. 2001, 2004; Tollefsen et al. 2007). In the Netherlands they are also widely used for evaluation of wastewater treatment techniques and monitoring of surface waters.

The discovery that the estrogenic effects in fish caused by effluents can be – for a large part – attributed to the presence of natural hormones that are excreted by humans illustrates the importance of the implementation of proper sewage treatment facilities. In the more densely populated, urban areas of the industrialized world such treatment practice has more or less become state-of-the-art. However, in regional areas where STP effluents are discharged on relatively small surface waters, adverse effects on male fish may still be observed (Vethaak et al. 2005). In the last decade, a lot of research has been dedicated to the technological improvement of the various stages of sewage treatment in terms of removal efficiency of micropollutants, and especially estrogenic chemicals, in municipal STPs. Removal of especially EE2 is not always near complete, as demonstrated by the findings of Kanda and Churchley (2008), Esperanza et al. (2007) and De Voogt et al. (2006).

The necessity of the reduction of the emission of hormones into the environment, often via effluents from sewage treatment plants to receiving surface waters is convincingly illustrated by the findings of Kidd et al. (2007). Recently, an aquatic Predicted No-Effect Concentration (PNEC) for EE2 was derived based on a large number of studies on the effects of EE2 on aquatic organisms. Caldwell et al. (2008) recommend the use of a PNEC of 0.35 ng EE2/L in order to adequately protect organisms in surface waters.

In the Netherlands in the year 2000, a comprehensive baseline study regarding the occurrence, potency and biological effects of estrogens and xeno-estrogens in the aquatic environment of the Netherlands was carried out (Vethaak et al. 2006). Part of that study described the efficacy of the removal of estrogens and xeno-estrogens from four representative wastewater treatment plants (De Voogt et al. 2006).

The study results that we present in this book chapter were obtained in the framework of a more in-depth study regarding the effects of the application of additional removal techniques that are used in combination with conventional as well as advanced sewage treatment works. The research objective was to investigate the effectiveness of additional treatment technologies focusing on natural and synthetic estrogenic hormones as well as nonylphenol (NP) and its ethoxylates. The treatment technologies that were studied included rapid sand filtration, active coal filtration, a membrane bioreactor, post-treatment with a membrane bioreactor and a constructed wetland. In addition to chemical analysis, the in vitro ER-CALUX® assay was applied in order to assess the overall estrogenic activity present in the samples.

15.2 Sampling Sites and Sampling Details

15.2.1 Selected STPs

For this study STPs were selected that are representative for the Dutch situation with regard to their treatment concept. Typically, for the STPS included in this study, sewage treatment involves three stages called primary, secondary and tertiary treatment. In the primary treatment step, oils, grease, fats, sand and larger particles are removed in a pre-sedimentation tank by filtration and/or sedimentation. The secondary treatment consists of an activated sludge tank, in which dissolved organic material (expressed as BOD) is converted into a solid mass by using indigenous, waterborne bacteria and carbon dioxide. In this process particulate matter is trapped as well and ammonia may be converted to nitrate and finally to nitrogen gas. In the tertiary treatment step, the sludge is removed by sedimentation in a post-sedimentation tank. The sedimentated sludge is then digested and disposed.

In total the influent and effluent waters of eight different STPs were sampled. Technical characteristics of the STPs are given in Table 15.1. STPs A and B are conventional activated sludge STPs, with no additional treatment techniques installed. Besides these two conventional STPs, plants with additional advanced treatment steps placed after the post-sedimentation tank were selected, either at

Table 15.1 Overview of compounds/parameters measured and the methods used

Parameter	Method
Natural estrogens: Estrone (E1) 17α-Estradiol 17β-Estradiol (E2) estriol (E3) *Synthetic estrogens:* 17α-Ethynylestradiol (EE2) mestranol (only in 1st and 2nd round)(MES) *Industrial plasticizer:* bisphenol A (BPA)	SPE-extraction using DVB Speedisk, cleanup with combined C_{18}/NH_2 SPE cartridges, HPLC fractionation, silylation, GC-ITD detection
Industrial detergents: Nonylphenol (NP) Nonylphenolmonoethoxylate ($NPEO_1$) Nonylphenoldiethoxylate ($NPEO_2$) Sum nonylphenol polyethoxylates ($NPEO_{3-16}$, represented as $NPEO_{10}$)	C_{18} SPE extraction, elution with methanol, cleanup, LC-MS detection
Total estrogenic effect	SPE-extraction using DVB Speedisk, cleanup with combined C_{18}/NH_2 SPE cartridges, assessment of total estrogenic activity with ER-CALUX® assay

full-scale or at pilot scale. Summarizing, the following treatment technologies were subjected to research: conventional treatment with and without primary treatment, conventional rapid sand filtration (continuous and discontinuous), activated carbon filtration, post-treatment with a membrane bioreactor (MBR) and a constructed wetland (horizontal and vertical). Furthermore, two MBRs without prior treatment were investigated, one pilot setup and one full scale. The MBRs combine biological treatment with a membrane filtration unit in a one-step treatment system.

15.2.2 Sampling

Twenty-four hour flow rate proportional composite influent and effluent samples were taken of the different treatment steps. These samples were stored under cool conditions (4°C) until further processing for analysis. Since the focus was on the effectiveness of additional treatment techniques with regard to removal of EDCs, effluents were sampled more intensively than influents. All samples were replicated at least two times in the period between July 2004 and April 2005. In total, 57 samples were taken, of which 12 were influents, 19 effluents of post-treatment tanks and 26 of the different additional removal techniques (see also Derksen et al. 2005). All measurements were done under dry weather conditions, representing about 80% of the operation time, and during normal functioning of the treatment plants. The latter was confirmed by measuring the routine parameters COD, BOD, suspended solids, NH_4, NO_3, N_{Kj}, PO_4, P_{total} and the amount of precipitation.

15.3 Analysis

15.3.1 General

Endocrine disrupting compounds, and in our case more specific those with estrogenic activity, comprise a variety of chemicals of which we have made a selection for inclusion in our study based on a few criteria. A first screening of candidate estrogenic substances, that is substances that were reported in the literature as possessing estrogenic activity to a certain extent, resulted in a list of 33 substances. From these a further selection was made using the following criteria: (1) STPs should be a relevant source for the (group of) substances; (2) the substance contributes significantly to the total observed estrogenic disruption, that is its estrogenic potency is significant and/or its concentration is considerable and (3) a reliable and well validated analytical method for the determination of the compound's concentration is available

Besides chemical analyses for the determination of the concentration of the selected estrogens, an effect assay was used to assess the total estrogenic activity in the samples. For this purpose, the in vitro ER-CALUX assay was included in the experimental design. The ER-CALUX assay was carried out on extracts that had been prepared in an almost identical way as those for the chemical analysis. The main differences were the addition of an (deuterated) internal standard and the inclusion of an extra cleanup step to enable chemical analysis by further removal of the relatively "dirty" matrix.

In Table 15.2, an overview is given of the compounds/parameters measured and the methods used. In the following subsections, the techniques will be described in more detail.

15.3.2 Determination of Estrogenic Activity by ER-CALUX

15.3.2.1 Sample Preparation for ER-CALUX

In order to avoid degradation, all samples have been extracted as soon as possible after they were taken from the various locations. Until extraction, they were cooled at 4°C. For removal of particulate matter, the influent samples (but not the effluent samples) were filtrated using a glass filter. Solid phase extraction on a sample size of 500 mL was carried out using an DVB Speedisk (Baker). After drying the disk elution was effected with acetonitrile, with subsequent evaporation of the excess solvent. The residue was taken up in 5 mL 0.2 M sodium acetate buffer pH 5.5 and cleaned-up over combined C_{18} and NH_2 cartridges (Brian et al. 2005; Belfroid et al. 1999). Two elution solvents were used: for the first two rounds of measurements ethyl acetate was used, for the third round methanol was used after an additional validation of this step.

Table 15.2 Technical characteristics of the STPs (data 2004).

		STP A	STP B	STP C	STP G	STP D	STP E	STP F	STP H	STP I
Type	Units	Conventional without PT	Conventional with PT and sludge digestion	Conventional without PT	MBR (pilot)	Conventional with PT	2-step STP without PT	Conventional without PT	MBR (full scale)	Conventional without PT
Additional post-treatment		Not applicable	Not applicable	Continuous SF after TT load 2.5-3.5 m/h	Not applicable	Vertical constructed wetland after TT	1) Discontinuous double layer SF after TT, load 10 m/h 2) Active coal after SF EBCT 20 min	MBR after TT	Not applicable	Horizontal constructed wetland after TT
P-removal		Bio-P	Bio-P + chem-P	Bio-P		Chem-P	Chem-P	Bio-P en Chem-P	Bio-P	Bio-P
Sludge digestion		No	Yes	No	Not applicable	No	Yes	Yes	Not applicable	Yes
% Industrial		19%	36%	5%		19%	0%	Unknown	Unknown	40%
Designed load	i.e.	118,000	364,000	7,800	Not applicable	63,200	530,000	250,000	Not applicable	175,000
Current load	i.e.	74,000	167,000	3,630	Not applicable	50,900	360,000	104,000	Not applicable	166,000
Designed flow rate	m^3/d	33,600	44,782	3,600	Not applicable	8,520	67,200	Unknown	Not applicable	35,000
Current flow rate	m^3/d	17,478	58,320	720	Unknown	11,055	63,777	48,848	36	34,800
Sludge load	g BZV/kg ds.day	0.022	0.05	0.027	Unknown	0.04	0.055	0.033	0.028	0.046
Sludge age	days	34	33	27	Unknown	32	14	24	49	15.5
Hydraulic retention time	hours	62	31	46	Unknown	55	7	20	Unknown	16

(continued)

Table 15.2 (continued)

		STP A		STP B		STP C	STP G	STP D		STP E		STP F		STP H		STP I	
		Influent	Effluent TT	Influent	Effluent TT	Influent	Effluent TT	Influent	Effluent TT	Influent	Effluent TT	Influent	Effluent TT	Influent	Effluent TT	Influent	Effluent TT
COD	mg/L	467	29	670	34	558	21	468	26	562	33	364	31	Unknown	19	465	48
BOD_5	mg/L	147	2.4	251	2.2	209	1	201	2	177	3.6	141	3.1	55	Unknown	141	7.1
N_{tot} -N	mg/L	46	3.1	53	7.1	5.8	3.3	44.6	3.2	Unknown	8.3	33	3.8	56	5.5	39	7.8
P_{tot} -P	mg/L	13	4.3	10	1.2	8.5	0.5	7.2	0.8	Unknown	0.4	6.3	0.7	9.4	1.5	8	
Suspended Solids	mg/L	249	4.8	290	4.2	234	3		5.5	Unknown	7	Unknown	5.1	144	0	156	5.1

PT = primary treatment, TT = tertiary treatment, SF = sand filter, MBR = membrane bio reactor, EBCT = Empty Bed Contact Time, Bio-P = biological phosphate removal, chem-P = chemical phosphate removal, COD = chemical oxygen demand, BOD = biological oxygen demand

15.3.2.2 ER-CALUX

The ER-CALUX assay uses T47D breast cancer cells that endogenously express estrogen receptors. These cells have been stably transfected with a luciferase reporter construct under control of Estrogen Responsive Elements (Legler et al. 1999). Because of this, upon binding of (unknown) estrogenic compounds to the estrogen receptors and thereby activating them, the cells produce the enzyme luciferase. The amount of luciferase produced is directly proportional to the extent of estrogen receptor activation and is thus a measure of estrogenic activity elicited by a compound or a mixture of compounds in an extract. The amount of luciferase produced can easily be quantified by adding the substrate luciferin. This results in a chemical reaction that produces light, which can be detected and quantified by a luminometer.

Because ER-CALUX cells cannot be exposed to the pure extracts in ethyl acetate, this solvent is evaporated to almost dryness using a gentle stream of nitrogen (37°C). After evaporation, the extracts (made from 500 mL water) are transferred to 50 μL DMSO. To determine the amount of estrogenic activity present in the water extracts, ER-CALUX cells are exposed to serial dilutions of the extracts as described by Murk et al. (2002). In short, cells are seeded into 96-well plates (5,000 cells per well) using medium that is supplemented with hormone-stripped serum. The next day, the medium is refreshed, after which the cells are incubated for another day. On day three, cells are exposed to medium that is supplemented with serial dilutions of the extracts (final DMSO concentration in the medium 0.1%). After 24 h of exposure, the cells are lysed and the amount of luciferase is quantified using a luminometer.

To be able to express the response of the samples as equivalents of the reference compound 17β-estradiol (E2), cells exposed to increasing concentrations of E2 are always included. An example of a typical calibration curve is given in Fig. 15.1. Using this calibration curve, the amount of luciferase produced by the samples can be compared by the amount of luciferase produced by E2. By interpolating, the response of the extracts can be expressed as amount of E2-equivalents per liter (EEQ/L) of water.

15.3.3 Chemical Analysis of Natural and Synthetic Estrogenic Hormones

15.3.3.1 Sample Preparation and Cleanup for Chemical Analysis

The SPE procedure on the samples for the chemical analysis was identical to that of the ER-CALUX assay, with the addition of deuterated internal standards prior to the SPE procedure being the only exception. For the recovery correction and quantification of BPA, its deuterated analogue was used (either BPA-*d6* or BPA-*d15*) while deuterated E2 in the form of E2-d4 was used for recovery correction and

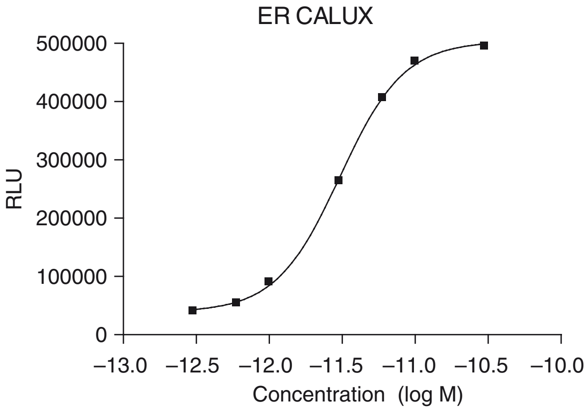

Fig. 15.1 Dose-response curve of ER-CALUX cells, exposed to increasing concentrations of the reference compound E2

quantification of the other compounds. In order to obtain sufficient sensitivity, a sample volume of 1.0 L was used.

For quantitative chemical analysis, an additional cleanup step was necessary using an isocratic fractionation on a C_{18} column (150 × 4.6 mm, with guard column). The mobile phase consisted of 65% methanol and was used at a flow rate of 1 mL/min. The fractions in which the hormones eluted from the column were pooled, the excess of solvent evaporated and the hormones were subsequently derivatized using a silylating reagent (Sigma Sil A, containing trimethylchlorosilane: hexamethyldisilazane: pyridine [1:3:9]). This cleanup procedure was adapted from the methods described by Belfroid et al. (1999) and Brian et al. (2005, 2007).

During the first two rounds of measurements, it turned out that the recovery of estriol (E3) was lower than expected. Therefore, after additional validation, the procedure for the determination was slightly modified in order to improve recovery of this compound. The stored cartridges that had already been eluted with ethyl acetate were then eluted with methanol, and the methanol extract was subjected to a slightly modified HPLC fractionation step using 50% methanol instead of 65%. For quantification of E3 no reliable correction could be made for the recovery, because the deuterated internal standard had already been (partly) eluted from the cartridge in the first elution step with ethyl acetate.

As E3 was primarily found in the influent samples, we chose to reanalyze the cartridges belonging to those samples. In addition, three effluent samples were also analyzed for E3 with the modified method to check whether our assessment that E3 was a less abundant compound in the effluents was true.

Although not as accurate as when a single elution step were used, summation of the two determined concentrations, the first in the ethyl acetate eluate and the second after methanol elution, gives a good indication of the level of E3 present in the samples that were investigated. Obviously, for the third round of measurements the cartridges were only eluted with methanol.

For quality assurance purposes, blank as well as spiked samples were included in the measurement series. Only BPA was found in the blank samples. Therefore, long term monitoring of blank values in our laboratory (i.e. over a period of several years) was ensured, indicating the presence of low concentrations of BPA, on average 7 ng/L. The concentrations presented in this study were corrected for this value.

15.3.3.2 Chemical Analysis

The silylated extracts have been analyzed using a Varian 38000 GC in combination with a Saturn 2000 ion trap detector (ITD). Cold splitless injection of 3 ul extract with a Gerstel CIS3 injector equipped with a Siltek liner was done onto a Varian CP-Sil-8-CB low bleed MS kolom (30 m, 0.25 mm i.d. and a film thickness of 0.25 um). A 1 m Siltek retention gap with an i.d. of 0.53 mm was used. Since there were quite large differences in matrix influences, the limits of detection (LODs) were determined specifically for each sample and each compound. LODs varied in the range of <0.05–5 ng/L for the natural and synthetic estrogenic hormones and from <8.3 to 18 ng/L for BPA.

15.3.4 Quantitative Analysis of NP and NP Ethoxylates

Samples aliquots of between 100 and 200 mL were acidified to pH = 2–2.5 and internal standards (^{13}C-NP, ^{13}C-NPEO$_2$) were added. Influents were filtered before taking aliquots to prevent clogging of SPE setups. Samples were extracted with Sep-Pak C$_{18}$-SPE cartridges (500 mg, Waters). After passing the sample aliquot and drying the cartridge using in a stream of N$_2$, analytes were eluted with 10 mL of methanol. The extract was then evaporated with nitrogen until dryness and redissolved in 1 mL of methanol/ Nanopure water 1:1 (v:v). Finally, the extract was filtered through a 0.2 μm Acrodisk filter.

All extracts were analyzed using reversed phase liquid chromatography coupled to electrospray mass spectrometry detection (LC-ESI-MS), according to a method published before (Jonkers et al. 2003). A Thermoquest Navigator LC-MS single quadrupole system was used with a Lichrosphere RP-C18 column (dimensions 125 × 2 mm, 3 μm) and a mobile phase flow rate of 0.25 mL/min. The mobile phase was made up of a mixture of pure methanol (A) and a water-methanol 3:1 (v:v) buffer (B) using a gradient from 30% A (positive ionization) or 50% (negative) A to 98% A in 20 min. For the detection of the ethoxylates, positive ionization was used with a sodium acetate buffer (0.1 mM), while NP was analyzed in negative ionization mode, using an ammonium acetate buffer (2 mM).

All analyses were performed in SIM mode, using the deprotonated molecular ion of NP during negative ionization and the sodium adducts of NPEO$_n$ in positive mode. For NPEO$_1$, the mass of the [NPEO$_1$+methanol+Na]+ adduct ((*m*/*z*) 319) was also selected. The electrospray interface was set at a probe temperature of

220°C, and probe and cone voltages of −3.8 kV and −20 V in negative ionization mode, and +4.0 kV and +20 V in positive ionization mode, respectively.

For all samples, $NPEO_1$ and $NPEO_2$ were quantified separately with pure standards, and the higher oligomers ($n = 3–16$) were quantified using a commercial mixture of on average ten ethoxylate units (represented as $NPEO_{10}$; content of $NPEO_1$ and $NPEO_2$ below 0.5%). All quantifications were done using 8-point quadratic calibration curves. Peak areas of sample extracts were always in the linear part of the calibration curves. The limits of detection for all analytes corresponded to a level of 0.05 μg/L in the samples.

15.4 Results

15.4.1 General

In Table 15.3, the results of the measurements of the natural and synthetic hormones, BPA, NP and its ethoxylates as well as the ER-CALUX results are represented for all STPs studied. Despite the fact that the sampling campaign was comprehensive from a logistic perspective, the results obtained in terms of removal efficiencies are only indicative, because the number of samples for certain treatment procedures was relatively limited. The concentrations are given as a range, determined by the lowest and highest result obtained taking all the measurements into account. The results for E3 are also only indicative, due to the unforeseen retention of E3 on the SPE cartridges resulting in problems for reliable quantification.

15.4.2 Natural and Synthetic Estrogenic Hormones

In the influents, the presence of all natural and synthetic hormones measured in this campaign was confirmed, except for MES that could not be measured in any of the influents. In general, the concentrations were in the order of a few to a few hundreds of ng/L. Highest levels were encountered for E1 and E3, with concentrations in the order of 41–150 ng/L and 34–334 ng/L, respectively. Apart from these two natural hormones, also 17α-estradiol and E2 were routinely analyzed at significantly lower levels, ranging from <0.6 to 9.9 ng/L for 17α-estradiol and 8–34 ng/L for E2. In the influents, concentrations of the synthetic estrogenic hormone EE2 were 2.2–9.2 ng/L, the average concentration being 3.8 ng/L.

For the effluents, the results from the quantitative analyses show that EE2 has not been measured above its LOD in any of the effluents analyzed. The relatively high LODs for EE2 that were obtained throughout the analyses, that is typically between 1 and 3 ng/L in most cases but in some even as high as 5 ng/L, imply that

Table 15.3 Results of quantitative determination of EDCs and ER-CALUX results for samples taken from various stages in the sewage treatment procedure. See for technical abbreviaations Table 15.3 NA = not analyzed; n = number of samples analyzed

Sampled stage		Influent		Post sedimentation tank		Continous SF		Discontinuous SF		MBR		MBR after TT		Active coal filter		Horizontal constructed wetland		Vertical constructed wetland	
STP code		A,B,C,D,G,H		A,B,C,D,F,I		C,D,F		E		G,H		F		E		I		D	
Compound/ assay	Units	range	*n*	range	*n*	range	*n*	range	*n*	range	*n*	range	*n*	range	*n*	range	*n*	range	*n*
BPA	µg/l	0.55–3.1	12	0.015–2.64	19	<0.017–0.15	8	0.11–0.77	3	0.01–0.082	4	0.008–0.094 3	3	0.013–0.026	3	0.15–0.18	3	<0.017	2
17a-estradiol	ng/l	<0.6–9.9	12	<0.5–<5	19	<0.5–<5	8	<0.5–<3	3	<1	4	<0.6–<2	3	<0.5–<2	3	<0.6–<1	3	<1–<2	2
E1	ng/l	41–150	12	<0.5–28	19	<0.5–10	8	<0.5–<3	3	0.6–6	4	<0.6–<2	3	<0.5–<2	3	<1–34	3	<1–7	2
E2	ng/l	8–34	12	<0.5–2.3	19	<0.5–1.2	8	<0.5–<3	3	<1.1	4	<0.6–<2	3	<0.5–<3	3	<1–10	3	<1–<2	2
E3[a]	ng/l	34–334	12	<1–<5	6	1.3–<5	5	<3	1	NA		<2	1	<2	1	<1	1	<1–<2	2
MES	ng/l	<1–<3.5	12	<1–<2.1	13	<1–<2	4	<1	2	<2–<2.3	4	<1.2–<2.1	2	<1	2	<1.1–1.2	2	NA	
EE2	ng/l	2.2–9.2	12	<1–<5	19	<1–<5	8	<1–<3	3	<2.9–<3.4	4	<1.2–<3.1	3	<1–<2	3	<1–<1.6	3	<1–<2	2
NP	µg/l	10–60	12	0.15–2.4	14	0.47–0.75	4	0.47–0.94	2	<0.07–1.6	4	0.32–1.2	2	0.37–0.67	2	0.24–1.0	2	NA	
NPEO1	µg/l	<0.05–52	12	<0.05–1.1	14	<0.05–0.11	4	0.27–0.39	2	<0.05–0.16	4	<0.05–0.39	2	0.35–0.37	2	0.30–0.41	2	NA	
NPEO2	µg/l	0.8–13.0	12	0.05–0.2	14	<0.05–0.08	4	0.07	2	<0.05–0.11	4	<0.05–0.08	2	<0.05–0.08	2	0.14–0.16	2	NA	
NPEO10	µg/l	12–290	12	<0.05–0.44	14	0.04–0.40	4	0.08–0.10	2	<0.13–0.16	4	<0.05–0.84	2	0.11–0.21	2	0.36–0.42	2	NA	
ER-CALUX	ng EEQ/l	9.1–71.0	12	0.18–5.2	20	0.20–2.9	8	0.80–1.9	3	0.09–1.6	4	0.06–0.10	3	0.21–0.73	3	3.0–22.7	3	0.12–0.14	2

[a] Results for E3 are only indicative

there may still be EE2 present in the effluents at a low but environmentally relevant level that may have consequences for aquatic wildlife (Kidd et al. 2007).

Even after the various treatment steps, the natural human estrogens E1 and E2 are regularly encountered in the effluents (see Fig. 15.2) with E1 at the highest concentrations, typically in the order of <0.5–10 ng/L. In the horizontal (STP I) and vertical constructed wetlands (STP D), low levels of E1 could be measured, 34 and 7 ng/L respectively. The presence of E1 may be explained by excrements of birds that populate these treatment locations. In addition to the presence of E1 in the samples from the horizontal constructed wetland, E2 could be measured at a level of 10 ng/L at this site. Low levels of E2, that is below 3 ng/L, were also encountered in the samples from the post sedimentation tank and the continuous sand filter, STPs C, D and F.

The only techniques capable of completely removing E1 until below LOD are the MBR after tertiary treatment in the setup of STP F and the STP that includes active coal filtration, STP E.

Calculation of removal efficiencies is only meaningful for E2 and E1, because the concentrations of the other estrogens were already close to their LODs even in the influents. For the conventional post sedimentation step, the

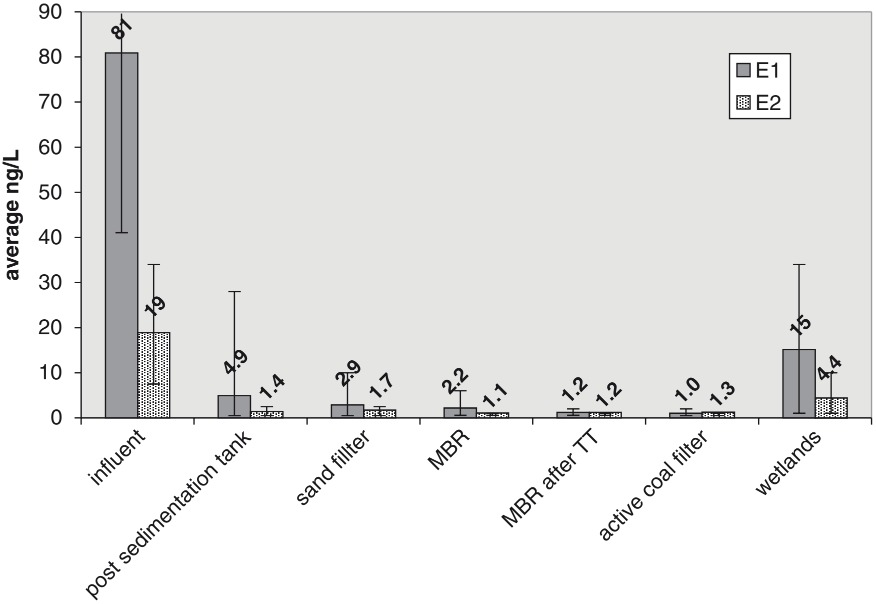

Fig. 15.2 Average concentrations of E1 and E2 per removal technique. The bars represent the minimum and maximum concentrations measured. The maximum E1 concentration in the influents is 150 ng/L. For levels below LOD, the average concentrations are calculated assuming that the specific compound is present at just its LOD

removal efficiency for E2 varies from >79% to >98%, while for E2 efficiencies of 90–>99% can be calculated. For the MBRs (STPs G and H), the removal efficiencies were >96% and >87%, respectively. For other treatment procedures, removal efficiencies could not be calculated properly due to the low concentrations (<LOD) encountered in the samples taken from the various stages of the treatment procedures.

15.4.3 BPA

In Fig. 15.3, the results of the determination of the BPA concentrations are represented for the various treatment technologies. In the influents, the average BPA concentration is in the order of 1.0 μg/L, with some peaks to 2.0–3.0 μg/L. Also in almost all the samples taken after sedimentation BPA was determined, at an average concentration of 80 ng/L. In the post sedimentation samples, extreme BPA levels of 1.5–2.5 μg/L were measured for STP A that could not be explained. None of the additional treatment steps were successful in removing all of the BPA. For the conventional treatment procedure (except STP A), the removal efficiencies for BPA are between

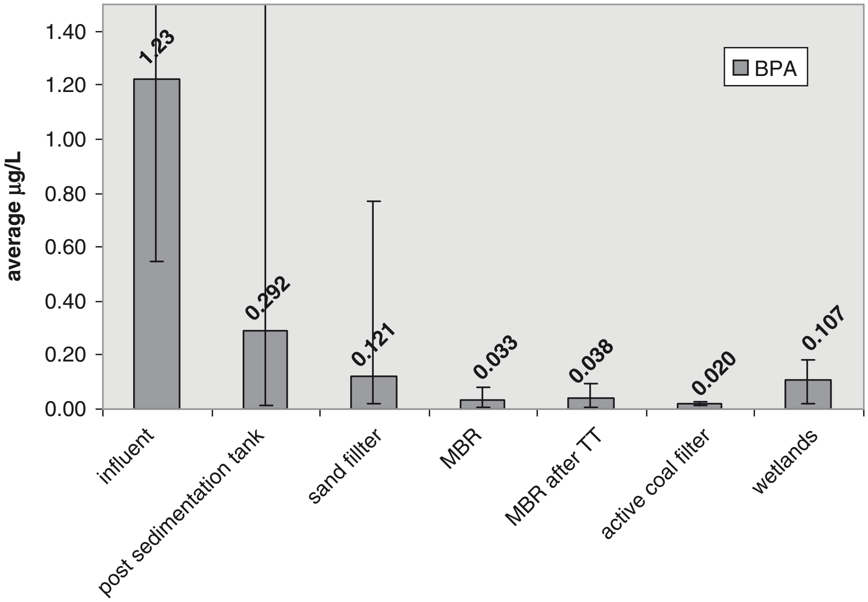

Fig. 15.3 Average concentrations of BPA per removal technique. The bars represent the minimum and maximum concentrations measured. The maximum concentration in the influents is 3.1 μg/L, the maximum post sedimentation concentration is 2.6 μg/L. For levels below LOD, the average concentrations are calculated assuming that the specific compound is present at just its LOD

96% and 99%. The results of the sand filtration steps (STPs C to F) are ambiguous, in some cases the concentration of BPA decreases, but in others an increase is measured. The horizontal constructed wetland (STP I) shows a slight increase in BPA level, while for the vertical constructed wetland the BPA level drops to below LOD.

15.4.4 NP and Ethoxylates

The results of the quantitative determinations of NP and its ethoxylates are given in Fig. 15.4. In the influents, high levels of both NP and the NPEOs have been determined, ranging from a few to a few hundreds of µg/L. For NP itself, the average concentration was 25 µg/L. The average levels of $NPEO_1$ and $NPEO_2$ were 19 and 6 µg/L, respectively, while the $NPEO_{10}$ concentration was much higher with an average of 125 µg/L.

After conventional treatment, in the post sedimentation samples the concentrations decreased drastically to concentrations well below 1 µg/L for both NP and the ethoxylates, indicating removal efficiencies of >98%. Especially the concentration of $NPEO_{10}$ decreased, with NP remaining as the most important contributor.

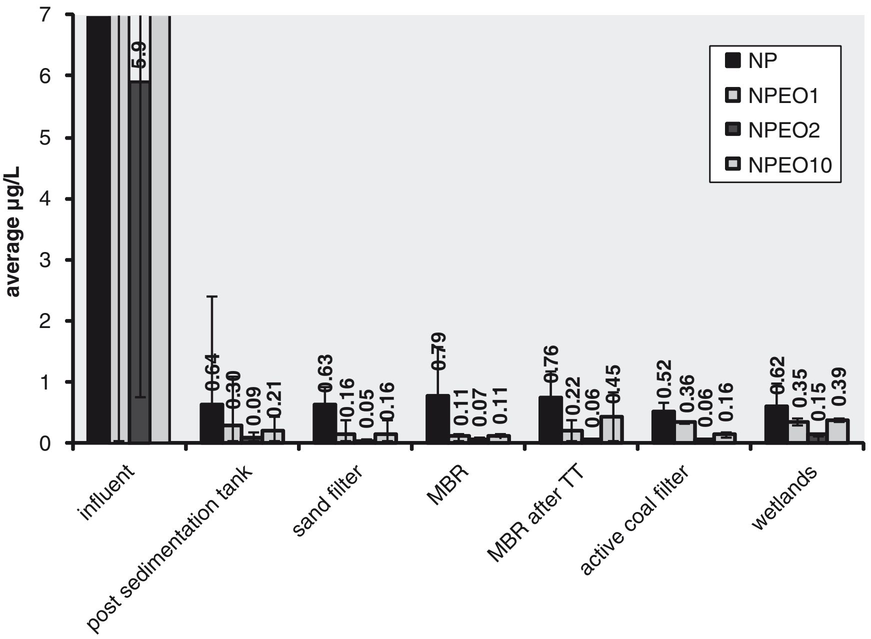

Fig. 15.4 Average concentrations of NP, $NPEO_1$, $NPEO_2$ and $NPEO_{10}$ per removal technique. The bars represent the minimum and maximum concentrations measured. The maximum concentration of $NPEO_{10}$ observed in the influents is 290 µg/L. For levels below LOD, the average concentrations are calculated assuming that the specific compound is present at just its LOD

All additional removal techniques demonstrate their capability to even further reduce the concentrations, resulting in levels in the order of a few 100 ng/L. After additional treatment, the $NPEO_{10}$ levels decreased most drastically, until <0.45 μg/L. No significant differences were observed between efficiencies of the separate additional removal techniques.

15.4.5 ER-CALUX

The results of the determination of the overall estrogenic activities by ER-CALUX for the various samples related to different removal techniques are represented in Fig. 15.5. For all techniques, the removal efficiencies were consistent with those calculated using the chemical analytical results.

In all the samples, estrogenic activity could be determined. For STPs equipped with additional removal techniques a remaining estrogenic activity in the order of 0.06–5.2 ng EEQ/L was established. Both the MBR after tertiary treatment (STP F) and the active coal filter (STP E) were capable of removal of estrogenic activity until a very low remaining activity of <0.10 and <0.73 ng EEQ/L, respectively. The removal efficiencies of the sand filters are not consistent, both an increase and a decrease are encountered depending on the STP. The remaining estrogenic activity in the horizontal constructed wetland (STP I) is relatively high (3–23 ng EEQ/L) and was, analogous to the chemical analyses, ascribed to the presence of birds and their excrements at this location. In contrast, the vertical constructed wetland gives a very good removal efficiency, with remaining estrogenic activities of 0.12–0.14 ng EEQ/L.

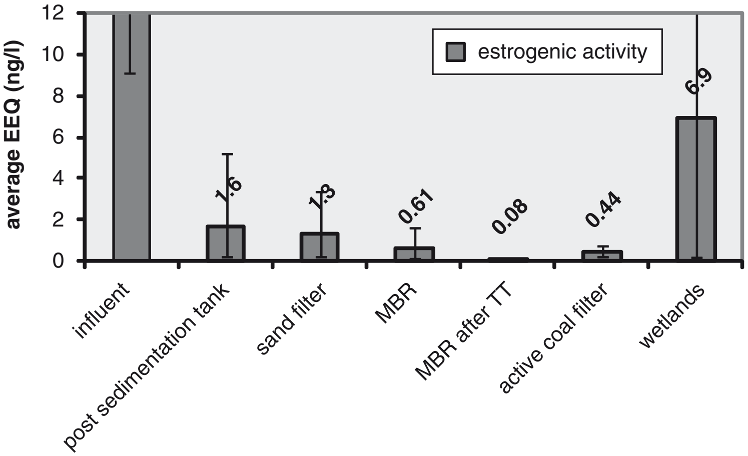

Fig. 15.5 Average estrogenic activity per removal technique as measured by the ER-CALUX assay. The bars indicate the minimum and maximum levels measured. The maximum estrogenic activity in the influents is 71 ng EEQ/L. The maximum value in the constructed wetlands (STPs D and I) is 23 ng/L. All activities are above LOD.

15.5 Discussion and Conclusions

It has been previously observed that concentrations of estrogenic hormones in STP effluents from The Netherlands are relatively low in comparison to levels reported in other countries, such as Sweden, Canada, the UK and Italy (De Voogt et al. 2006), but that they show similarities to effluent concentrations in Germany (Karbe et al. 2006). The results of the present study confirm those findings. The low concentrations of hormones in effluents in The Netherlands may be the result of the high efficiencies of Dutch STPs, however, comparison of data is often difficult because of missing details on for example the exact sampling locations and the analytical methods used. In general, Dutch sewage treatment facilities include various levels of conventional treatment (i.e. primary, secondary, tertiary). In many cases additional removal techniques such as sand or coal filtration or a membrane bioreactor are implemented in the wastewater treatment procedure.

Because all STPs were fully operational during the sampling campaigns for this study, the efficiency of removal of the estrogenic substances after additional treatment was sometimes difficult to assess because the concentrations of the compounds studied were already very low or even below their LODs when they were introduced in the additional treatment process. Of the natural estrogens, only E1 and E2 were measured in effluents after tertiary treatment (see Table 15.3). Of the synthetic estrogenic hormones covered in this study, MES was not found above its LOD in any of the samples. The highly potent EE2 could only be measured in the influents in the range 2.2–9.2 ng/L, while in none of the effluents EE2 was present above its LOD. The interpretation of this result is somewhat hampered by the fact that unfortunately in this study the LOD of EE2 turned out to be relatively high, in the order of a few ng/L, which is already the level where population effects may be expected after chronic exposure (Kidd et al. 2007).

In the influents, the average level of NP is 25 μg/L, while the corresponding ethoxylate concentrations range from 5.9 μg/L for $NPEO_2$ and 19 μg/L for $NPEO_1$ to 125 for $NPEO_{10}$. Filtration of the influents prior to the SPE procedure, which is part of the sample treatment procedure used in this study, may lead to an underestimation of the total load of NP and ethoxylates, because these chemicals are known to (partly) associate with suspended particulate matter (De Voogt et al. 2000; Derksen et al. 2005). BPA levels in the influents are in on average 1.23 μg/L, that is in roughly the same order as NP and the ethoxylates.

After conventional treatment, NP and its ethoxylates as well as BPA are still present at concentrations in the low μg/L range, but the contributions of these compounds to the overall estrogenic activity as measured by the ER-CALUX are still not very high, due to their limited estrogenic potencies (Houtman et al. 2006b). The pathways of removal, such as degradation and/or adsorption to solids of the endocrine disrupters in the STPs have not been addressed in the present study. However, it should be mentioned that suspended particulate matter can contribute significantly to the total load of the chemical in a wastewater sample, especially for NP and the ethoxylates

Considering the additional removal techniques, the results of sand filtration are sub optimal because both for the estrogenic hormones and the other compounds studied the levels after treatment were still in the low ng/L range for the hormones and the low μg/L range for BPA, NP and the ethoxylates (i.e. corresponding to efficiencies mostly below 50%). The discontinuous filter setup performed better than the continuous sand filter, although the low number of measurements does not permit elaborate conclusions regarding these techniques. As for the constructed wetlands, the horizontal wetland seemed to be prone to introduction of estrogenic hormones by aquatic wildlife, while the vertical wetland was capable of reducing the estrogenic activity to 0.12–0.14 ng EEQ/L, despite the measurable levels of E1 (up to 7 ng/L) that were observed in the effluents.

Summarizing the other additional removal techniques, all were shown to be capable of significantly reducing the estrogenic activity and consistently also the concentrations of the EDCs in the effluents. In the samples taken after tertiary treatment from the post sedimentation tank the remaining estrogenic activity was on average 1.6 ng EEQ/L. Especially the MBR in combination with prior (tertiary) treatment performed well in reducing the estrogenic activity, to an average level of 0.08 ng EEQ/L, based on three separate measurements ranging between 0.06 and 0.10 ng EEQ/L. In none of these samples, estrogenic hormones were found. The implementation of an MBR with no prior treatment resulted in an average remaining estrogenic activity of 0.61 ng EEQ/L (0.09–1.6 ng EEQ/L, n = 4). The natural estrogen E1 could be measured in all four samples at a concentration between 0.6 and 6 ng/L. Active coal filtration enabled the reduction of the estrogenic activity to an average of 0.44 ng EEQ/L (0.21–0.73 ng EEQ/L, n = 3), with no measurable natural hormones in the effluents.

An important conclusion of this study is that the effluents of conventional treatment only – consisting of two or more steps addressing primary, secondary and tertiary treatment – still show a considerable estrogenic activity and that they contain average concentrations of E1 and E2 of 4.9 and 1.4 ng/L, respectively. Although E1 and E2 are slightly less potent estrogens than the synthetic hormone EE2, for which a PNEC of 0.35 ng/L was derived by Caldwell et al. (2008), it cannot be excluded that aquatic wildlife, especially fish, experience adverse and sex-related health effects after chronic exposure to these effluents (Kidd et al. 2007; Filby et al. 2007). In order to achieve a further reduction of the estrogenic activity and a further decrease of the concentrations of the endocrine disrupting compounds analyzed, the implementation of additional removal technique (mostly after prior conventional treatment) has shown promising results. The MBRs, whether or not with prior treatment, and active coal filtration have shown to be capable of reducing the estrogenic activity to – in most cases – levels below 1 ng EEQ/L. In the light of the environmental relevance of the presence of even very low concentrations, that is in the low ng/L range, of especially the estrogenic hormones, the implementation of additional removal techniques after conventional treatment seems necessary.

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Chapter 16
Criteria for Designing Sewage Treatment Plants for Enhanced Removal of Organic Micropollutants

Francisco Omil, Sonia Suárez, Marta Carballa, Rubén Reif, and Juan M. Lema

Abstract This work addresses the problem of micropollutants removal in sewage treatment plants trying to identify the main factors influencing their fate and behaviour. Firstly the most significant groups of substances that are continuously emitted into the environment are presented and the physico-chemical properties and biodegradability of representative compounds are discussed. This information is crucial to understand the main removal mechanisms occurring in sewage treatment plants, such as sorption, biodegradation and chemical transformation, as well as the distribution pathways of micropollutants once released into the environment. Selected case studies are discussed to identify some key operational factors which influence the removal of these compounds, including the use of additives, temperature, biomass concentration and characteristics (microbial diversity, structure, etc.), as well as hydraulic and sludge retention time. A discussion focused on comparison of data corresponding to several configurations of activated sludge systems and membrane biological reactors is presented. So far, it is not clear how the type of technology affects micropollutants removal. A number of conclusions trying to explain the influence of different factors and some guidelines useful to enhance the removal of micropollutants in sewage treatment plants are presented.

Organic micropollutants refer to a wide group of carbon containing chemical compounds, mainly of xenobiotic nature, created by industrial processes either intentionally or as by-products, such as pharmaceuticals, personal care products, hormones, pesticides, brominated flame retardants, plasticizers, perfluorinated compounds, etc. Some of these substances are being considered for inclusion in the list of Persistent Organic Pollutants (POPs), i.e. compounds that are resistant to environmental degradation through biological, chemical or photochemical processes, thus capable of long-range transport, bioaccumulation in human and animal tissue,

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F. Omil (✉), S. Suárez, M. Carballa, R. Reif, and J.M. Lema
School of Engineering, Rua Lope Gómez de Marzoa s/n Campus Sur – University of Santiago de Compostela, 15782, Santiago de Compostela, Spain
e-mail: francisco.omil@usc.es

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biomagnification in food chains, and exerting potential significant impacts on human health and the environment (Katsoyiannis and Samara 2007; Clarke et al. 2008; Stockholm Convention on Persistent Organic Pollutants 2009). Moreover, a significant number of these substances, those defined as Endocrine Disrupting Compounds (EDCs), may exert estrogenic activity on various higher organisms (Kester et al. 2000).

During the last decade, the focus of environmental research has been extended from the more "classic" POPs such as organochlorine pesticides or Polychlorinated Biphenyls (PCBs) to the so called "emerging contaminants" such as Pharmaceuticals and Personal Care Products (PPCPs). Recent advances in analytical techniques, mainly related to the increasing use of Liquid Chromatography (LC) coupled with Mass Spectrometry (MS), have enabled the possibility of determining a wide variety of micropollutants which, although denoted as "emerging" because information about occurrence is fairly recent, have been discharged into the environment along decades, mainly in water bodies (Ternes 2007). That is the case of PPCPs or the most recently reported Perfluorinated Alkylated substances (PFAs), a large group of chemicals widely used to create inert surfaces for different industrial and consumer products since the 1950s, but recently detected in waste dumps or sewage (Clara et al. 2008). Although these compounds are present at low concentrations, many of them raise considerable toxicological concerns, either as sole compounds or also when present as components of complex mixtures.

The objective of this chapter is to present the main removal mechanisms that take place throughout Sewage Treatment Plants (STPs), since municipal wastewaters represent a significant emission source of micropollutants (Neumann et al. 2002; Joss et al. 2005). Most of the existing units operate with variations of the well known Activated Sludge (AS) process. However, one innovative technology that is nowadays gaining popularity is the Membrane Biological Reactor (MBR). Postreatment methods, such as activated carbon or through ozone or advanced oxidation technologies, although very interesting as a polishing step leading to almost complete removal of these substances, can be considered as an "externality" of the common primary-secondary treatment, and are not discussed in this chapter.

16.1 Types of Organic Micropollutants, Physico-chemical Properties and Biodegradability

It would be unrealistic to address the problem of organic micropollutants which can be found in wastewaters considering each one of the hundreds of different existing compounds. On the contrary, the scope here is to select some representative compounds belonging to the main groups of organic micropollutants and by considering their physico-chemical and biological properties, trying to understand the main mechanisms involved in their removal in Sewage Treatment Plants (STPs). Figure 16.1 shows the chemical structures of selected representative organic micropollutants.

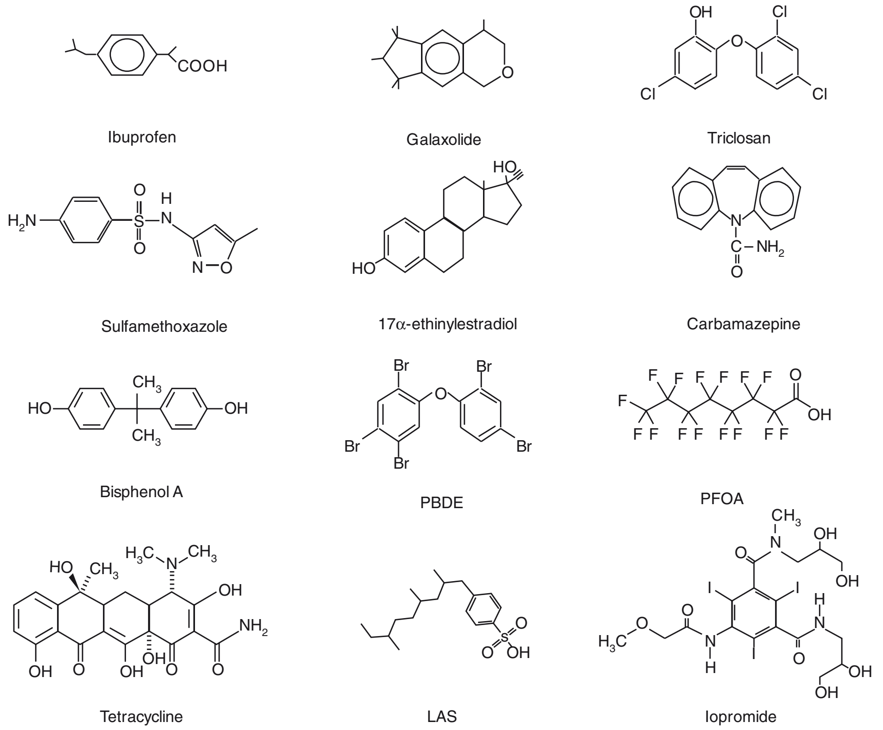

Fig. 16.1 Chemical structures of selected representative organic micropollutants

16.1.1 Types of Organic Micropollutants

Among the wide number of substances that can be present in sewage, the following groups can be considered as the most important and representative according to the following criteria: (a) wide occurrence in sewage reported in different areas of the world; (b) available analytical methodology; (c) high consumption; and, (d) research works already available.

Endocrine-Disrupting Compounds (EDCs). This group comprises a diverse range of both natural and synthetic chemicals which include hormones, phthalates (used in the manufacture of plastics), alkylphenols (present in detergents and surfactants and discharged from industrial or municipal treatment systems), polychlorinated biphenyls (PCB; formerly used in electrical equipment), dioxins (released from incinerators), organochlorine pesticides and organohalogens (used as flame retardants). Bisphenol A and the synthetic hormone 17α-ethinylestradiol (EE2) can be selected as representative EDCs found in environmental water compartments. Because the types of substances that may alter endocrine function are so diverse, many substances included in the following groups below may also cause endocrine disruption at a certain extent.

Pharmaceuticals. Several pharmaceutical compounds belonging to different therapeutical classes have been detected in urban wastewaters and their fate and behaviour along STP treatment varies according to the type of compound. In this study, carbamazepine, ibuprofen, iopromide, sulfamethoxazole and tetracycline are used to illustrate the different behaviours observed in STPs.

Personal Care Products (PCPs). The choice of personal care products (PCPs) was based on their high annual usage in a wide range of household products and concern over their possible effects on human and aquatic organisms (United States National Library of Medicine 2008a, b). Polycyclic musk fragrances such as galaxolide, sunscreen agents such as benzophenones and preservatives such as methylparaben are selected as representative compounds.

Disinfectants, Antiseptics and Other Biocides. Antiseptics and disinfectants are extensively used in hospitals and other health care settings for a variety of topical and hard-surface applications (McDonnell and Russell 1999). A wide variety of active chemical agents are found in these products, many of which have been used for hundreds of years, including alcohols, phenols, iodine, and chlorine. Triclosan is selected as a representative compound of this group.

Brominated Flame Retardants. Brominated Flame Retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol-A (TBBP-A), have routinely been added to consumer products for several decades in a successful effort to reduce fire-related injury and property damage. Recently, concern for this emerging class of chemicals has risen because of their occurrence in the environment and in human biota (Covaci and Dirtu 2008). Here decabromodiphenyl ether (BDE209), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) are considered (Breitholtz et al. 2008).

Polyfluorinated Alkylated Substances (PFAs). In recent years, Polyfluorinated Chemicals (PFCs) have increasingly been used as surfactants in various industrial and consumer products, because of their unique properties as repellents of dirt, water and oils (Clara et al. 2008). Recently, this group of substances has entered scientific and political discussions. The most studied compounds are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), which are the most important degradation products of PFAs.

Pesticides. Pesticides are used widely to kill unwanted organisms in crops, public areas, homes and gardens and for medicinal purposes to kill parasites and many of them are proven or suspected to be EDCs (McKinlay et al. 2008). Among them, the chlorinated pesticides are the most commonly associated substances of this group with health and environmental problems, such as lindane.

Linear Alkylbenzene Sulfonates. Linear alkylbenzene sulfonates (LAS) are the most widely used anionic surfactants, with an annual European production estimated at 400 million kg (Lara-Martin et al. 2008). LAS are present in commercial formulations as a complex mixture of C10 – C13 homologues and positional isomers resulting from the attachment of the phenyl ring to the successive carbon atoms (from the second to the central one) of the linear alkyl chain.

16.1.2 Physico-chemical Properties and Biodegradability

Once a micropollutant is discharged into wastewater, it will be distributed between the different environmental compartments (e.g. surface water, soil, sediment) according to its physico-chemical properties, including the solubility, volatility, acidity, lipophilicity and sorption potential. Moreover, its persistence will depend on its resistance to be degraded biologically or abiotically. Table 16.1 shows the physico-chemical characteristics and biodegradability of selected organic micropollutants.

16.1.2.1 Volatility

The selected micropollutants (Table 16.1) posses very low Henry coefficients ($H < 10^{-5}$), except galaxolide ($H = 4.5 \times 10^{-3}$). Ternes and Joss (2006) observed that a significant amount of a compound will be stripped in a bioreactor with fine bubble aeration if $H > 0.003$. Therefore, it can be concluded that stripping process is in general not relevant for the removal of micropollutants during wastewater treatment.

16.1.2.2 Acidity

Acidity (i.e. dissociation constant pK_a) indicates if a specific ionic interaction is or not relevant for the sorption potential of a given compound. Moreover, for compounds containing functional groups which can be protonated and de-protonated, the pH value might play a crucial role.

For most of the compounds considered in this work, a specific ionic interaction is not relevant, since the molecule is non-ionised at the ambient neutral pH value. Only for ibuprofen (pKa of 4.9–5.7) and perfluorooctanoic acid (pK_a of 2.8), a higher fraction might be negatively charged at neutral pH, and thus electrostatic interactions with positively charged molecules, such as coagulants, could be expected.

16.1.2.3 Lipophilicity

The octanol-water partition coefficient (K_{ow}) is an indication of the substance hydrophobicity (lipophilicity) and thus it indicates if a specific compound tends to migrate from the aqueous phase into the liphophilic cell membrane of lipid fraction of the biomass. Jones et al. (2002) have observed that compounds exert: (a) low sorption potential if $\log K_{ow} < 2.5$, (b) medium sorption potential if $\log K_{ow}$ between 2.5 and 4.0, and, (c) high sorption potential if $\log K_{ow} > 4.0$.

From the compounds considered in this work, sulfomethoxazole, carbamazepine and methylparaben show low lipophilicity, while brominated flame retardants, galaxolide and triclosan are highly hydrophobic.

Table 16.1 Physico-chemical characteristics and biodegradability of selected organic micropollutants

Category	Compound	Notation	MW	s ($mg{\cdot}L^{-1}$)	H ($atm{\cdot}m^3{\cdot}mol^{-1}$)	pKa	log K_{ow}	log K_d	k_{biol} ($L{\cdot}g^{-1}SS{\cdot}d^{-}$)
EDCs	Bisphenol A	BPA	228	120.0	$1.0{\cdot}\times 10^{-11}$	–	3.1–3.3	$8.9{\cdot}\times 10^{3a}$	–
	17α-ethinylestraidol	EE2	296	4.8–11.3	$7.9{\cdot}\times 10^{-12}$	10.5–10.7	2.8–4.2	2.3–2.8	7–9
Pharmaceuticals	Carbamazepine	CBZ	236	17.7	$1.1{\cdot}\times 10^{-7}$	7.0–13.9	2.3–2.5	0.1–1.7	<0.01
	Ibuprofen	IBP	206	21	$1.5{\cdot}\times 10^{-7}$	4.9–5.7	3.5–4.5	0.9–1.4	9–35
	Iopromide	IPM	791	23.8	$1.0{\cdot}\times 10^{-28}$	–	–	0.7–1.2	1–2.5
	Sulfamethoxazole	SMX	253	610	$6.4{\cdot}\times 10^{-13}$	5.6–6.0	0.5–0.9	1.2–2.6	<0.1
	Tetracycline	TCN	444	231	$4.7{\cdot}\times 10^{-24}$	3.3, 7.8, 9.6	−1.37	–	–
Personal care products	Galaxolide	HHCB	258	1.8	$1.3{\cdot}\times 10^{-4}$	–	5.9–6.3	3.3–4.1	<0.03
	Benzophenone	BZPN	182	137	$1.9{\cdot}\times 10^{-6}$	–	3.2	–	–
	Methylparaben	MTPB	152	2,500	$2.2{\cdot}\times 10^{-9}$	8.4	2.0	–	–
Antiseptic	Triclosan	TRI	290	10	$1.5{\cdot}\times 10^{-7}$	7.9	4.8	–	–
Brominated flame retardants	Decabromodiphenyl ether	BDE209	959	0.0001	$1.2{\cdot}\times 10^{-8}$	–	12.1	–	–
	Hexabromocyclododecane	HBCD	632	$8.6{\cdot}\times 10^{-3}$	$4.6{\cdot}\times 10^{-5}$	–	7.7	–	–
	Tetrabromobisphenol A	TBBPA	544	0.001	$7.1{\cdot}\times 10^{-11}$	–	7.2	–	–
Polyfluorinated alkylated substances	Perfluorooctanoic acid	PFOA	414	3,400	–	2.8	–	−0.5 to 1.6	–
	Perfluorooctane sulfonate	PFOS	500	370^b	$2{\cdot}\times 10^{-6}$	–	–	0.3–1.6	–
Pesticides	Hexachlorocyclohexane(lindane)	HCH	291	7.3	$5.1{\cdot}\times 10^{-6}$	–	–	–	–
Linear alkylbenzene sulfonates	C10 homologue	LAS	320	20	–	–	–	2.3	$1.3–2.0^c$
	C11 homologue	LAS	334	15	–	–	–	3.0	$1.7–2.6^c$
	C12 homologue	LAS	348	10	–	–	–	3.5	$2.3–3.4^c$
	C13 homologue	LAS	362	5	–	–	–	4.0	$2.9–4.4^c$

MW: molecular weight; s: solubility in water ($mg{\cdot}L^{-1}$); H: Henry coefficient ($atm{\cdot}m^3{\cdot}mol^{-1}$); pKa: dissociation constant; K_{ow}: octanol-water partition coefficient; K_d: sludge-water distribution coefficient; k_{biol}: pseudo first-order degradation constant ($L{\cdot}g^{-1}SS{\cdot}day^{-1}$); "–": data not available

[a] K_{oc} values in sediments

[b] Solubility of the K salt

[c] Biodegradability constant in day^{-1}

United States National Library of Medicine 2008c; (http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB); United States National Library of Medicine 2008a (http://chem.sis.nlm.nih.gov/chemidplus); Liu et al. 2005; Penteado et al. 2006; Gómez-Gutiérrez et al. 2007; Ben et al. 2008; EFSA 2008; Kasprzyk-Hordern et al. 2008; Suárez et al. 2008

16.1.2.4 Sorption Potential

The sorption potential of a given compound is indicated by the solid-water distribution coefficient (K_d), which combines two driving forces for sorption: acidity and lipophilicity. Ternes and Joss (2006) indicated that only compounds having K_d values higher than 500 L kg^{-1} will be sorbed significantly onto sludge during primary and secondary treatment. In the case of sludge treatment, Carballa et al. (2007) showed that the limit of relevance below which sorption can be neglected is around $K_d < 1$ L kg^{-1}, since the sorbed amount is not only dependent on the distribution coefficient but also on the concentration of solids.

From data available in literature (Table 16.1), it can be observed that linear alkylbenzene sulfonates and galaxolide exert a high sorption potential followed by the hormone 17α-ethinylestradiol, while the other compounds tend to remain in the water phase.

16.1.2.5 Biodegradability

Biodegradability of micropollutants will depend on their bioavailability, i.e. the potential of microorganisms to interact with them, which is related to the solubility of trace pollutants in the aqueous phase (in general very low), but also on the chemical structure of the compound. In this way, complex structures or toxic groups will make the breaking down of molecules more difficult. In order to have a measurement of the degree of biodegradability of micropollutants, kinetic constants (k_{biol}) can be experimentally determined. As a consequence of the very low substrate concentrations, the approach commonly used to model the kinetic behaviour of micropollutants is pseudo first-order degradation (Joss et al. 2006) with direct proportionality of the transformation rate to the soluble substance concentration, as well as to the sludge concentration, although in a system operated under steady-state conditions the sludge concentration can be considered as constant.

From Table 16.1, it can be observed that carbamazepine, sulfamethoxazole and galaxolide did not reach the minimum k_{biol} in the examined system required for any degree of degradation to occur (0.1 L g^{-1}SS d^{-1}). The biodegradation of the other listed compounds will strongly depend on the reactor configuration and only ibuprofen is expected to be easily degraded in STPs (9–35 L g^{-1}SS d^{-1}).

16.2 Removal Mechanisms in Sewage Treatment Plants

There are four possible removal mechanisms of organic micropollutants in STPs, which are sorption to solids, stripping (volatilisation) and biological and chemical transformation, although as stated previously, volatilisation of the micropollutants considered can be in general neglected.

16.2.1 Sorption

Sorption onto particulate matter is an important removal mechanism when the tendency of organic micropollutants to partition onto primary and secondary sludge is high. Two mechanisms are assumed to be relevant for sorption onto particulate matter: absorption (micropollutants move from the aqueous phase and enter into the lipophilic cell membrane of biomass or into the lipid fraction of the sludge due to their hydrophobicity) and adsorption (micropollutants are retained onto solids surface due to electrostatic interactions between positively charged compounds and the negatively charged surface of biomass cells).

A common approach to determine the fraction of PPCPs sorbed onto sludge is the use of the solid–water distribution coefficient (K_d, in L kg^{-1}), defined as the ratio between the concentrations in the solid and liquid phases at equilibrium conditions.

16.2.2 Biodegradation

Biodegradation is the most important process resulting in transformation (structural changes) of organic micropollutants and it can vary from partial transformation to complete mineralisation. During biotransformation, metabolites are produced, whose character in terms of toxicity and fate in the environment may be different from the parent compounds. The same may be applied to conjugates. It is expected that deconjugation (conversion back into the original compounds) occurs in sewers, in STPs (mainly during primary treatment) or in the environment.

Biological degradation rates show big differences between compounds. There are few studies focused specifically on biological degradation of PPCPs. Joss et al. (2006) have determined pseudo first-order degradation kinetics (k_{biol}) for a large number of compounds under aerobic conditions with biomass from urban STPs. According to these degradation constant values, three groups of compounds can be differentiated into: (a) hardly biodegradable, with $k_{biol} < 0.1$ L g^{-1}SS d^{-1}; (b) highly biodegradable, with $k_{biol} > 10$ L g^{-1}SS d^{-1}; and (c) moderately biodegradable with $0.1 < k_{biol} < 10$ L g^{-1}SS d^{-1}.

16.2.3 Chemical Transformation

Apart from chemical oxidation that can be applied as postreatment using Advanced Oxidation Processes (AOPs), the main chemical transformation that can occur along the STP is the deconjugation of certain micropollutants. Other natural processes such as photo- degradation are not relevant in STPs, although it should be considered in low turbidity waters such as rivers or lakes (Matamoros et al. 2008).

16.3 Factors Affecting Removal of Different Types of Compounds

In sewage treatment plants a number of separation processes (settling, volatilization, adsorption, etc.) and biochemical reactions take place and accordingly there is a vast number of factors that may affect the final results. Furthermore, it is important to realise that physical characteristics of sludge might influence biochemical reactions rate, considering the diffusion-reaction process, and also the development of particular biocenosis.

16.3.1 Use of Additives (e.g. Coagulants, Activated Carbon)

Some modifications, such as the use of chemical additives, can be implemented in STPs in order to improve solid and fat separation and, consequently, to enhance the removal of those substances with high sorption properties. The basis is that natural partitioning between micropollutants and particles can be influenced by the presence of substances, such as coagulants, commonly used in some activated sludge processes for phosphorus co-precipitation.

Coagulation-flocculation has been shown to be a suitable pretreatment option for decreasing at some extent the amount of certain type of micropollutants in urban or hospital wastewaters. Carballa et al. (2005) showed that the use of ferric and aluminium salts enhances the removal of substances with high sorption properties, such as musk fragrances, up to 50–70%. Furthermore, the presence of trivalent cations could enhance the elimination of acidic compounds (such as naproxen) by ionic or quelating interactions. Similar conclusions were obtained by Suárez et al. (2009) working with hospital wastewaters, who found high removal efficiencies for fragrances such as galaxolide (>90%) which was attributed to their strong lipophilic character. This explains also the fact why better results were obtained in wastewater streams with higher fat content. For other compounds, such as the acidic and slightly lipophilic diclofenac (which is mainly deprotonated at pH-values from 6.5–7.5), the conclusion between both works points to a correlation between removal efficiencies and coagulant doses applied, probably related to the establishment of covalent interactions between the deprotonated pharmaceutical and the trivalent cations of coagulants that enhance adsorptive interactions. This fact may also explain the higher removal efficiencies reported for diclofenac in STP in which phosphorus is precipitated during secondary treatment with the addition of inorganic (ferric) salts (Suárez et al. 2008).

In a similar way, flotation systems have shown to produce similar results as coagulation-flocculation, which could be improved when treating wastewaters with high fat content (Carballa et al. 2005).

Powdered or granular activated carbon (PAC and GAC) have been shown to effectively enhance sorption of organic micropollutants like pesticides or taste and odour compounds (Newcombe et al. 1997). The most common applications of these adsorbents is as a final step in drinking water plants or as postreatment in STP effluents. Although there are differences based on the type of activated carbon, all of them have been proven to significantly remove a large number of micropollutants especially in waters containing very low amounts of dissolved organic matter. In this way, Nowotny et al. (2007) obtained high eliminations of compounds such as bisphenol A, carbamazepine, galaxolide or triclosan treating effluents from STPs, and even the highly polar compound iopromide could be highly removed when applying ten-fold higher dosages of activated carbon.

On the other hand, it is commonly considered that the adsorbability of micropollutants is significantly lower when they are in competition with background organic matter (Snyder et al. 2007), as would be the case of direct activated carbon additions into biological aeration tanks. In this case activated carbon efficiency could be greatly reduced by the presence of other organic compounds which compete for binding sites and can block pores within the activated carbon structure.

However, this configuration has been successfully used to reduce the toxicity caused by certain substances in the activated sludge process, as well as to maintain a lower concentration of potential harmful compounds that might inhibit the process. Although there is no information concerning micropollutants removal so far, the addition of powdered activated carbon enhanced removal efficiency of organic pollutants such as phenol and cyanide due to the combined action of biodegradation and adsorption processes (Papadimitriou et al. 2009). There are also interesting results in the use of hybrid systems which combine coagulation, activated carbon adsorption and MBR in order to achieve higher eliminations of certain organic pollutants such as dyes, which appear of interest for the removal of micropollutants (Lee et al. 2006).

Recent works treating the effluents containing the persistent carbamazepine in an AS system showed that no significant removal was found until 500 $mg{\cdot}L^{-1}$ of GAC was added directly in the aeration tank. Previous operation with 100 $mg{\cdot}L^{-1}$ caused no effect, and the further increase of GAC concentration up to 1,000 $mg{\cdot}L^{-1}$ caused an increase in the removal efficiency of that compound to up to 43% (Serrano 2008).

16.3.2 Temperature

Seasonal variations in removal rates of some micropollutants in full scale STPs were reported in several studies when comparing the total loads of compounds in the influent and effluent (Vieno et al. 2005; Castiglioni et al. 2006), in a way that higher removals were measured at higher temperatures. Considering the target substances individually, Castiglioni et al. (2006) reported that removal of some compounds was positively affected by summer temperatures (average 18.6ºC) compared to winter values (average 9.7ºC), while for other micropollutants the behaviour was similar during both seasons. However, in none of the mentioned studies, the different efficiencies in micropollutant removals could be exclusively

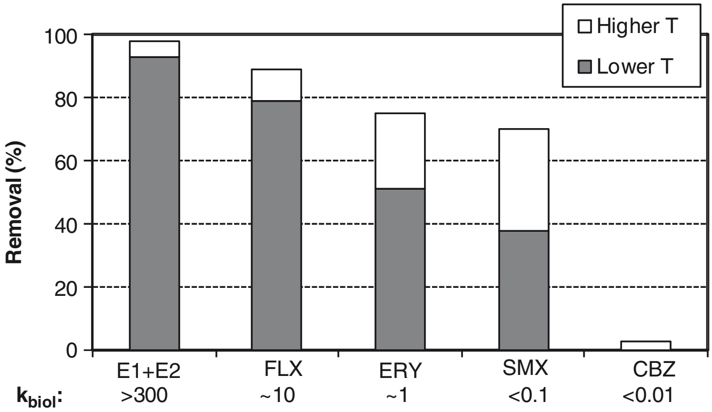

Fig. 16.2 Removal efficiency of selected compounds (estrone and 17β-estradiol (E1 + E2), fluoxetine (FLX), erythromycin (ERY), sulfamethoxazole (SMX) and carbamazepine (CBZ)) in an AS pilot plant (Suárez 2008) as a function of temperature (*lower*: 14–18ºC and higher: 18–23ºC). k_{biol} is the pseudo first-orderdegradation constant (L.g_{SS}^{-1} day^{-1})

attributed to the effect of operation temperature, since in Vieno et al. (2005) a simultaneous inhibition of nitrifying bacteria was observed, while in Castiglioni et al. (2006) the comparison was performed between data from different STPs. The exclusive effect of temperature on the removal of some pharmaceuticals can be observed in Fig. 16.2 (Suárez 2008), in which data obtained in a denitrifying/nitrifying pilot plant, fed with a synthetic mixture with similar chemical characteristics as a medium-strength urban wastewater (500 mg·L^{-1} of COD, 40 mg·L^{-1} of N-NH_4 and 8 mg·L^{-1} of P-PO_4) and spiked with a set of 16 PPCPs including antibiotics, anti-epileptics, anti-depressants, tranquilizers, anti-inflammatory drugs, fragrances and hormones in the μg·L^{-1} range (between 10 and 40 μg·L^{-1}) , are shown.

It is known that temperature can affect sorption and biodegradation rates of micropollutants during sewage treatment. For most compounds, equilibrium sorption decreases with increasing temperature (Hulscher and Cornelissen 1996), while microbial activity is enhanced at higher temperatures. However, taking into account that biological treatment in common STPs is based on activated sludge, which is typically operated at Hydraulic Retention Times (HRT) in the range of 4–24 h, sorption equilibrium can be assumed to be reached independently of operation temperature (Ternes et al. 2004). Regarding microbial activity, the effect of temperature is dependent on the magnitude of the pseudo first-order degradation constant of the considered compound in the following way (Fig. 16.2: k_{biol}): (a) highly biodegradable substances, such as natural estrogens (estrone (E1) and 17β-estradiol (E2)) and fluoxetine (FLX), are transformed to a high degree independently of operation conditions; (b) hardly biodegradable compounds such as carbamazepine (CBZ) is not removed even at higher temperatures and (c) the effect of temperature is especially noticeable for micropollutants with moderate k_{biol} as for example erythromycin (ERY) and sulfamethoxazole (SMX).

16.3.3 Microbial Diversity, Adaptation and Co-metabolism

Biodegradation of pollutants can in principle either be achieved by metabolism, using the pollutant as a source of primary carbon or nutrients for growth and/or as energy source; or by co-metabolism, in which the pollutant is transformed by the action of extracellular enzymes produced by the cells, but without any benefit for the microorganism. There is little information so far concerning this specific issue in the case of micropollutants, although due to the very low concentrations of such compounds it seems more plausible that bacteria grow on a primary substrate. This means that the presence of specific microorganisms which exclusively metabolize micropollutants is less probable, although bacteria may express some specific enzymes in order to change the substrate to a product that is not further transformed by the other enzymes. Forrez et al. (2008) linked the enzyme ammonium monooxygenase, involved in nitrification processes, with the degradation of xenobiotic substances such as EE2. The need of expression of the required enzymes to break the target compounds can be difficult due to the extreme low concentrations at which micropollutants occur. In this way, it has been reported (Jones et al. 2007) that systems operating at high Sludge Retention Times (SRT) could promote a higher and less specific enzymatic activity due to the increased cell lysis. The enzymatic mechanism responsible for degradation of certain micropollutants is often not activated as long as there are readily degradable carbon or nutrient sources available, which is the common situation in STPs. This was reported by Drillia et al. (2005) who found that the antibiotic sulfomethoxazole was used as carbon and nitrogen source by an enriched consortium. However, it was degraded whenever there was a depletion of carbon and nitrogen or both in the medium, while in the presence of acetate and ammonium nitrogen (alternative carbon and nitrogen sources, respectively), sulfomethoxazole was not degraded and remained intact.

Acclimation phenomena are also possible to occur, during which microorganisms present in a given system are able to degrade at a larger extent certain pollutants after a period of time due the establishment of a more diverse biocoenosis with broader physiological capabilities. Suárez (2008) describes the work with a denitrifying/nitrifying pilot plant which was fed without the selected micropollutants during the start-up period of the reactor which lasted around three times the implemented SRT (~100 days) so as to ensure the development of a diversified biota, including slowly-growing bacteria, as well as the achievement of stable operational conditions. After the addition of target compounds to the synthetic feed, their fate inside the plant was regularly followed. Concerning naproxen a gradual increase in its removal from 27% up to 99% was observed during the first 300 days (Fig. 16.3). Taking into account that removal of naproxen remained stable during the following 300 days, this initial enhancement was attributed to a possible acclimation of bacteria to this pharmaceutical. The possibility that existing microorganisms in biological processes can acclimate to the presence of xenobiotic compounds by broadening their enzymatic spectrum was pointed out by several authors under different operational conditions (Najean et al. 1990; Layton et al. 2000; Zwiener et al. 2000; Chin et al. 2005).

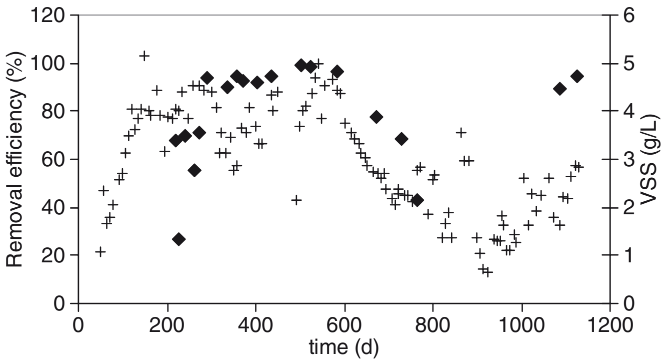

Fig. 16.3 Removal of naproxen in the pilot plant (Suárez 2008) along the complete operation period (◆). Concentration of VSS inside the reactor (+)

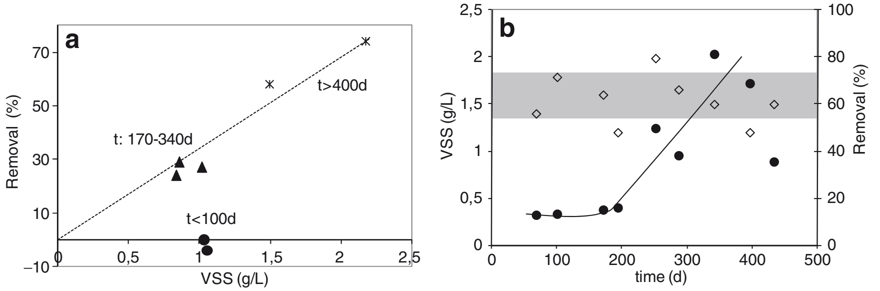

Fig. 16.4 (**a**) Correlation between removal of diclofenac and biomass concentration (expressed as VSS) in the aerobic reactor for the different sampling dates (t). (**b**) Correlation between removal of ibuprofen in the anoxic reactor (•) and its biomass concentration (◆). The *grey* shade area indicates the interquartile range of biomass concentration

When biomass from the pilot plant previously mentioned (Suárez 2008) was used to inoculate two completely mixed lab-scale reactors, one working under anoxic conditions and the other under a nitrifying aerobic ambient, a different behaviour was observed for some micropollutants (Fig. 16.4). For example diclofenac removal increased from 0% to 25% during the first 170 days, which coincides with the death and wash out of heterotrophic bacteria and the development of strict nitrifying biomass (Fig. 16.4a). Similarly, transformation efficiencies for ibuprofen in the anoxic reactor increased gradually with time from below 16% (until day 200) up to ~75% (on day 340). Although the reactor was inoculated with activated sludge, the operation in the absence of aeration and with nitrate as the sole electron donor in the system caused the development of a specific denitrifying biomass. These two examples are a clear indication that the type of bacteria developed in a biological system can influence the behaviour of micropollutants in a very significant extent. These findings might explain the SRT influence over the elimination of specific substances. Presently, there is little information available concerning the identification and isolation of enzymes present in the activated sludge which might be involved in biodegradation pathways of organic micropollutants. Further research must be accomplished in order to identify cometabolic routes as well as enzymatic oxidation kinetics.

16.3.4 Biomass Concentration and Structure

In Fig. 16.3 a decrease in the removal efficiency of naproxen in the pilot plant (Suárez 2008) after day 600 is clearly stated. This occurred simultaneously with a wash-out of sludge from the reactor as indicated by the decrease in VSS concentration. Similarly in Fig. 16.4a the growth of nitrifying bacteria implied an increase in the removal efficiency of diclofenac to maximum levels of around 75%. These two examples indicate that removal efficiency of some micropollutants can be correlated with biomass concentration, although its effect will only be noticeable for compounds with moderate biological degradation constants ($k_{biol,naproxen}$ 0.4–1.9 and $k_{biol,diclofenac}$ $< 0.1\ L{\cdot}gSS^{-1}{\cdot}d^{-1}$).

The structure of biomass is expected to have an impact on the removal of micropollutants, as it affects mass transfer between the target compound and microorganisms (i.e. the availability of the compound), the viability of bacteria and their enzymatic activity, although this aspect should be further investigated. Several operational parameters, such as SRT, composition of the treated wastewater, selection of technology, etc., may have an impact on the structure of the biomass developed in the system. This was illustrated by Cicek et al. (2001) when comparing the characteristics of biomass developed in a membrane bioreactor operated under different SRT, where the lowest SRT led to the highest biomass production rates, biomass viability and overall enzymatic activity. Similarly, in a previous study, Cicek et al. (1999) reported different biomass structure depending on the technology used for wastewater treatment, indicating that MBR sludge was composed of smaller flocs and contained many free-living bacteria, while the AS system was composed of larger flocs and higher amounts of filamentous organisms. Additionally, biomass developed in the MBR had a higher viable fraction and a consistently higher overall activity than the AS.

16.3.5 Hydraulic Retention Time (HRT)

Taking into account that HRT determines the mean residence time of soluble compounds inside the system, the biological degradation kinetics will be the key point in establishing if this parameter does or not affect the efficiency of the process. An example of this was illustrated by Huang et al. (2008) for the degradation of plasticizer di-(2-ethylhexyl)phthalate (DEHP) in an anaerobic-anoxic-aerobic activated sludge reactor, in which the overall removal efficiency of the compound was independent of the considered HRT, although the contribution of the individual processes to that removal was influenced by the HRT. The study revealed that anaerobic degradation of DEHP increased from 14% to 23% when the HRT of the reactor was incremented from 5 to 14 h, indicating that the process with the slowest kinetics was positively influenced by higher HRT. Similarly, Tauxe-Wuersch et al. (2005) determined the influence of HRT on the removal of acidic drugs in full-scale STP with primary and secondary treatment showing that the behaviour depended on the physico-chemical properties of the compound: (a) hardly biodegradable compounds as clofibric acid and diclofenac were not removed independently of HRT; (b) ibuprofen, which is a soluble compound with a moderate biological degradation constant (k_{biol} 9–35 $L \cdot g_{SS}^{-1} \cdot d^{-1}$), was principally removed during biological treatment with efficiencies varying from 0% to 79%. These differences were attributed to the fact that the three STPs did not have the same HRT and a correlation was obtained indicating that an increased residence time resulted in higher ibuprofen degradation. Additionally it was observed that absolutely no removal of this compound was observed during a heavy-raining week; (c) ketoprofen can be partially removed during primary treatment according to its moderate lipophilicity (log K_{ow} 3.1), although the efficiency showed to depend on the HRT of the primary sedimentation tank.

16.3.6 Sludge Retention Time

As shown in Clara et al. (2005), SRT of biological reactors may influence the removal efficiency of degradable micropollutants, such as bisphenol A, ibuprofen, bezafibrate and natural estrogens, for which a positive effect on their removal was observed when working at higher SRT, although only until a critical value of 10 days. Considering that SRT defines the mean residence time of bacteria inside the system and influences consequently the microbial diversity developed in biological reactors, a minimum SRT of 10–15 days was proposed as necessary to ensure the development of a diverse biocoenosis, which comprises nitrification, denitrification, and phosphorus removal. This main conclusion in Clara et al. (2005) implies that once the growth of the whole set of microorganisms which may be involved in wastewater treatment is guaranteed, SRT does not further influence the removal of micropollutants.

Transformation of galaxolide and tonalide (musk fragrances) during biological treatment in a nitrifying/denitrifying pilot plant of around 90% was reported in Suárez (2008), although it had been previously shown that removal of these compounds was mainly driven by absorption (Bester 2004; Joss et al. 2005; Kupper et al. 2006). These differences could be attributed to the higher SRT applied to pilot plant operation, since musks are highly lipophilic compounds, implying that the retention time inside the reactor is determined by SRT, rather than by HRT. This fact explains how compounds with a very low k_{biol} (<0.03 $L \cdot g_{SS}^{-1} \cdot d^{-1}$) can be biologically transformed during the secondary treatment step.

16.4 Does Technology Influence Micropollutants Removal?

Although the experience is still limited, it can be pointed out that there is an impact of the selected technology on xenobiotic substances removal. In this way, Miège et al. (2008) compared removal rates of a wide number of micropollutants in different technologies (pretreatment plus primary treatment, activated sludge with and without nitrogen treatment, membrane biological reactors, etc.). Fig. 16.5, adapted from Miège et al. (2008), compares the average removal rates reported for different micropollutants in AS systems and in other technologies.

As a main conclusion, activated sludge processes with nitrogen and phosphorus removal appear to be one of the most efficient technologies, together with MBRs combined with nitrogen elimination, in terms of micropollutants removal. However, conclusions can not be generalised because in some cases the number of data are quite limited. For example only 2 and 4 sets of data are available for fixed biomass and submerged biofilters respectively. Moreover, it is still not clear if such systems succeed in enhancing micropollutants removal when compared with conventional systems working with similar operational parameters.

MBR technology, which is based in the combination of a suspended biomass biological reactor and a membrane microfiltration or ultrafiltration step, has gained wider acceptance throughout the industry. One of its major advantages is the potential production of a high quality effluent which can be even appropriate for water reclamation. However, membrane filtration does not enhance the elimination of most micropollutants by means of a size-exclusion mechanism.

There is quite generalised tendency that consider MBRs as a definite technology for urban wastewater treatment, including micropollutants removal. Although the know-how accumulated in the last years by these systems has been enormous and

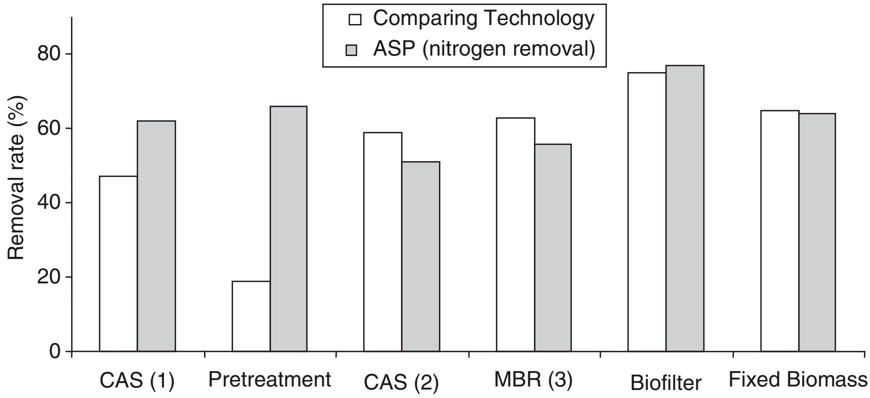

Fig. 16.5 Removal efficiencies (%) corresponding to the compilation of data of more than 50 different PPCPs obtained for Activated Sludge Process (ASP) with nitrogen treatment compared with various treatment processes. (CAS 1): without nitrogen treatment; (CAS 2): nitrogen and phosphorus removal; (MBR 3): nitrogen removal (Adapted from Miège et al. 2008)

a number of well-known advantages are now clearly stated, some of the limitations of these systems (such as capital and energy costs) should be also considered. Moreover the results reported so far concerning micropollutants are not significant enough to clearly show its advantage with respect to AS systems. In fact, both technologies, MBRs and AS systems, have been shown to achieve comparable results in terms of micropollutants removal when operating at similar conditions.

Table 16.2 summarizes the information gathered by Weiss and Reemtsma (2008) from different studies comparing MBR and AS efficiencies. The substances reported

Table 16.2 Average removal efficiencies for 49 xenobiotics in MBR and AS treatment (Adapted from Weiss and Reemtsma 2008)

	Removal		Operating Conditions			
Substance	MBR	AS		MBR	AS	References
BTSA	++	+	*Scale*	Lab	full	Weiss and Reemtsma 2008
Btri	++	+	*SRT*	26–102	15	
5-TTri	++	–	*HRT*	7–14	18	
4-Ttri	–	–	*Redox*	Aerobic	ana-anx-aer	
1,6-NDSA	+	–	*MLSS*	5	5	
2,7-NDSA	+	–				
1,7-NDSA	+	–				
2-NSA	+++	+++				
1-NSA	+++	+++				
1,3-NDSA	–	–				
1,5-NDSA	–	–				
2,6-NDSA	–	+				
bayrepel-acid	+++	+	*Scale*	Pilot	Full	Zuehlke et al. 2006
DEET	++	–	*SRT*	15 and 65	7	
MCPP	+	–	*HRT*	6.7	12	
TCEP	+	+	*Redox*	Aerobic	Aerobic	
carbamazepine	–	–	*MLSS*	3 and 12	2	
SPC C11	+++	+++				
2,4-dichlorobenzoic acid	++	++				
EDTA	–	–				
TCPP	–	–				
LAS C9–C13	+++	+++				
phenazone	++	+	*Scale*	Pilot	Full	Bernhard et al. 2006
acetylaminoantipyrin	++	+	*SRT*	∞	n.m.	
formylaminoantipyrin	++	–	*HRT*	10	9	
17β-estradiol	+++	+++	*Redox*	Aerobic	Aerobic	
estrone	+++	+++	*MLSS*	11–20	4	
17α-ethinylestradiol	+++	++				
propyphenazone	++	–				

(continued)

Table 16.2 (continued)

Substance	Removal		Operating Conditions			References
	MBR	AS		MBR	AS	
AMDOPH	–	–				
benzothiazole	++	+	*Scale*	Lab	Full	González et al. 2007
2-aminobenzothiazole	++	+	*SRT*	400	12–14	
2-methylthiobenzothiazole	–	–	*HRT*	7 and 10	22	
BTSA	–	–	*Redox*	Aerobic	ana-anx-aer	
2-mercaptobenzothiazole	++	++	*MLSS*	15	4.6	
2-hydroxybenzothiazole	+++	++				
clofibric acid	++	++	*Scale*	Pilot	Full	Kloepfer et al. 2006
diclofenac	++	+	*SRT*	15–26	15	
ketoprofen	+++	++	*HRT*	18	18	
ibuprofen	+++	+++	*Redox*	ana-anx-aer	ana-anx-aer	
mefenamic acid	+++	++	*MLSS*	13	4	
naproxen	+++	++				
CDEA	+++	+++	*Scale*	Pilot	Full	Kimura et al. 2007
NP	+++	+++	*SRT*	8 and 26	15	
NP1EO	+++	+	*HRT*	11 and 18	18	
NP2EO	+++	++	*Redox*	ana-anx-aer	ana-anx-aer	
NP3EO + NP15EO	+++	++	*MLSS*	13	13	
OP	++	++				
OP1EC	++	++				
OP2EC	++	+				

"ana-anx-aer": anaerobic-anoxic-aerobic; SRT in days; HRT in hour; MLSS in g·L^{-1}Legend for removal efficiencies: <20% (–); 20–40% (+); 40–90% (++); >90% (+++); "n.m." not measured

are of hydrophilic nature, and therefore sorption onto primary or secondary sludge was neglected. Only one reference per compound is given since no significant differences were found in the different studies reported, with the sole exception of benzothiazole-2-sulfonate (BTSA), which was partially eliminated in the work of Weiss and Reemtsma (2008) and no significant removal was reported by Kloepfer et al. (2006).

Eight substances were identified as recalcitrant (–) in both treatments: 4-Ttri (4- Tolyltriazole), 1,3-NDSA and 1,5-NDSA (1,3 and 1,5-naphthalene disulfonate), EDTA (Ethylen Diamine Tetra Acetic acid), TCPP (tris(1-chloro-2-propyl) phosphate), AMDOPH (1-acetyl-1-methyl-2-dimethyloxamoyl-2-phenylhydrazide), 2-methylthiobenzothiazole and carbamazepine. When elimination is not feasible through a biodegradation pathway and sorption is not relevant due to the physico-chemical properties of the pollutant, it is not expected that any technology based on biodegradation will succeed in removing these substances. Similarly, those compounds exhibiting a rapid degradation rate (+++) such as ibuprofen, 1-NDSA and 2-NDSA, NP (nonylphenol), SPC C11 (sulfophenylundecanoic acid) or estradiol, were efficiently removed in both conventional and MBR systems.

There is a number of compounds with slower degradation kinetics (+ or ++), for which removal efficiencies are affected by the type of reactor. In fact, removal efficiencies corresponding to 20 compounds listed in Table 16.2 increased by at least 25% when MBR was used, although a complete depletion was hardly achieved. The explanation for the increased efficiency should be mainly attributed to the higher sludge concentration and higher sludge retention time rather than the hydraulic retention time that was not, in general, so different between the two technologies.

It is important to have in mind that, up to now, no additional works have managed to operate AS and MBR systems with the same operational parameters. Other factors might play a crucial role, such as the different biomass structure found in MBRs (Massé et al. 2006), the higher enzymatic activity derived from a more important cell lysis, better conditions to achieve acclimation or the development of a stable population of nitrifiers, among others. However, a direct link between MBR biomass properties and micropollutants removal has not been established.

16.5 Guidelines to Enhance the Removal of Micropollutants in STPs

A number of conclusions can be derived from the joint analysis of all factors discussed along this paper. For this, two main characteristics of each micropollutant, biodegradability (k_{biol}) and partition coefficient between the solid and liquid phase (K_d) are considered. In Table 16.3 a summary of those conclusions, giving some examples, is presented.

- Compounds with high k_{biol}, such as 17β-estradiol, are very well transformed independently of operational conditions.
- The extension of transformation of compounds with moderate k_{biol} and low K_d values, such as ibuprofen, depends on the HRT.
- Compounds with low k_{biol} and high K_d values, such as musk fragrances, are retained in the aeration tank by sorption and significantly transformed when the SRT is high enough to permit biological degradation.

Table 16.3 Factors affecting removal in biological treatment

	Removal	Influencing factors	Example
$k_{\mathbf{biol}}\downarrow\ K_{\mathbf{d}}\downarrow$	–	None, as not degraded	Carbamazepine, diazepam
$k_{\mathbf{biol}}\ \downarrow\uparrow\ K_{\mathbf{d}}\downarrow$	++	HRT	Ibuprofen
$k_{\mathbf{biol}}\uparrow\ K_{\mathbf{d}}\downarrow\uparrow$	++	None, as quickly degraded	17β-estradiol
$k_{\mathbf{biol}}\downarrow\ K_{\mathbf{d}}\uparrow$	++	SRT	Galaxolide
$k_{\mathbf{biol}}\downarrow\uparrow\ K_{\mathbf{d}}\downarrow\uparrow$	+	SRT	17α-ethinylestradiol
$k_{\mathbf{biol}}\downarrow\uparrow$	+	T, VSS	Fluoxetine, citalopram, naproxen
$k_{\mathbf{bio}}\downarrow$	+	Sludge type	Diclofenac
Ionisable	+	Coagulants, pH	Diclofenac
$K_{\mathbf{ow}}\uparrow$	++	Fat content	Galaxolide

Removal efficiency <20% (–); 40–70% (+); >80% (++)

- Compounds with moderate k_{biol} and K_d values, such as 17α-ethinylestradiol, are moderately transformed during biological treatment, being the removal efficiency positively affected by higher SRT.
- Compounds with low k_{biol} and K_d values, such as carbamazepine, are not removed and not biotransformed regardless of operational conditions.
- Transformation of compounds with moderate k_{biol}, as for example fluoxetine, depends on factors affecting their pseudo-first order kinetics, such as temperature and sludge concentration.
- Microbial diversity influences degradation of certain micropollutants which showed to be recalcitrant (low k_{biol}) in AS processes, as observed for diclofenac.
- Removal of acidic substances, as diclofenac, which are partially deprotonated at neutral pH, can be enhanced by the addition of cationic coagulants.
- Removal of ionisable substances during primary treatment can be improved by pH control. This is the case of carbamazepine, for which the protonation of its amide group improves its removal through adsorption.
- Removal of lipophilic compounds (high K_{ow}), such as musks, can be enhanced during primary treatment in presence of fat that favours absorption.

Most of the research dealing with micropollutants removal in STP has been focussed on the determination of efficiency of different technologies or different working conditions whereas there is very scarce information about the scientific background concerning the main removal mechanisms (volatilisation, sorption, chemical and biological transformation), the influence of the characteristics of the target compound (physico-chemical and biodegradability) and the role of biomass properties (microbial diversity, structural conformation, enzimatic activity, etc.). In order to be able to develop new strategies for the successful treatment of micropollutants, more detailed knowledge about those issues is still required.

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Chapter 17
Xenobiotics Removal by Membrane Technology: An Overview

Andrea J.C. Semião and Andrea I. Schäfer

Abstract Small molecular weight xenobiotics are compounds of extreme concern in potable water applications due to their adverse human health and environmental effects. However, conventional water treatment processes cannot fully and systematically remove them due to their low concentrations in natural waters and wastewaters. Biological limitation to degrade such compounds is another cause for inefficient removal.

Physical barriers like membranes possessing pore sizes smaller than the compounds to be removed emerged as a good solution. Nanofiltration and reverse osmosis proved to be quite effective for xenobiotics removal in potable water production in the Paris purification plant of Méry-sur-Oise. However, even these very narrow pore membrane processes may result in incomplete removal: xenobiotics retention is high but factors such as adsorption, size exclusion and charge repulsion affect unpredictably their retention. The water solutions complexity to be treated renders xenobiotics removal predictions even more difficult due to interactions between xenobiotics and compounds in water.

Removal of xenobiotics by microfiltration and ultrafiltration is very low because adsorption on the membrane is the main retention mechanism. Combining those with other processes (e.g. activated carbon) can considerably improve xenobiotics removal.

The least studied processes in xenobiotics removal are electrodialysis, membrane distillation and pervaporation. Electrodialysis removal of organic xenobiotics shows a breakthrough through the membrane possibly due to adsorption followed by diffusion. Membrane distillation presents high removal rates of xenobiotics due to the compounds low vapour pressure. For volatile organic xenobiotics or solutions of trace amounts both membrane distillation and pervaporation can be used, xenobiotics interaction with the membrane being the key factor.

A.J.C. Semião (✉) and A.I. Schäfer
School of Engineering, The University of Edinburgh, Edinburgh EH9 3JL, United Kingdom
e-mail: A.Correia-Semiao@ed.ac.uk; Andrea.Schaefer@ed.ac.uk

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In this book chapter a thorough synopsis of current knowledge on xenobiotics removal is presented and balanced with recent fundamental studies of underlying mechanisms, informing both the practitioner regarding membrane capabilities for xenobiotics removal and the researcher with the current state-of-art.

17.1 Introduction

17.1.1 Xenobiotics Removal by Conventional Water Treatment Processes and Natural Water Contamination

Xenobiotics are compounds foreign to a living organism or introduced in the environment by artificial means. The implications of xenobiotics on human health, including endocrine disruption, have been intensively debated recently (Tyler et al. 1998; Younes 1999; Safe 2000). Although studies are to date not conclusive, it is important to remove xenobiotics from wastewaters discharged to surface waters as well as protecting drinking water sources.

Concentrations of xenobiotics up to μg/L were measured in wastewater treatment plant (WWTP) effluents, showing an incomplete removal by conventional treatment processes all over the world (Baronti et al. 2000; Körner et al. 2000; Zuccato et al. 2000; Johnson and Sumpter 2001; Kolpin et al. 2002; Williams et al. 2003; Schultz and Furlong 2008). Batt et al. (2008) measured a total concentration of active pharmaceuticals up to 3,000 ng/L in New Mexico of which carbamazepine concentration was up to 800 ng/L. Carbamazepine and paracetamol were found at high concentrations, 300 ng/L and 11.3 mg/L respectively, in the Hérault area, France (Rabiet et al. 2006). High concentrations of antidepressants in Minnesota, USA (Schultz and Furlong 2008) and pharmaceuticals in the Berlin area, Germany (Heberer 2002) were also measured.

These effluents are discharged into surface and groundwaters where concentrations up to μg/L were measured for pharmaceuticals, anti-depressants and hormones (Kim et al. 2007; Batt et al. 2008). Rabiet et al. (2006) showed that wells tapped for drinking water in the vicinity of WWTPs had concentrations of pharmaceuticals up to 300 ng/L compared to other wells with <50 ng/L upstream from the plant. The same phenomenon was found with surface waters downstream of a WWTP in the Berlin area (Heberer 2002). In a UK survey on two rivers in the southeast of England an increase in estrone concentration was measured caused by a WWTP discharge (Williams et al. 2003). Although hormones were measured at trace level concentrations in these effluents, in USA streams concentrations of more than 100 ng/L were quantified (Kolpin et al. 2002).

There are thousands of xenobiotics of concern most of which are small and occur at low concentrations making them very difficult to remove effectively. Due to an insufficient removal by conventional treatment processes, the application of advanced technologies such as membrane processes have been the focus of attention since they have the potential to efficiently remove xenobiotics down to very low levels.

17.1.2 Target Xenobiotics

Six organic xenobiotics were chosen as example compounds for this chapter due to the extensive availability of data from different types of membrane filtration studies and due to their different physico-chemical properties. This choice allows the illustration of different behaviours of xenobiotics in different membrane processes. The chemical properties of the xenobiotics are described in Table 17.1. The pK_a and Log K_{ow} represent the acid dissociation constant and the partition coefficient in octanol-water, respectively. The latter is a measure of the compound hydrophobicity.

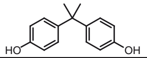
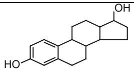
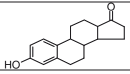
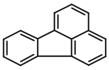
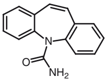
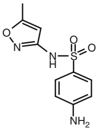
Sulfamethoxazole (SMX), estrone, estradiol, bisphenol-A (BPA), fluoranthene and carbamazepine (CBZ) have approximately the same molecular weight (MW). They differ in their dipole moment, Log K_{ow} and pK_a. They are all bipolar, with the exception of fluoranthene, meaning they can act either as a proton (H) acceptor or donor, being able to form H-bonds with other molecules (Goss and Schwarzenbach 2003).

17.1.3 Membrane Processes

Membranes work as a physical barrier to the passage of contaminants, with pores or molecular channels incorporated into a polymeric material. The most common membrane processes for water treatment applications are pressure driven. Exerting pressure perpendicular to the membrane (driving force) allows the passage of water through, the permeate, and the retention of solutes and contaminants, the concentrate, from a feed solution that circulates tangentially to the membrane surface (see Eq. 17.4 and Fig. 17.1).

Membranes are either porous, for example ultrafiltration (UF) and microfiltration (MF), or dense, for example reverse osmosis (RO). Nanofiltration (NF) membranes are considered to be between porous and dense (Schäfer et al. 2005). These differences dictate how the contaminant is transported through the membrane. MF and UF membranes are characterised by the molecular weight cut-off (MWCO), an indication of the compounds size they remove, corresponding to the MW at which 90% rejection is obtained (Mulder 1996). NF can be either characterised by MWCO or ionic retention of salts such as NaCl or $CaCl_2$. RO membranes being dense are characterised by salt rejection, although

Table 17.1 Selected xenobiotics chemical properties

Compound	Molecular Formula	CAS No.	Molecular Structure	Molecular weight (g/mol)	Solubility (mg/L)	pK_a	Log K_{ow}	Dipole moment (Debye)	H acceptor (A)/ donor (D) capacity of the compound[1]
Endocrine Disrupting Chemicals									
Bisphenol A (Endocrine Disruptor)	$C_{15}H_{16}O_2$	80-05-7		228	120^{a,b}	9.28^{c}	3.32^{d}	1 -1.4^{a,b,e}	2 strong D [OH]/2 weak A [π electrons]
Estradiol (Natural Steroidal Hormone)	$C_{18}H_{24}O_2$	50-28-2		272	3.6 -13^{b,f}	10.23^{c}	4.01^{g}	2.2^{h}	2 strong D [OH]/1 weak A [π electrons]
Estrone (Natural Steroidal Hormone)	$C_{18}H_{22}O_2$	53-16-7		270	13 -30^{f,i}	10.34^{c}	3.13^{g}	2.1^{h}	1strong D [OH]/1 strong and 1 weak A [=O, π electrons]
Fluoranthene (Polycyclic Aromatic Hydrocarbon)	$C_{16}H_{10}$	206-44-0		202.3	<1	NA	5.2^{j}	NA	3 weakA [π electrons]
Pharmaceuticals									
Carbamazepine (Antiepileptic)	$C_{15}H_{12}N_2O$	298-46-4		236	17.7^{b,k}	<1^{d}	2.45^{d}	3.2-3.6^{b,k}	1strong D [NH_2]/2 strong and 2 weak A [=O, N, 2π electrons]
Sulfamethoxazole (Sulfonamide antibiotic)	$C_{10}H_{11}N_3O_3S$	723-46-6		253	600-610^{b,k}	1.8, 5.7^{d,k}	0.89^{b,d,k}	5.4 -6.3^{b,k}	2 strong D [NH, NH_2]/4 strong and 1 weakA [2 =O, N, O, π electrons]

[1] The H-acceptor and donor groups of the compound are identified in brackets [group]
[a] Nghiem et al. 2005a
[b] Kimura et al. 2004
[c] Kwon et al. 2006
[d] Ternes and Joss 2006
[e] Nghiem 2005
[f] Nghiem et al. 2004
[g] Hansch et al. 1995
[h] Kubli-Garfias 1998
[i] Schäfer et al. 2003
[j] Yoon et al. 2004
[k] Nghiem et al. 2005b

some researchers have modelled molecular retention to determine a MWCO (Kimura et al. 2004).

Retention of a contaminant is defined as:

$$R_{\text{xenobiotic}}(\%) = 100 \times \left(1 - \frac{c_P}{c_F}\right) \tag{17.1}$$

Where c_P and c_F are the permeate and feed concentrations, respectively.

Other common performance parameters for membrane processes are:

$$Q_F = Q_C + Q_P \tag{17.2}$$

$$\text{Recovery} = \frac{Q_P}{Q_F} \tag{17.3}$$

$$J = \frac{1}{A}\frac{dV}{dt} = L_P\left(\Delta P - \Delta\pi\right) \tag{17.4}$$

Where Q_F, Q_C and Q_P are feed, concentrate and permeate flow rates, recovery is the amount of clean water produced per feed water treated, A is the membrane area, V is the permeate volume, t is time, L_P is the membrane permeability, ΔP is the applied transmembrane pressure and Δπ is the osmotic pressure difference between feed and permeate.

Several types of membrane processes are available for water treatment depending on their separation principle, pore size d_P (see Fig. 17.1), and driving-force for separation. The different membrane processes found are pressure driven as described in Fig. 17.1 (MF, UF, membrane bio-reactor MBR, NF and RO), electrical potential driven (electrodialysis ED), thermally driven (membrane distillation MD) and due to vapour pressure differences between feed and permeate (pervaporation PV). A comparison between different membrane separation processes described in this chapter and solutes they remove is presented in Table 17.2.

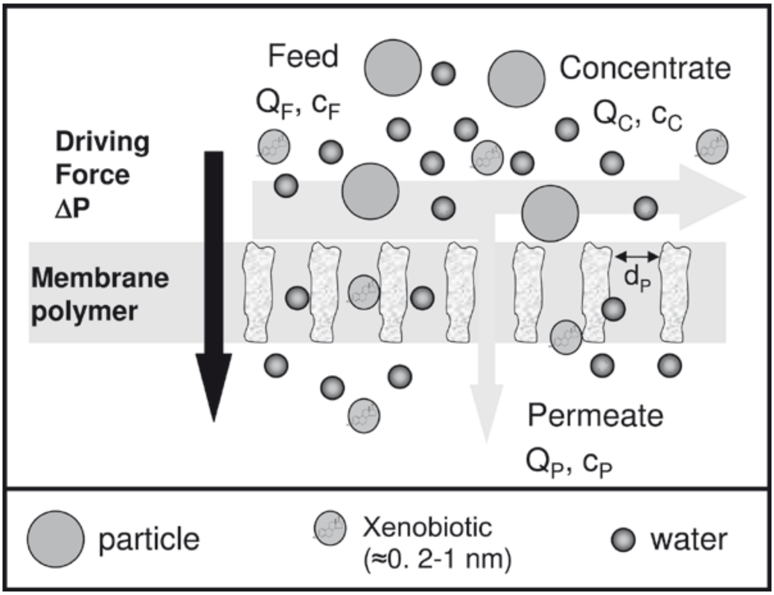
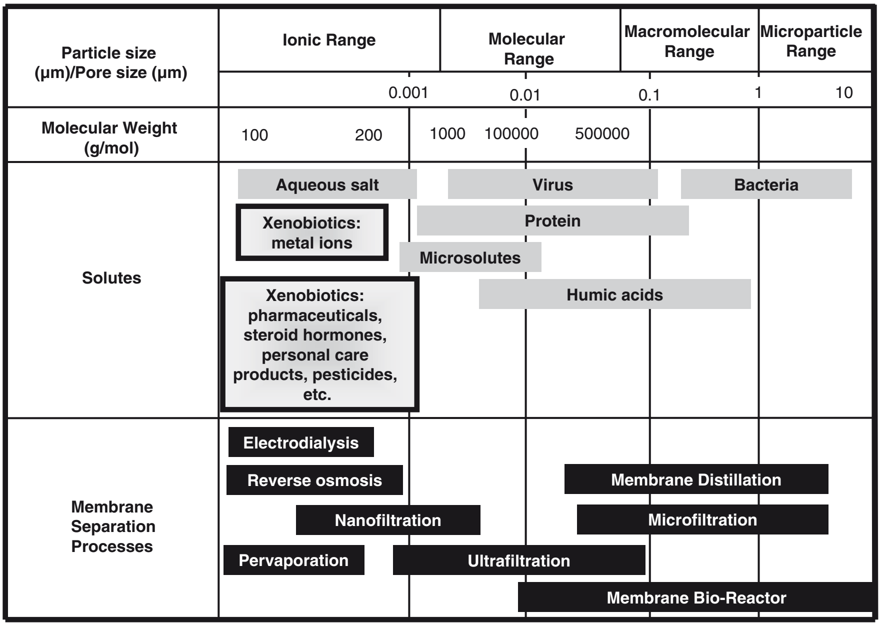


Fig. 17.1 Pressure-driven membrane schematic with pore size d_p (microfiltration, ultrafiltration, nanofiltration and reverse-osmosis)

Table 17.2 Membrane processes and contaminants dimensions (adapted from [Anselme and Jacobs 1996; Aptel and Buckley 1996; Manem and Sanderson 1996; Mulder 1996; Schäfer 2001])



The MW range of the compounds and membrane pore sizes or particle sizes are also presented.

Membrane separation processes are in principle able to remove from contaminants as big as bacteria (e.g. MF, UF, membrane bio-reactor, NF and RO) to small contaminants such as xenobiotics and metal ions (e.g. NF, RO and ED).

17.2 Microfiltration, Ultrafiltration and Membrane Bioreactors

MF and UF processes use porous membranes that act as a sieve, with pore size ranging between 50–10,000 nm (MF) and 1–100 nm (UF) (Mulder 1996). Separation of molecules takes place by steric hindrance at the inlet of the pore and by frictional resistance inside the pores (Bitter 1991). UF membranes separate smaller contaminants than MF given their smaller pore size as can be seen in Table 17.2. A key advantage of UF over MF in water treatment is that UF removes bacteria and most viruses and is hence a physical disinfection process.

To separate small molecules such as xenobiotics it is necessary for these compounds to precipitate, adsorb or coagulate to a bigger size to allow for MF or

UF retention. However exceptions have been found where high apparent retentions are obtained although xenobiotics sizes are much smaller than membrane pore size, as described next.

A simplified schematic of the several mechanisms involved in xenobiotics retention by MF and UF membranes is shown in Fig. 17.2.

17.2.1 *Xenobiotics Removal by MF and UF*

Due to the relatively large pore sizes of MF and UF membranes (see Table 17.2) xenobiotics generally of MW lower than 400 g/mol are not retained even by the lowest MWCO membranes (Devitt et al. 1998; Yoon et al. 2006, 2007). However studies show the occurrence of adsorption by some of the membrane polymers (Schäfer et al. 2002) leading to apparent high retention.

Chang et al. (2003) obtained 100% removal of estrone in a MF dead-end process due to adsorption on the membrane. A sieving effect is discarded since the membrane pores are much larger than the estrone molecule. This occurs due to low estrone feed concentrations, where the amount of adsorption sites available on the membrane allows for adsorption of almost all the contaminant. High adsorption of xenobiotics have also been obtained in several UF studies (Yoon et al. 2004, 2006; Comerton et al. 2007). Fluoranthene and 17β-estradiol adsorbs onto UF membranes from >70% for fluoranthene and >34% for estradiol (Yoon et al. 2004).

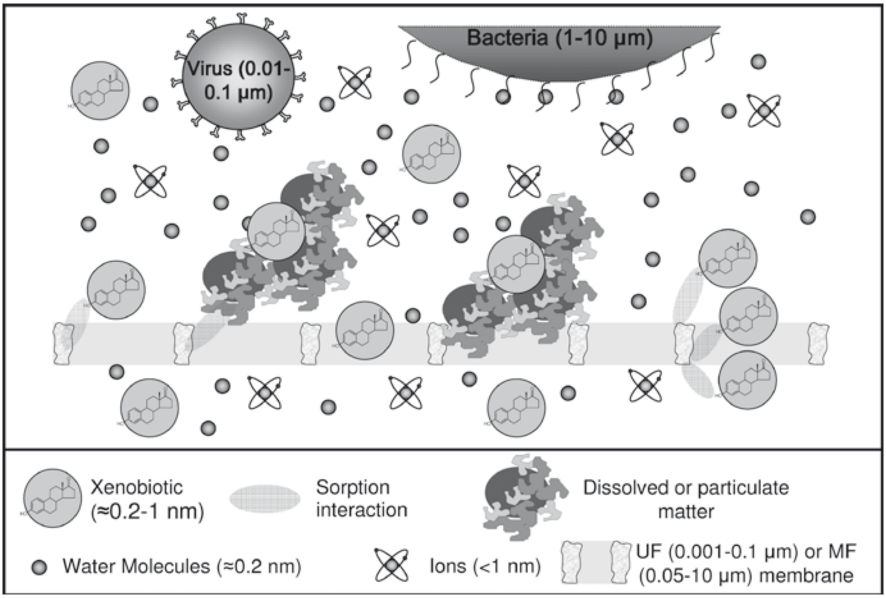


Fig. 17.2 Retention mechanisms by MF and UF membranes

Although MF and UF have apparent high retentions for small xenobiotics they are related with adsorption on the membrane surface. Once adsorption sites saturate, retention is low and these processes are not effective in removing xenobiotics sustainably.

Solution pH affects the extent of xenobiotics adsorption. Lyko et al. (2005) measured a UF retention of 36% for BPA at pH 5 and none at higher pH. Schäfer et al. (2006) obtained similar UF retentions (30%) for this compound in pure water from pH 4–9, when BPA is neutral. These high retentions are associated with adsorption on the membrane. The UF process does not exhibit any retention capacity though once BPA dissociates at $pH > 9.3$ (Table 17.1). Adsorption decreases dramatically accompanied by a decrease in retention due to charge repulsion between BPA and the membrane. Adsorption of xenobiotics is thought to occur through H-bonding which BPA loses when dissociated, also contributing to a decrease in adsorption.

It has to be noted that adsorption of xenobiotics to MF and UF membranes can lead to losses in xenobiotic analysis if polymeric filters (e.g. cellulose acetate and polyamide) are used in sample pre-treatment. Given that MF and UF retain particulates and some molecules, xenobiotics that are associated with such particulate or dissolved matter can also be retained and will be unaccounted for (Neale et al. 2009). However, interactions of xenobiotics with particulates and molecules can be exploited to enhance the retention by MF and UF.

17.2.2 Solute–Solute Interaction and Retention by MF and UF

Organics in wastewater play a role in xenobiotic retention, as they interact with xenobiotics and enhance their removal (Devitt et al. 1998). This case was illustrated by Schäfer et al. (2006) in a submerged UF process where higher retentions of BPA at $pH < 9$ are obtained in the presence of natural organic matter (NOM) compared to retentions of BPA without NOM. BPA partitions into the NOM and is better retained. At $pH > 9$ due to charge repulsion between BPA, NOM and the membrane no enhancement of BPA retention is obtained since no adsorption and partitioning of BPA on the membrane and on NOM occurs.

When adsorption of xenobiotics on the membrane is the main retention mechanism, the presence of NOM can decrease their retention. NOM possesses hydrophobic moieties (Haslam 1996; Yuan and Zydney 2000), H-bonding capacity (Piccolo 1994) or gel formation capacity (Davis et al. 2003; Fatin-Rouge et al. 2006) and therefore adsorbs onto the membrane surface and competes for adsorbing sites with the xenobiotics. Pore blockage by NOM also causes less access for adsorption sites, decreasing the rate of adsorption and therefore decreasing retention of xenobiotics. This has been shown to happen for steroid hormones, pharmaceuticals and pesticides (Chang et al. 2003; Yoon et al. 2004, 2006; Comerton et al. 2007).

Solute–solute interactions of xenobiotics with organic compounds from water and wastewater are very compound and solution chemistry specific. Interaction and their effects on xenobiotic transport and removal are important. However mechanisms are to date poorly understood.

17.2.3 Hybrid Processes on Xenobiotics Removal by Large Pore Size Membranes

Pre-treatment processes such as coagulation, adsorption, oxidation, complexation or precipitation enhance xenobiotic retention. The formation of larger complexes enhances the removal by large pore membrane processes.

Oxidation, pH adjustment or polymer assisted filtration can lead to the precipitation or complexation of metals and subsequent removal of the precipitate by MF or UF (Broom et al. 1994; Uludag et al. 1997; Sanli and Asman 2000; Teng et al. 2001; Kryvoruchko et al. 2004; Fatin-Rouge et al. 2006).

Coagulation appears to be a poor treatment method for trace organics removal from aqueous solutions. No interaction of steroid hormones was obtained by Chang et al. (2004) and Bodzek and Dudziak (2006) when mixed with iron and aluminium based coagulants. The reason for this low efficiency is most likely a lack in affinity for inorganic solids as well as the low concentration of xenobiotics.

Considering sorption of steroid hormones on activated carbon (AC) is generally high (Chang et al. 2004; Bodzek and Dudziak 2006), combining MF to remove AC with the sorbed xenobiotic from solution is an option. Chang et al. (2004) obtained an estrone removal as high as 96%, providing a minimum AC dosage is met.

In real life applications xenobiotics removal enhancement by hybrid MF and UF processes is a difficult task. These processes rely on an effective interaction between xenobiotics and the sorbent. This interaction depends on sorbent and xenobiotic characteristics and the solution chemistry that may both enhance or hinder the process. This makes such processes inherently complex and unlikely to function effectively for a vast number of xenobiotics or solution chemistries. A physical separation such as NF and RO is therefore an attractive option.

17.2.4 Xenobiotics Removal Using Membrane Bioreactors

The combination of MF/UF with biological degradation into a single process is called an MBR, considered to be a MF/UF hybrid process. Suspended solids and microorganisms responsible for biodegradation are separated from the treated water by a membrane filtration unit. In this case a biological rather than a physico-chemical process is coupled with the membrane filter. The inhibitive end product of the bioconversion by enzymes and microorganisms is continuously removed to proceed with the reaction (Manem and Sanderson 1996; Mulder 1996).

MBR are partially effective in xenobiotics removal (Joss et al. 2006; Hu et al. 2007a). Removal is higher when compared to conventional activated sludge processes (CASP) possibly due to a higher specific surface obtained in MBR processes (Joss et al. 2004; Lyko et al. 2005). Kim et al. (2007) obtained >95% removal of hormones and some pharmaceuticals (e.g. ibuprofen) by treating wastewater from University campus dormitories and student apartments. Xenobiotics removal can be effective if they are biodegraded after an association with the biomass in the MBR which is obtained for contaminants such as BPA, nonylphenol (NP), pharmaceuticals and endocrine disrupting chemicals (EDC) (Clara et al. 2005). Removal is also effective when the xenobiotic adsorbs on the biomass suspended solids (Joss et al. 2005, 2006) and is later separated from the treated water by MF or UF. Adsorption on the sludge is found to be the highest at lower pH where there is less charge repulsion between the sludge and the xenobiotics (Schäfer et al. 2002; Melin et al. 2006). Removal is also enhanced for xenobiotics with lower dipole moment or higher hydrophobicity (Baumgarten et al. 2006; Hu et al. 2007a). Due to gel formation or fouling on the membrane surface there is thought to be a shift of the membrane MWCO which can partly remove macromolecular organic carbon to which xenobiotics are adsorbed to (Schäfer et al. 2002; Lyko et al. 2005; Melin et al. 2006).

However removal of compounds such as CBZ and SMX has been found to be very low or nonexistent for MBR and conventional processes due to a low sorption capacity on the sludge (Clara et al. 2005; Joss et al. 2006; Göbel et al. 2007; Kim et al. 2007; Radjenovic et al. 2007).

Xenobiotics that are not removed are discharged and in consequence often found in natural waters (Heberer 2002; Rabiet et al. 2006) or in river, ocean and soil sediments (Kuster et al. 2004; Weston et al. 2004; Braga et al. 2005). Degradation of compounds into smaller, more hydrophilic, polar, persistent and sometimes more toxic molecules also occurs and is to date poorly understood (Baumgarten et al. 2006; Göbel et al. 2007; Hu et al. 2007a). For example Hu et al. (2007a) obtained higher concentrations of NP in the effluent compared to the influent concentration due to NP production from parent compounds. Although MBR processes show enhanced xenobiotics removal compared to conventional treatment processes, this removal is still insufficient and poorly understood.

17.3 Nanofiltration and Reverse Osmosis

NF pores are in the <2 nm range while RO "pores" are to be seen as non-discernable voids between polymer chains. Transport of a liquid through a dense membrane is described in terms of the solution-diffusion mechanism which is a function of solubility on the membrane and its diffusivity. Each permeant dissolves in the membrane material and passes by diffusion due to its chemical potential gradient (Bitter 1991). In NF the transport of liquid through the membrane is considered to be between UF and RO with a contribution of both convection and sorption-diffusion.

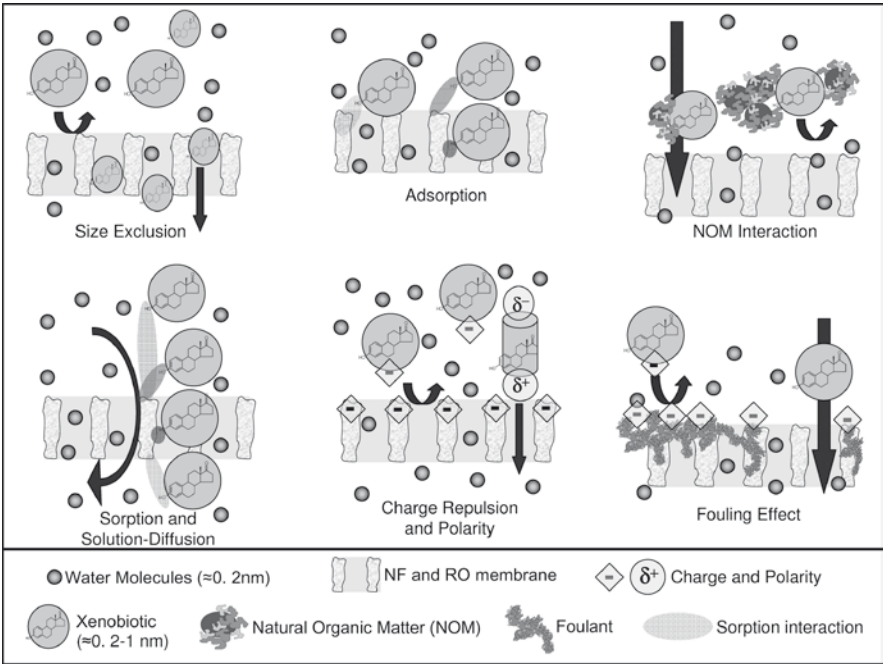


Fig. 17.3 Retention mechanisms by NF and RO membranes

The retention of contaminants by NF and RO membranes involves several mechanisms such as steric exclusion, adsorption followed by diffusion and electrostatic interactions. These mechanisms depend on the membrane properties such as surface charge and pore size, the xenobiotic properties such as H-bonding capacity, molecular size and polarity and the solution chemistry involved such as pH, ionic strength and the presence of NOM.

A simplified schematic of the several mechanisms involved in xenobiotics retention by NF and RO membranes is shown in Fig. 17.3.

17.3.1 Size Exclusion

Size exclusion mechanism is directly related with molecular size. In general it increases with increase of compound MW (Berg et al. 1997; Ducom and Cabassud 1999; Kimura et al. 2003b) and retentions are usually higher than 90% (Rosa and de Pinho 1995; Raff and Wilken 1999; Weber et al. 2004; Kim et al. 2007; Kosutic et al. 2007) for compounds with MW higher than the MWCO of the membrane (Berg et al. 1997; Van der Bruggen et al. 1999; Koyuncu et al. 2008) (see Fig. 17.4a). MW has been shown to be a good indicator of the retention trend obtained by NF and RO membranes compared to other molecular sizes, for example Stokes diameter (Van der Bruggen et al. 1999).

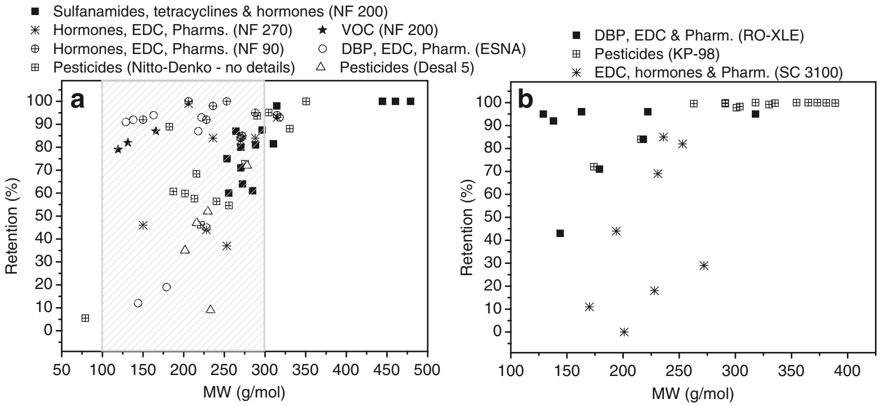


Fig. 17.4 Xenobiotics retention by NF (**a**) and RO (**b**) membranes as a function of MW – the shaded area corresponds to the MWCO of the NF membranes (adapted from [Chian et al. 1975; Berg et al. 1997; Ducom and Cabassud 1999; Kiso et al. 2000; Kimura et al. 2003b, 2004; Nghiem 2005; Koyuncu et al. 2008]) with EDC: Endocrine Disrupting Chemicals, Pharm: Pharmaceuticals, VOC: Volatile Organic Carbon, DBP: Disinfection By-products and the membrane used specified in [ ]

However, this trend is not always obeyed and deviations occur in NF and RO (see Fig. 17.4). For NF this happens especially when the contaminant size is of the same order as the membrane pores (Kimura et al. 2004) (see Fig. 17.4a). The retention is affected by the occurrence of adsorption phenomena, charge interactions between the contaminant and the membrane material and the presence of a third component in solution such as NOM. Presence of ions such as monovalent and divalent salts also affects retention.

17.3.2 Adsorption

Many polymeric membranes adsorb xenobiotics. Adsorptions of pesticides, steroid hormones, volatile organic carbon (VOCs) and pharmaceuticals of up to 100% are obtained (Chian et al. 1975; Ducom and Cabassud 1999; Kiso et al. 2000; Nghiem et al. 2002, 2005a, 2008; Kimura et al. 2003b, 2004; Schäfer et al. 2003; Ng and Elimelech 2004; Yoon et al. 2004; Pronk et al. 2006b; Zhang et al. 2006; Koyuncu et al. 2008).

Adsorption plays an important role in membrane retention. Until saturation of the membrane sites is achieved the real retention is overestimated (Kimura et al. 2003a, b; Nghiem et al. 2004). While adsorption occurs, the apparent retention is often >90% but once the membrane becomes saturated this latter decreases drastically, sometimes to <10% (Kimura et al. 2003a, b; Hu et al. 2007b; Jin et al. 2007; McCallum et al. 2008). The permeate concentration shows a breakthrough curve similar to an AC process, with a slow increase in the initial phase until it reaches equilibrium translated in a constant permeate concentration with time (see Fig. 17.5a). This is accompanied by a feed concentration decrease until saturation occurs. In this later phase steric hindrance and electrostatic interactions as well as solution diffusion govern retention.

However contaminants such as SMX and CBZ do not show any breakthrough curve during filtration (see Fig. 17.5b) where adsorption on the membrane does not occur. Retention is mainly governed by size exclusion and charge interactions.

Besides giving apparent retention values at initial stages of filtration, adsorption also causes the accumulation of important amounts of xenobiotics on the membrane polymers which can be of significant risk in water treatment. Release of high concentrations of xenobiotics that are sorbed on the membrane may occur during the periodical cleaning procedure of the membranes and hence contaminate the water where it is discharged to (Nghiem and Schäfer 2006). Changes in solution pH causing the contaminant to dissociate and desorb can also occur, where both permeate and feed concentration become contaminated. It is therefore important to understand how adsorption occurs and what governs it. Adsorption on the membrane is highly dependent on the membrane material used (Kiso et al. 2000; Kimura et al. 2003a), the contaminant and their properties. The solution chemistry, such as pH and ionic strength, also affects adsorption on the membranes.

When comparing adsorption of SMX, estrone, BPA, fluoranthene and CBZ the latter four show much higher adsorptions on NF and RO membranes at neutral pH (Yoon et al. 2004, 2006; Comerton et al. 2007).

Since SMX and the membrane are both negatively charged at neutral pH, charge repulsion occurs and no adsorption is obtained. SMX is also more hydrophilic compared to other contaminants so sorptive interactions are not favoured (Nghiem et al. 2005b). As a general trend, the more hydrophobic the compound is the more it will adsorb on the membrane (Kiso et al. 2000; Yoon et al. 2004;

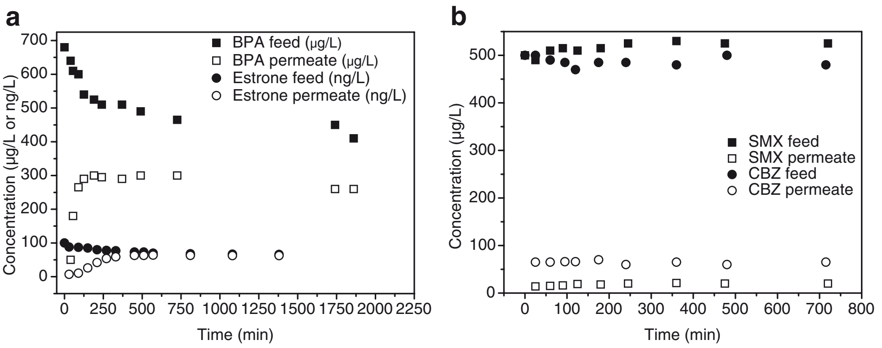


Fig. 17.5 BPA, estrone (**a**), SMX and CBZ (**b**) feed and permeate concentrations progress with time in NF (a and b adapted from (Nghiem et al. 2005a; Jin et al. 2007) and (Nghiem et al. 2005b) respectively)

Nghiem et al. 2005a; 2006; Yoon et al. 2006, 2007; Comerton et al. 2007) since this requires less free energy compared to forming a "cavity" in the water phase (Goss and Schwarzenbach 2003).

It is argued that sorption interactions between the membrane and trace contaminants occur through H-bonding capacity which is lost for some contaminants when they dissociate (e.g. BPA). When SMX dissociates it does not lose its full H-bonding capacity due to $–SO_2$, $–NH_2$, –N, –O and the benzene groups (Table 17.1). However no adsorption occurs for SMX. Charge repulsion and hydrophilicity overcome the H-bonding capacity and SMX does not adsorb when compared to estrone for example (Koyuncu et al. 2008). Adsorption between the membrane and SMX could occur at low pH, when the compound is neutral and charge repulsion does not take place. However, SMX adsorption is negligible for a membrane of the same polymer material (Nghiem et al. 2006). It is striking that compared to other bipolar molecules, SMX although capable does not form H-bonding with the membrane material. Being highly hydrophilic SMX does not need to bind with a hydrophobic membrane to be stable in solution.

CBZ adsorbs less when compared to estrone and BPA (Comerton et al. 2007). Although estrone and CBZ are both bipolar and possess =O groups, estrone adsorbs more. CBZ is neutral so charge repulsion does not play any role. On the other hand, as SMX, CBZ is more hydrophilic which might explain the lower interaction with the membrane (Nghiem et al. 2005b).

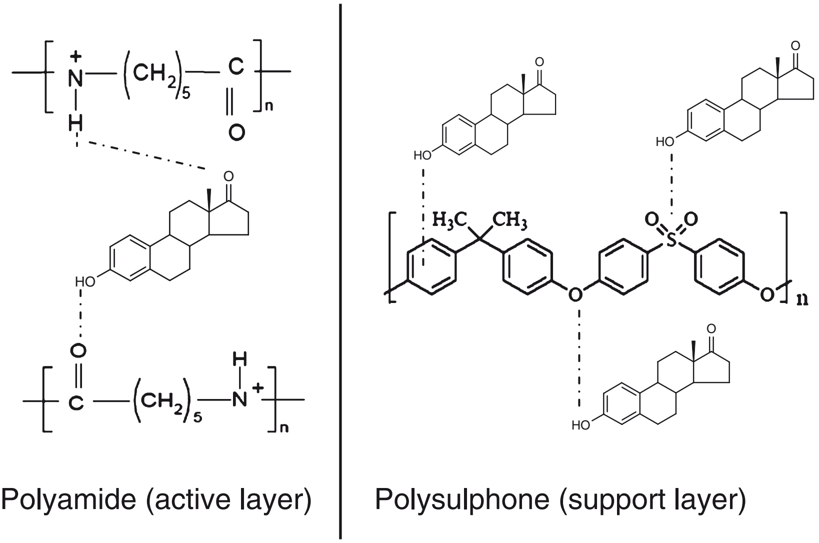
Fluoranthene readily adsorbs on the membrane when compared to estradiol (Yoon et al. 2004) although it does not possess any strong H-bonding groups. However, fluoranthene is the most hydrophobic of the studied contaminants (Log K_{ow} of 5.2 in Table 17.1) and adsorbs therefore on the membrane showing the influence of hydrophobic interactions on adsorption (Nghiem and Coleman 2008). This was also shown in the study by Chang et al. (2003) where high adsorption of estrone is obtained on a polypropylene membrane. Since this material is not able to form H-bonds, hydrophobicity explains the strong adsorption.

Estrone and BPA have similar size, Log K_{ow} and pK_a (Table 17.1) and both readily adsorb on the membrane although estrone has higher adsorption. This adsorption causes lower retentions than expected for membranes with smaller pores than the compound (Kimura et al. 2003b) due to diffusion of the xenobiotic through the membrane. The main difference between estrone and BPA is in their molecular structure. Estrone and BPA are bipolar, although estrone has one =O, one benzene ring and one –OH and BPA has only two –OH and two benzene rings. The =O group forms stronger H-bonds than the –OH group explaining the higher adsorption of estrone compared to BPA. This was showed by Neale et al. (2008) when studying the interaction between hormones and organic matter. Estrone and progesterone bind more than estradiol and testosterone due to their =O groups in the molecule which are very strong H-acceptors.

Commercial membranes are usually thin film composite membranes (TFC) with a very thin active layer and a support layer made of a different material. The active layer is the selective layer with pores in the nm level and the support layer with wider pores does not give any resistance to flux. Most commercial membranes have a polyamide active layer and a polysulphone support layer although cellulose acetate active layers are also found. No comprehensive study has been made on what material adsorption occurs onto. According to McCallum et al. (2008) adsorption of estradiol occurrs mainly in the polysulphone layer compared to the polyamide layer. When looking at Fig. 17.6 one can see that H-bonding between the bipolar estradiol molecule can be formed in both layers. A high adsorptive interaction between BPA, another bipolar contaminant, was also noticed by Lyko et al. (2005) with a polyethersulphone membrane. Williams et al. (1999) on the other hand obtained a higher adsorption of organic pollutants such as 2-chlorophenol on the polyamide layer when compared to the polysulphone layer showing that interactions are compound and membrane material specific.

Operational conditions such as flow and pressure can also affect xenobiotics adsorption. When comparing batch adsorption (membrane exposed to xenobiotic without pressure) with adsorption obtained in pressurised experiments, higher adsorption and lower extraction is obtained in the latter showing adsorption occurs either inside the pores (Kimura et al. 2003a; Plakas et al. 2006) or is enhanced by pressure.

Metals, ions and saccharides retentions tend to increase with pressure in NF and RO, for example uranium, magnesium and raffinose (Seidel et al. 2001; de Pinho et al. 2002; Bowen and Welfoot 2005; Favre-Reguillon et al. 2008), while the opposite is noticed for some xenobiotics and organic molecules, for example with sucrose (Geraldes et al. 2002), hormones (Nghiem et al. 2004; Weber et al. 2004), pesticides (Berg et al. 1997; Xu et al. 2005), VOCs (Ducom and Cabassud 1999), EDCs (Gallenkemper et al. 2003) and pharmaceuticals (Xu et al. 2005). This phenomenon has not been well explained, but it is thought to be related with the adsorptive interactions that occur between the contaminants and the membrane that can lead to diffusion.



Polyamide (active layer)

Polysulphone (support layer)

Fig. 17.6 H-bonding between xenobiotics and polyamide and polysulphone membranes

17.3.3 Charge Repulsion

The surface charge of commercial membranes becomes more negative with increase of pH (Elimelech et al. 1994; Childress and Elimelech 1996; Schäfer et al. 2003; Nghiem et al. 2005b; Hu et al. 2007b). Xenobiotics that dissociate, do so at the pH corresponding to their pK_a (e.g. estrone at pH > 10.3). When this occurs, charge repulsion between the membrane surface charge and the dissociated compound occur enhancing the retention of the xenobiotic (Van der Bruggen et al. 1999; Kimura et al. 2003a, b; Nghiem et al. 2005a, b, 2006; Xu et al. 2005, 2006; McCallum et al. 2008). This effect is especially pronounced with molecules smaller than the pore size of the membrane. For example, Berg et al. (1997) obtained an increase in the pesticide mecoprop rejection from 10–90% when increasing the pH from 3 to 7. Solution pH can also affect pore size due to repulsion of negatively charged groups on the membrane polymer or due to membrane structural changes which in turn affect the rejection of xenobiotics (Berg et al. 1997; Ahmad et al. 2008).

CBZ retention does not vary much with pH as can be seen in Fig. 17.7. This compound is neutral and governed by steric interactions only (Nghiem et al. 2005b). In the previous section it was shown that this compound does not adsorb. SMX which practically does not adsorb either on the other hand changes from neutral to negatively charged at pH 5.6. Retention increases from 20% to 100% with increase of pH due to charge repulsion between the membrane and the compound (see Fig. 17.7). Although CBZ is smaller, when these two compounds are both neutral (pH < 5.6) SMX is significantly less retained. The authors explained this is due to differences in dipole moment where a higher dipole moment for the SMX

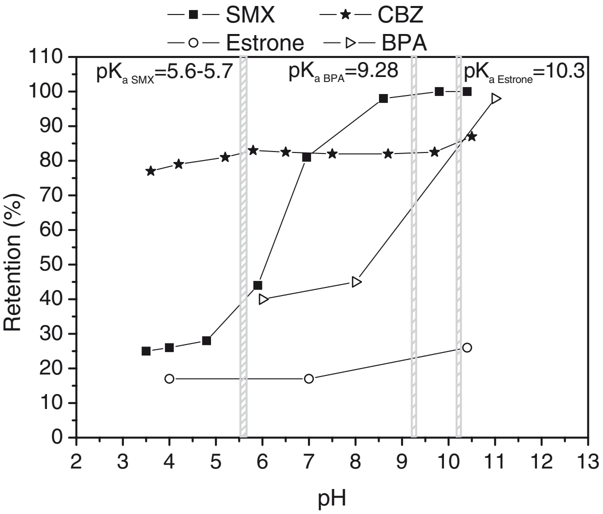


Fig. 17.7 SMX, estrone, BPA and CBZ retention as a function of pH (adapted from [Nghiem et al. 2005a, b, 2008; Hu et al. 2007b])

causes a lower retention, as argued by other authors for different compounds (Chian et al. 1975; Van der Bruggen et al. 1998, 1999; Gallenkemper et al. 2003; Nghiem et al. 2005b, 2006; Yoon et al. 2006). Molecules with high dipole moment are directed towards the pore with the side of the dipole with opposite charge closer to the membrane pore, entering more easily into the membrane (Chian et al. 1975). Kimura et al. (2004) however found that a higher dipole moment enhances retention when a cellulose acetate membrane is used instead of a polyamide membrane as Van der Bruggen et al. (1999) used in their study. Retention of polar and non-polar compounds is therefore affected by the membrane material used and no generalised trend can be obtained at present.

Although estrone is also negatively charged at high pH an opposite trend compared to SMX was obtained by Schäfer et al. (2003). When estrone dissociates at higher pH, retention decreases dramatically from >90% to 50%. Neutral estrone adsorbs on the membrane and gives an apparent high rejection. At higher pH when the molecule dissociates, charge repulsion occurs, decreasing adsorption and consequently retention. These results with estrone seem to contradict what Hu et al. (2007b) obtained, where estrone retention increases from 15% to 25% with increase of pH once the membrane is saturated in estrone (see Fig. 17.7). This is caused by charge repulsion between the membrane and estrone. In the latter case the membrane was saturated with estrone which did not occur in the study by Schäfer et al. (2003). Another possible explanation for this discrepancy is the different membranes used. Although both polyamide they can have different properties which are propriety of the manufacturer.

Nghiem et al. (2005a) showed an increase of BPA retention with pH (see Fig. 17.7) following the same trend as SMX (Nghiem et al. 2005b) and estrone (Hu et al. 2007b). When BPA dissociates at high pH it loses its H-bonding capacity, which only remains through the benzene ring, a weak H-acceptor. No adsorption is therefore expected to occur and retention increases due to charge repulsion.

Although most studies are focused on xenobiotics that become negatively charged and are repelled by the membrane, Heijman et al. (2007) and Pronk et al. (2006b) showed that attraction between the negative membrane and positively charged xenobiotics translates into lower retentions. However Radjenovic et al. (2008) obtained rejections >90% for positively charged pharmaceuticals in a Spanish drinking water treatment plant.

The increase of ionic strength in solution decreases membrane rejection of charged compounds due to charge shielding between the membrane and the contaminant (Seidel et al. 2001; Favre-Reguillon et al. 2003, 2008; Nghiem et al. 2006), with calcium ions shielding more effectively than sodium ions (Nghiem et al. 2006). Zhang et al. (2006) also showed a decrease in BPA rejection with increase of ionic strength due to swelling of the membrane pores or due to a decrease in the BPA hydrodynamic radius.

As with charged organic xenobiotics metals and heavy metals are mainly removed through the Donnan exclusion mechanism where the metal ion with the same charge as the membrane has a retention higher than 80% (Raff and Wilken

1999; Favre-Reguillon et al. 2003) due to charge repulsion (Raff and Wilken 1999; Oh et al. 2000; Seidel et al. 2001; Choo et al. 2002; Favre-Reguillon et al. 2008). Metal speciation study is therefore important to understand the rejection mechanisms not only due to different charges the metal species carry but also due to different species the metal can form for example with carbonates and NOM, which affects its size and therefore its retention.

While many studies on the retention of xenobiotics by NF/RO exist, mechanisms are to date not fully understood and hence it is difficult to predict the removal of a particular xenobiotic correctly. The presence of another compound in water renders this prediction even more difficult due to several types of interactions that take place.

17.3.4 Solute–Solute Interactions and Fouling

Although MW is still a good guidance to predict retention by the membrane, the solution characteristics where the contaminant is found in, such as presence of NOM, can affect the retention and overcome the size exclusion prediction.

17.3.4.1 Solute–Solute Interaction with Retained Organics Increases Xenobiotics Retention

When NOM is present in solution enhanced retention is generally obtained for xenobiotics (Agbekodo et al. 1996; Devitt et al. 1998; Nghiem et al. 2004, 2005a; Xu et al. 2005; Jin et al. 2007; Koyuncu et al. 2008; Radjenovic et al. 2008) due to partitioning of the contaminant into the retained NOM (Plakas et al. 2006; Pronk et al. 2006b). Agbekodo et al. (1996) showed that increasing organic carbon concentration from 2 to 2.8 mg/L increases pesticide removal from 67% to 90%.

17.3.4.2 Absence of Solute–Solute Interaction of Xenobiotics with Retained Organics does not Affect Xenobiotic Retention

Certain types of NOM, for example surfactants, are found not to affect xenobiotics retention (Berg et al. 1997; Nghiem et al. 2004; Jin et al. 2007), showing that the nature of NOM plays a fundamental role in NOM-contaminant interaction and consequent retention by the membrane. According to Neale et al. (2008) estradiol bounds less to surfactants because partitioning is expected to occur through weak H-bonding with the hydrophilic surfactant head in contrast with other types of NOM, such as humic acid, which form stronger H-bonding.

17.3.4.3 Membrane Fouling Increases Xenobiotics Retention

Fouling by NOM modifies the membrane surface and pore properties and affects the retention of small compounds (Plakas et al. 2006; Xu et al. 2006) especially for NF membranes when compared to RO (Comerton et al. 2008). NOM can block the membrane pores or change the membrane surface properties enhancing contaminant removal by steric exclusion and charge repulsion (Pronk et al. 2006b; Heijman et al. 2007; Jin et al. 2007; Kosutic et al. 2007; Nghiem and Hawkes 2007; Comerton et al. 2008; McCallum et al. 2008; Nghiem and Coleman 2008; Nghiem et al. 2008).

17.3.4.4 Membrane Fouling Decreases Xenobiotics Retention

A decrease in xenobiotics retention as a consequence of fouling can also occur. NOM adsorption and increase in membrane negative surface charge increases the MWCO of the membrane due to charge repulsion between the functional groups on the membrane (Xu et al. 2006) resulting in lower rejection of ionic solutes.

Colloidal fouling also causes a decrease in xenobiotics retention by NF and RO membranes (Ng and Elimelech 2004; Nghiem and Coleman 2008). Due to the cake formed on the membrane surface, back diffusion to the feed is hindered which causes accumulation on the membrane surface and consequent diffusion through the membrane polymer (Agenson and Urase 2007; Nghiem and Hawkes 2007; Nghiem et al. 2008).

Other types of foulant decrease the membrane surface charge when adsorbed, decreasing the repulsion between the membrane and the xenobiotic (Heijman et al. 2007; Nghiem and Hawkes 2007).

17.3.4.5 Membrane Fouling Affects Xenobiotics Adsorption

When NOM is present two main trends are found in the xenobiotic adsorption mechanism on membranes. Higher adsorption of the contaminant is obtained, possibly on both membrane and NOM layer that is formed on the membrane surface (Agbekodo et al. 1996; Nghiem et al. 2002; Xu et al. 2006; Hu et al. 2007b; Jin et al. 2007). In the case of hydrophobic HA presence for example, it renders the membrane more hydrophobic, enhancing estrone adsorption (Hu et al. 2007b; Jin et al. 2007). Jin et al. (2007) found that estrone interaction with NOM depends on the NOM specific functional groups, such as the presence of phenolic groups, which enhance estrone retention by partitioning into the NOM, but do not seem to readily affect estrone adsorption on the membrane.

On the other hand, a decrease in xenobiotics adsorption also occurs when there is competition between the NOM and the contaminant for adsorbing sites (Yoon et al. 2004, 2006; Plakas et al. 2006; Zhang et al. 2006; McCallum et al. 2008; Nghiem and Coleman 2008; Nghiem et al. 2008). Competition for adsorption between different xenobiotics also take place (Kiso et al. 2000; Plakas et al. 2006) decreasing the retention when compared to a single xenobiotic solution.

Complexity of natural waters renders the removal prediction of xenobiotics difficult due to all the interactions that take place between the xenobiotic, the compounds in water and the membrane. Removal mechanisms are to date poorly understood.

Studies on the removal of xenobiotics by membranes not involving pressure driven processes are scarcer because water treatment applications are currently dominated by pressure driven processes. From the studies presented next it can be seen though that membrane processes share some of the mechanisms of xenobiotics removal such as adsorption followed by diffusion through the membrane material amongst others. They depend on the contaminant chemical characteristics, for example hydrophobicity.

17.4 Electrodialysis

Ions or charged molecules can be removed by ED where an electrical potential difference acts as the driving force for separation. Uncharged compounds are unaffected and can be separated from charged compounds. Electrically charged membranes (cation-exchange membranes allow the passage of cations and anion-exchange membranes allow the passage of anions (Mulder 1996)) are alternately stacked between the positive electrode (anode) and negative electrode (cathode). Cations migrate to the cathode and anions migrate to the anode (Strathmann 2004). Two phases are obtained: the diluate which is purified and free from charged solutes and the concentrate where the charged solutes migrate to and concentrate.

ED studies have mainly focused on wastewater treatment of metals and heavy metals from industrial wastewaters (Marder et al. 2004; Lambert et al. 2006). In general, high removals of metals are achieved by this process although membrane type affects metal removal (Green et al. 2001; Van der Bruggen et al. 2003; Banasiak et al. 2007; Turek et al. 2007; Banasiak and Schäfer 2009). Metal speciation plays an important role. In some cases the pH of the solution has to be adjusted and/or controlled since it affects the metal solubility, charge and therefore the metal mobility (Green et al. 2001; Marder et al. 2003; Marder et al. 2004; Turek et al. 2007).

Less attention has been given on the application of ED for the removal of xenobiotics, despite the fact that some deprotonate at a certain pH and could be removed. The only studies are on the applicability of ED for salts recovery from a urine solution containing xenobiotics (Escher et al. 2006; Pronk et al. 2006a). Although high removal of 17α-ethinylestradiol is obtained (Escher et al. 2006), Pronk et al. (2006a) showed that xenobiotics such as CBZ and propranolol readily adsorb on the membranes, where electrostatic, size exclusion and hydrophobic interactions play a role in the adsorption behaviour. More hydrophobic compounds seem to adsorb more. This adsorption governs the permeation of these contaminants through the ED membranes since both increase with time and breakthrough eventually occurs. Pronk et al. (2007) studied the application of ED followed by ozonation in a pilot scale for the production of a fertiliser from urine. Whilst the conductivity decreases substantially to almost 100% removal of salts, all xenobiotics are below detection limit with the exception of ibuprofen. Ibuprofen adsorbs on the membrane and, after saturation of the membrane sites, significant permeation occurs.

17.5 Pervaporation

In PV the permeate is removed as vapour from the feed stream in contact with a dense hydrophobic membrane due to a low vapour pressure on the permeate side.

This process was first applied in the removal study of VOCs. Most xenobiotics such as EDCs have low volatility, high MW and low water solubility when compared to VOCs. Although PV does not seem to be an appropriate treatment process it has been applied for the treatment of water containing trace amounts of xenobiotics. According to Higuchi et al. (2004) removal of trace amounts of EDCs is >90% and a function of the contaminant hydrophobicity. A high removal by more hydrophobic compounds was also obtained by other authors (Nguyen and Nobe 1987; Higuchi et al. 2002). Interactions between the contaminant and the membrane are crucial in the removal performance by PV (Nguyen and Nobe 1987).

However, due to the xenobiotics low vapour pressure and high MW when compared to VOCs, the driving force needs to be enhanced to increase removal rates (Higuchi et al. 2002; Urkiaga et al. 2002), translating into higher energy requirements.

Contrary to NF and RO, in PV the higher the interaction of the xenobiotic with the membrane the better, since the contaminant is to be removed on the permeate side. The more hydrophobic compounds permeate better, but in general xenobiotics have large MW and low vapour pressures, translating into a higher driving force, accompanied by energy costs.

17.6 Membrane Distillation

In a MD process two liquids at different temperatures are separated by a very hydrophobic microporous membrane. This temperature difference results in a vapour pressure gradient, the driving force for separation. Thus transport occurs by evaporation on the high-temperature side followed by transport of the vapour molecules through the membrane pores. Finally the molecule condenses on the permeate side which is either a liquid or a gas at a lower temperature (Mulder 1996; Couffin et al. 1998).

The application of MD to xenobiotic contaminated water is appealing since most xenobiotics have low vapour pressures and the solution they are found in can be concentrated, with pure water obtained on the permeate side. Wu et al. (1991)

studied the application of MD in the treatment of a taurine rich pharmaceutical wastewater effluent where the concentrate obtained is very rich in taurine (66% purity). Cartinella et al. (2006) studied the removal of natural steroid hormones using MD. Rejections of estrone and estradiol are >99.5% without having much affect on the water recovery. Solutions containing urine and humidity condensate with trace amounts of organic acids do not affect the performance either and rejections are maintained >99.5%. Zolotarev et al. (1994) studied the removal of heavy metals from wastewater and obtained a pure distillate of water and a heavy metal selectivity of 99.8% which only decreased to 99.7% when the feed metal concentration increased. MD can therefore be used to very high concentrations of metals without losing its selectivity. However, this is accompanied with a decrease in trans-membrane flux.

MD can also be used by applying vacuum on the permeate side (vacuum membrane distillation) to remove volatile xenobiotics from the feed solution. Couffin et al. (1998) and Banat et al. (1996) showed that MD can be used to remove halogenated VOCs and benzene (87% removal) from water, respectively.

17.7 Large Scale Applications

Despite the pessimistic picture previously painted in the efficiency of xenobiotics removal by membrane processes, large scale applications have shown very good results with high water quality obtained. These applications are motivated by the need to remove xenobiotics for water treatment where the water supply is contaminated, or for water recycling where wastewater is treated to a potable water standard. Increasing water pollution awareness combined with increased water demand and water scarcity is rapidly expanding the number of large scale plants. A number of such applications will be outlined here.

17.7.1 Méry sur Oise

The Méry-sur-Oise water purification plant in Paris, France, treats water for potable usage directly from the river Oise to 650,000 people with a daily maximum production of 340,000 m^3. The majority of the treated water produced (80%) originates from MF pre-treatment followed by NF treatment, while the remaining (20%) originates from conventional biological treatment. The NF area used is 340,000 m^2, corresponding to 9,120 modules of Dow Filmtec NF 200 membranes (polyamide on a polysulphone support and polypripazine as an ultrathin top layer). The choice of the membrane technology was due to its high removal of organic carbon and pesticides when compared to conventional processes (Ventresque et al. 2000; Cyna et al. 2002).

The Oise generally has very high concentrations of pesticides (e.g. >1.6 µg/L in May, June and August of 2007 (Sindicat des Eaux d'Ile de France 2007a)). The highest concentrations were measured for glyphosate and aminomethyll phosphon acid (AMPA) ranging from 0.2–0.9 µg/L. Removal of pesticides remains very high with single pesticide concentration lower than 0.1 µg/L and 0.5 µg/L for total pesticide concentration in the treated water. In 2007 the atrazine and desethylatrazine concentrations in treated water were always lower than the detection limit of 50 ng/L (Sindicat des Eaux d'Ile de France 2007b).

The total organic carbon (TOC) removal is also very high with a drinking water concentration of about 2 mg/L (2007). Disinfection by-products (DBP) such as trihalomethanes are removed in the process to concentrations lower than 90 µg/L. Metals such as aluminium have concentrations lower than 12 µg/L in the treated water (Sindicat des Eaux d'Ile de France 2007b).

17.7.2 NEWater

The NEWater facilities in Singapore are advanced water reclamation plants designed to produce a total of 75,000 m^3/day of water (Tortajada 2006) with MF followed by RO and UV disinfection. The water influent originates from a clarified secondary effluent with CASP. This treated water can be further reused as high grade industrial water (e.g. microelectronics industry) or for indirect potable reuse applications. For a typical input of 12 mg/L of TOC removals higher than 99% were achieved in 2000 (Seah et al. 2003). Sample analyses from 2000 to 2002 showed concentrations of pesticides in the treated water lower than 0.1 µg/L and of DBP lower than 75.9 µg/L (Singapore Public Utilities Board 2002).

17.7.3 Water Factory 21 (WF21)

WF21 in California, USA, was built to treat and purify wastewater from the Orange County District to drinking water standards. This treated water was then injected into the groundwater basin (Orange County Water District – Groundwater Authority 2002) that supplies drinking water to a population of more than 2 million people. Groundwater is protected from seawater intrusion by injecting up to 19,000 m^3/day of treated reclaimed water to be blended with deep-well water into coastal aquifers. A RO treatment with Hydranautics ESPA2 polyamide membranes was added to reduce salts and organics, with MF as a pre-treatment process.

DBP such as N-Nitrosodimethylamine (NDMA) were detected in several drinking water wells in California (California Department of Public Health 2006). The presence of this compound in the injected water from WF21 forced the interruption of the plant in 2000–2001, reducing water treatment by more than 85% (Mitch et al. 2003b). The levels of NDMA in the discharged water were higher than 20 ng/L (Mitch et al. 2003a; California Department of Public Health 2006). A UV treatment was subsequently installed to remove the NDMA. According to a study by Plumlee et al. (2008), the RO process in WF21 removes NDMA between 24% and 56%, depending on the sampling season. With the addition of UV treatment the overall removal increases up to 75%. As expected MF does not remove any of the NDMA. On the contrary, due to chlorination pre-treatment to avoid MF fouling the NDMA concentration increases in the MF influent.

Metals and heavy metals concentrations in 2003 were below 5 μg/L, organic carbon was below 0.7 mg/L and trihalomethanes were below 2.7 μg/L (Wilf and Hydranautics, a Nitto Denko Corporation 1998).

WF21 has stopped working since 2007 to be replaced by an improved and larger water purification plant (Groundwater Replenishment 2004; Orange County Water 2007).

17.7.4 Luggage Point Water Reclamation Plant

The Luggage Point Water Reclamation Plant (LPWRP) was built to convert effluent from a WWTP into high quality reclaimed water for industrial reuse (e.g. BP refinery cooling towers) with MF pre-treatment followed by BW30 RO membranes from Dow Filmtec (polyamide on polysulphone support). Its maximum production is 10,600 m^3/day (Al-Rifai et al. 2007).

According to a study by Al-Rifai (2008) in 2006 the MF process does not reject any of the studied xenobiotics. The removal of acidic pharmaceuticals (e.g. ibuprofen) by the RO membranes on the other hand is high and varies between 30% and 100% and increases with the increase of compounds log K_{ow} and pK_a. Rejection of neutral pharmaceuticals (e.g. CBZ) ranges from 63% to 100%. For EDCs (e.g. BPA) removal varies greatly between 0% and 100%. No relationship with the compounds characteristics was found for the latter two classes of compounds.

Other membrane plants applying NF and RO processes have reported good removal of xenobiotics to very low concentrations. In the Debden Road Plant UK, pesticide concentration is lower than 0.1 μg/L in the permeate (Gaid et al. 1998). According to Khan et al. (2004) RO shows the best results in removing hormones and pharmaceuticals compared to NF, UF and MF in a water recycling demonstration plant in Queensland, Australia.

Despite the high removal percentages of xenobiotics by NF/RO processes, some compounds are not readily removed and show high concentrations in the treated water (e.g. NDMA and BPA) meaning that removal by membrane processes is insufficient. Furthermore the concentrate stream obtained in these processes which is very rich in xenobiotics poses a disposal problem that needs to be addressed. Disposal of the washing solutions for both MF/UF and NF/RO processes can also present a problem since polymeric membranes are capable of adsorbing high rates of xenobiotics, which desorb under certain washing conditions such as backwashes and alkaline washes.

17.8 Conclusions

Xenobiotics removal by NF and RO has progressed to full scale applications in water and wastewater treatment with particular interest in water recycling applications. The key advantage of membrane filtration for xenobiotics removal is the fact that treatment is a physical process that does not result in unwanted by-products. Removal of many xenobiotics by membrane filtration is effective albeit compound and membrane specific. In fact, removal mechanisms for each process are governed by xenobiotics characteristics, membrane type, water matrix and solution chemistry (such as the presence of other xenobiotics or organics, pH and ionic strength) and operational parameters (such as pressure, feed flow rate). This makes removal prediction of specific compounds for a specific water difficult. Long term phenomena such as membrane fouling further affect xenobiotics retention which means that removal can vary with time as well as season. The underlying mechanisms for xenobiotics removal are size exclusion, adsorption followed by diffusion and charge repulsion. These mechanisms are currently not understood well enough to allow prediction of removal of xenobiotics. Different waters require a tailored process which requires individual design and pilot testing.

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Chapter 18
Membrane BioReactors: A Cost-Effective Solution to Enhance the Removal of Xenobiotics from Urban Wastewaters?

Francesco Fatone

Abstract Membrane bioreactor is no longer just a promising technology. Full scale applications in urban wastewater treatment plants are rapidly growing in number and in terms of treatment capacity. This modification of the conventional activated sludge process may enhance the removal of xenobiotics for two main reasons: (1) the effluent (permeate) is virtually free from suspended solids and associated pollutants; (2) there is a major flexibility for the operation of the biological process, which is distinguished from the sedimentation properties of the activated sludge. This chapter deals with the removal of xenobiotics from real urban wastewater showing and discussing a 10-year activity carried out in Italy on pilot, demonstration and full scale membrane bioreactors. Target xenobiotics were metals (As, Cd, Cr, Hg, Ni, Pb), industrial organic chemicals and products, such as PAHs, BTEXs, PCBs, PCDDs/PCDFs, etc. As far as metals are concerned, besides Cd and Hg, which were almost completely removed both in conventional and membrane systems, generally the enhanced biosorption and/or retention capability allowed the membrane bioreactor to be more effective than the conventional activated sludge systems in removal of Cr, Cu and Ni. High sludge age seemed to enhance the bioconversion of hydrophobic and partially recalcitrant substances such as dioxins, hexachlorobenzene and poly-chlorinated bi-phenyls. As for the power requirements of the membrane bioreactors, which still represent a bottleneck for the widespread urban application of the technology, full scale data demonstrated were close to sustainable values, especially when membrane filtration is coupled to energy-saving biological processes such as the intermittent and automatically controlled aeration. Moreover, although a significant decrease is being observed for investment costs, land cost still represents a real major driver for membrane bioreactors urban implementation.

F. Fatone
Department of Biotechnology, University of Verona, Strada Le Grazie 15,
Cà Vignal, I-37134, Verona-Italy
e-mail: francesco.fatone@univr.it

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18.1 Introduction

Although numerous questions still remain unanswered about the actual effects of trace xenobiotics discharge on aquatic life and human health (Schwarzenbach et al. 2006), many studies have been already carried out to explore the best available techniques (BATs) able to enhance the xenobiotics removal mechanism within urban wastewater treatment (Joss et al. 2005, 2008; Cirja et al. 2008). In particular, major attention has been paid to the techniques also able to upgrade the huge number of existing conventional activated sludge plants (CASPs), which were not originally designed for removal of xenobiotics. Among the BATs, membrane bioreactors may represent an option for activated sludge systems to enhance the xenobiotics removal mechanisms and efficiencies (Byrns 2001).

A number of studies discussed key treatment conditions, such as sludge retention time (SRT), biomass characteristics and concentration, temperature, pH value, all of which are important for the removal of micropollutants from wastewater (Clara et al. 2005; Cirja et al. 2008). In any case, the necessity to maintain good sludge sedimentation properties in conventional activated sludge properties (CASPs) limits the flexibility for the operation of the biological processes. Also, since the fraction of the xenobiotics (bio)sorbed to the mixed liquor suspended solids (MLSS) may be significant, a solid-free effluent might allow one to drastically reduce their discharge in the water bodies. Therefore, major flexibility in the operation of the biology and almost complete removal of suspended solids are two of the major aims to improve the activated sludge process for xenobiotics removal.

The Membrane BioReactor (MBR) achieves these two major goals. This, in fact, constitutes a modification of the CASP, where the final solid/liquid separation is performed by the membrane filtration (micro- or ultra-filtration) instead of the traditional secondary gravitational clarifier.

If, from one side, the membrane capital, operation and maintenance costs still represent a drawback for MBRs widespread application in urban wastewater treatment plants, from a practical viewpoint the advantages of these systems are nowadays almost well accepted and include features such as: compactness and small footprint; easy and reliable remote operation; stable high quality of the effluent in terms of suspended solids, turbidity, virus and pathogens, so to be suitable for reuse applications or as a high quality feed water source for Reverse Osmosis treatment (Chapman et al. 2003; Le-Clech et al. 2005).

Literature reports numerous MBR properties which may enhance xenobiotics removal (Cirja et al. 2008). In particular, the possibility to operate high SRTs seems to deserve major attention. This condition, in fact, may be essential for the removal and degradation of xenobiotics from wastewater. It allows for the enrichment of slowly growing bacteria and the establishment of a more diverse biocoenosis able to degrade a large number of xenobiotics. The possibility for genetic mutation and adaptation of microorganisms to assimilate persistent organic compounds increases at higher SRT (Cicek et al. 2001). Furthermore, some enzymatic activities increase proportionally to the higher specific surface area of MLSS, which is directly related to the floc-structure. The activated sludge composition varies both with the influent composition and operating conditions adapted to the wastewater treatment system (Chang and Judd 2003). This phenomenon can be attributed to improved mass-transfer conditions in the MBR favoured by smaller flocs and the presence of many free-living bacteria. The size of bacterial flocs contained in the activated sludge can be another factor causing the difference between CASP and MBR wastewater treatment processes (Evenblij 2006). The small size of microorganisms and the flocs surface implies short distances to be overcome for substrate diffusion into the flocs and this phenomenon may enhance xenobiotics biodegradation.

A controversial topic is the role of the fouling/cake layer with respect to its role on xenobiotics retention. Fouling is the general term given to the process by which a variety of species present in the water increase the membrane resistance, by adsorbing or depositing onto its surface, by sorpting onto the pore surfaces within the bulk membrane material (pore restriction) or by complete pore-blocking (Le-Clech et al. 2006). Membrane fouling in MBRs is one of the drawbacks which limits the MBRs application. This phenomenon, in fact, leads to frequent membrane replacements and cleaning procedures. In these systems membrane fouling is a result of the interaction between the membrane material and the components in the activated sludge bulk, including feed components, cells, microbial metabolites, such as extracellular polymeric substances (EPS), etc. However, an important, and rather unknown, point regarding the fouling/cake layer concerns its role in enhancing the xenobiotics retention.

Although MBRs were initially claimed to be a sort of “revolution” to enhance xenobiotics removal, and notwithstanding the numerous scientific papers concerning this topic, the actual advantages for the treatment of real urban wastewaters are still not quantified.

Taking into account this lack of knowledge, this chapter deals with a 10-year activity carried out by three Italian universities (University of Verona, University of Venice “Cà Foscari”, Marche Polytechnic University) which studied the advantages of MBR technology also in terms of xenobiotics removal from real urban wastewaters. The investigations ranged from pilot to full scale urban wastewater treatment plants (WWTPs) and focused on target xenobotics, mainly originated from local industrial production and/or selected on the basis of their actual occurrence in Italian urban wastewaters.

Besides the investigations of the effect of operating parameters such as the SRTs, the behaviour of the MBRs are compared with that of the parallel conventional activated sludge plants, operating alongside the membrane systems with same operating parameters. Finally, the operating costs of the full scale MBRs are discussed, so to globally evaluate the actual efficiency of MBRs for the treatment of real urban wastewater. In this way, costs and environmental benefits will allow the reader to estimate the industrial feasibility of MBRs for widespread urban wastewater treatment.

18.2 Xenobiotics in the Urban Water Cycle in Italy: The Lagoon of Venice as Precursor

The necessity to extend the focus of wastewater treatment, from traditional sanitary-environmental aims (Metcalf and Eddy 2003), to priority and hazardous micropollutants emerged in Italy more than a decade ago, in relation to the special measures necessary to protect the ecosystem and the environment of the Lagoon of Venice. This is, in fact, one of the most important wetlands of Europe and of the Mediterranean region and cohabits with one of the main industrial and productive areas in Italy, which is located at the border of the Lagoon (Carrer and Leardi 2006). Also, the high population density and commercial/productive activities in this area increase the potential risks for the environmental equilibrium of the lagoon ecosystem. Therefore, in Italy this area was actually a precursor to investigating and applying the technologies to safeguard the aquatic environment from xenobiotics discharge and accumulation. Therefore, the activity of the authors on MBRs started right on the border of the Lagoon of Venice in 1999. They installed and operated a pilot MBR in parallel with a large urban wastewater treatment plant, which also collects a remarkable fraction of industrial wastewater, mainly from local chemical and oil refining industries. Further to these investigations, Cecchi et al. (2003) claimed that MBRs would have been a must for the WWTPs discharging in the Lagoon of Venice. A few years later, in fact, the industrial area of Porto Marghera adopted the MBR technology to enhance the removal of micropolutants from industrial wastewater before the discharge into the Lagoon of Venice (Cattaneo et al. 2008). Then, over the following 10 years, the scale of the experiments increased from pilot to demonstration up to the full scale MBRs. (Fig. 18.1).

The plants were equipped with hollow fibre submerged membranes ZeeWeed®500 (GE Infrastructure) whose main characteristics are provided in Table 18.1.

Table 18.2 includes the main features of the plants shown in Fig. 18.1.

As for the treated sewage, the conventional pollutants demonstrated diverse ranges of concentration as shown in Table 18.3:

18.2.1 *Objectives of the Experiments and Main Operating Parameters*

18.2.1.1 Pilot 1

Generally, the operation of "Pilot 1" was aimed at finding out the suitability of MBRs to reach and overcome the strict standards proposed for discharge in the Lagoon of Venice. In this context, one of the main objectives for Pilot 1 was to

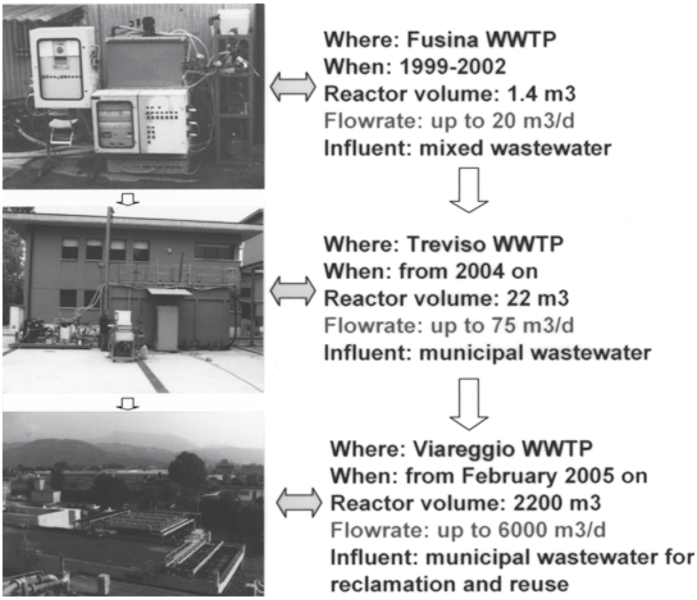

Fig. 18.1 Evolution of the main experimentations carried out in Italy by the author's research group

Table 18.1 Characteristics of the membrane used in the experimentations

Parameter	
Membrane type	Hollow-fibres
Nominal pore size	35 nm
Module configuration	Submerged
Material	PVDF
Membrane surface chemistry	Neutral and hydrophilic
Filtration mode	Vacuum filtration
Operating pH	5–9.5
Cleaning pH	2–11
Maximum hypochlorite exposure	1,000 ppm
Maximum operating temperature	40°C

define the effect of SRT. So, three experimental runs were carried out according to different sludge retention times (SRTs). Finally (Run 4), the bioreactor was hybridised by the addition of granular activated carbon (GAC – Norit CGRAN) to the suspended activated sludge (Table 18.4) as of 1% w/w, in order to study the effect on the sorption potential.

Table 18.2 Main characteristics of the MBRs

MBR	Reaction volume (m^3)	Membrane area (m^2)	Biological process
Pilot 1	1.4	21.6	SBR
Pilots 2[a]	22 (11 per line)	69.9 per line	Alternate Cycles and Predenitrification-Nitrification
Full scale	2,200	12,130	Alternate Cycles

[a] Pilot 2 is a container-based MBR with two separate parallel and continuously fed lines: one operating the predenitrification-nitrification scheme and the other the intermittent aeration automatically controlled

Table 18.3 Conventional pollutants in the urban raw wastewaters

MBR	TSS (mg/L)	COD (mg/L)	TN (mg/L)	TP (mg/L)
Pilot 1	150–400	250–500	35–50	3–6
Pilots 2	80–100	90–160	20–23	1–2
Full scale	200–310	550–650	45–55	4–8

Table 18.4 Operating parameters for the MBR-SBR experimentations

Parameter	Run 1	Run 2	Run 3	Run 4[a]
SRT (day)	11	~200	>1,000	>1,000
HRT (h)	14	14	14	14
MLSS (g/L)	4	9	18	16
MLVSS/MLSS (%)	80	63	53	53

[a] Addition of GAC (1% w/w) to the mixed liquor

18.2.1.2 Pilots 2

One of the main objectives of the research activity "Pilots 2" was to define the xenobiotics removal and behaviour in two continuously fed schemes for biological process: the conventional multi-zone predenitrification-nitrification and the intermittent aeration automatically controlled on the basis of dissolved oxygen (DO) and oxidation-reduction potential (ORP) (Battistoni and Chemitec 1999; Battistoni et al. 2003, 2006, 2007; Fatone et al. 2005, 2006, 2007, 2008a, Fatone 2007). This allowed us to study, on one side, the effect of dynamic and stable redox conditions in the MBRs and, on the other, the effects of an energy-saving strategy, such as the automatic control of the intermittent aeration (Charpentier et al. 1987; Battistoni et al. 2008), on micropollutants removal. Nine steady state experimental runs were carried out (Fatone et al. 2008a) according to the ranges of operating conditions given in Table 18.5.

18.2.1.3 Full Scale Urban MBR: Viareggio (Central Italy)

The Viareggio municipal WWTP was originally built more than 30 years ago and adopted primary sedimentation, Carousel tanks, and, before the disinfection contact

Table 18.5 Ranges of main operating conditions in the experimentations Pilots 2

	T	HRT	SRT	MLSS	MLVSS/MLSS
MBR	°C	h	d	kg/m^3	%
Pilots 2	11–23	8–11	22–48	5–9	62–70

tank, conventional secondary clarifiers for the final solid/liquid separation. Year by year, the system underwent hydraulic and mass overloading and became due for retrofitting. At first, the existing primary longitudinal clarifier was retrofitted, adopting the alternate cycles process (reaction volume 2,200 m^3). Later, the water shortage for the local floricultures suggested the plant undertake wastewater reuse as the most sustainable remedy. So, an ultrafiltration chamber was coupled to the alternating anoxic/oxic bioreactor in order to obtain the alternate cycles-membrane bioreactor (AC-MBR) (Battistoni et al. 2006; Fatone et al. 2007, 2008a).

In addition to the filtration chamber, adequate pretreatments (sieving and degritting) and an off-line equalization basin were built. After the pre-treatments, the off-line equalization volume is about one-fifth of the following bioreactor (450 m^3). Although this was possible because a parallel conventional treatment line could cope with the wet weather flows, the equalization volume is anyway rather small if compared to multi-zone MBRs that need larger buffer tanks (Gnirss et al. 2008).

The membrane tank is equipped with eight GE-Zenon cassettes disposed in four parallel and separately fed trains. Basically the UF section was engineered according to the usual practice for GE-Zenon hollow-fiber membranes, with coarse aeration at the bottom of the modules for the membrane scouring. To avoid possible accumulation of biological foam and floating materials, the UF chamber was provided with a continuous weir in the side opposite to the feeding.

At the moment the AC-MBR line operates at the side of the pre-existing conventional plant (Fig. 18.2).

As for the biology, the alternate cycle (AC) is an automatically controlled process, where the intermittent aeration of the continuously fed bioreactor is managed on the basis of on-line signals of DO and ORP, which are processed in real time by the control device. In particular, these signals, coming from consolidated and inexpensive probes, are able to indirectly detect the exhaustion of the ammonia, during the aerobic phases, and of the nitrates, during the anoxic phases. Therefore, the control device can establish the optimal alternation of the aerobic and anoxic phases with relation to the actual influent loadings and, thus, optimizing the energy consumed for the biological oxidation.

The plant was supervised for the first-year operation (Battistoni et al. 2006; Fatone et al. 2007) and the main operating parameters are shown in Table 18.6.

In this case study, the operating choices met the present trend of the full-scale MBRs to operate MLSS under 10 g/L (Daigger et al. 2004) and SRT was as low as necessary to match the nitrification potential of the plant with the influent nitrifiable loadings. This is necessary to avoid low α-factor (Germain et al. 2007) and consequent rise of the energy use for biological oxidation. Therefore, the operating strategy was addressed by the nitrogen removal which actually was the main focus

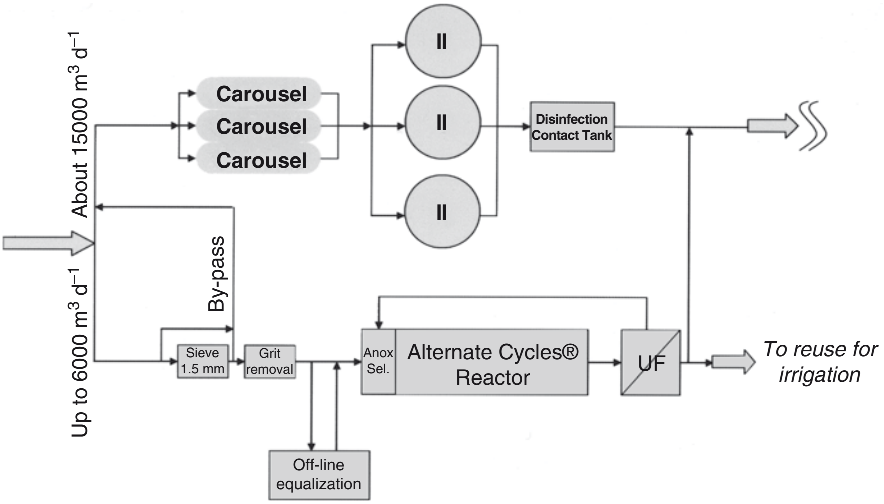

Fig. 18.2 Present flowscheme of the Viareggio municipal WWTP

Table 18.6 Ranges of main operating conditions in the full scale MBR

	T	HRT	SRT	MLSS$_{\text{ACtank}}$	MLVSS/MLSS
MBR	°C	h	d	kg/m^3	%
Full scale	13.8–26.5	9–11	13–21	6–8	62–77

of the plant operators. On the other hand, xenobiotics were monitored to study their behaviour and final fate.

18.3 Results and Discussion

18.3.1 Metals

As far as the metals removal in activated sludge systems is concerned, the biosorption phenomenon is crucial (Vegliò and Beolchini 1997), and the significant role of extracellular polymeric substances (EPS) has been reported in literature (Comte et al. 2006). Dissolved organic matter, primarily unbound extracellular polymeric substances (EPS) and sometimes referred to as the soluble microbial product (SMP), may encourage solubilization through chelating with the metals (Holakoo et al. 2006). On the other hand, bound EPS may be expected to encourage accumulation of metals in the biomass by encouraging their attachment to the solid phase (Brown and Lester 1979; 1982). Thus, the distribution of EPS between the bound and unbound phases is likely to be crucial in determining metals removal and this in turn may be expected to be affected by the SRT.

At the same time, SMP are reported not to be completely retained in MBRs (Liang et al. 2007). As a result, MBRs have the potential to enhance the metals removal from wastewater for a number of reasons, but there is great uncertainty to quantify the actual advantages coming from this technology.

To date, many research papers have dealt with the treatment of wastewater containing high levels of metals (some milligrams per litre concentration), that could be representative for industrial wastewater from mining, metal refining or other industries. However, metals in urban wastewater are much less concentrated (micrograms to nanograms per litre) and may be found in many different chemical/physical forms (dissolved ions, labile and non-labile complexes, associated with the suspended particulate). Furthermore, large urban wastewater treatment plants are often used to treat also non-hazardous liquid wastes (e.g., municipal landfill leachate) which may constitute another source of heavy metals to be removed. Anyhow, the abundance of the heavy metals in the influent remains almost in concentrations much lower than the milligram per litre, but the heterogeneity of their physical-chemical form is very high.

As a result, estimating the real MBRs potential for metals removal in urban treatment systems becomes complicated. The urban raw wastewaters hereby analyzed showed contents of metals as follows: As, Hg, Pb, Cd were present in the range of 0.1–10 μg/L, while Cu, Ni, Cr were in the range 10–70 μg/L. Generally, the occurrence of metals followed the sequence: Hg ~ As < Pb < Ni < Cu < Cr < Fe < Zn < Al.

The authors studied the effect of SRT in the first experience (Pilot 1) and the metals removals are reported in Table 18.7 vs the values observed in the parallel full scale conventional WWTP (Fatone et al. 2008b).

Besides Cd and Hg, which were almost completely removed both in conventional and membrane system, generally the MBR was more effective than the conventional plant for Cr, Cu and Ni. These results are in good agreement with previous studies on biosorption phenomena (Battistoni et al. 1993; Comte et al. 2006) and may be explained as follows: Cd and Hg had high affinity with biomass or biomass-bound ligands, which can be well separated from the secondary liquid effluent through a conventional gravitational clarifier; Cr, Cu and Ni were bound also to the soluble ligands, which might undergo a better solid/liquid separation through membrane filtration. On the other hand, As was of major concern as already found by Innocenti et al. (2002) and Pb underwent similar removal in both the conventional and mem-

Table 18.7 Metals removal in the full scale CASP and in the parallel pilot MBR

	CASP – aver. one year (±var. coeff.)	MBR-Run 1	MBR – Run 2	MBR – Run 3	MBR – Run 4
As (%)	34 (±76)	29	37	33	35
Cd (%)	>90 (±10)	>90	>90	>90	>90
Cr (%)	60 (±52)	>95	>95	>95	>95
Cu (%)	55 (±42)	85	89	72	90
Hg (%)	>95 (±31)	>95	>95	>95	>95
Ni (%)	25 (±77)	40	46	66	64
Pb (%)	69 (±22.5)	58	63	50	70

brane-assisted treatment systems. As far as the operating parameters are concerned, in fact, the experimental results were not consistent with the expected ones: operating high sludge ages did not involve significant effects. In fact, switching from 10–15 to more than 200 days the removal performances were well comparable. From a practical point of view, these results indicate that high SRTs and MLSS may be not the correct strategies to reach the "heavy metals zero discharge" from such a municipal/industrial wastewater treatment. In fact, that practice involves significant increases of the power requirements for the biomass aeration (Germain et al. 2007) and seems to lead to insignificant enhancements of metals retention.

Furthermore, the final hybridization of the bioreactor by the addition of active carbon was not significantly effective, in contrast with the results found by Pirbazari et al. (1996) for treatment of landfill leachate. Therefore, basically the major role of the MBR was supposed to consist of the sieving effect on the metal complexes present into the bioreactor.

Considering the experimentations at larger scale, Pilots 2 (Fatone et al. 2006) and the full scale experience, allowed us to confirm that MBRs could enhance the removal of Cr, Cu and Ni, while Hg was effectively removed also by CASP. As expected, major problems were represented by As which demonstrated it was not prone to biosorption on the activated sludge. Finally, the influence of the different biological processes (intermittent aeration and conventional multi-zone DN scheme) was not significant.

18.3.2 Organic Xenobiotics: Focus on Industrial Chemicals and Products

The number of synthetic contaminants of possible toxicological concern is huge and among these, we decided to focus on industrial chemicals and products, which were directly studied in the investigations hereby discussed.

First of all the role of headworks (screening, grit and sand removal) has to be mentioned with relation to their influence on xenobiotics removal. This is because hydrophobic molecules, such as PAHs, can adhere to street particles (Lau and Stenstrom 2005; Villar et al. 2006) which are usually removed in the conventional headworks of a WWTP. Additionally, the role of the headworks cannot be ignored for volatile compounds such as BTEXs.

Since MBRs require adequate pre-treatments, in order to protect the membranes from accumulation of trash and fibre materials (Frechen et al. 2007), the role of headworks and pre-treatments were investigated in both full scale CASPs and MBRs. The results showed high variability of the pollutants associated with grit and sand, but the influence of the fine screens (punched holes with openings = 1 mm) and/or oversized grit removal sections were not significant.

As a matter of fact, the PAHs and BTEXs were removed in the headworks of both CASP and MBR in similar ranges. Table 18.8 reports the ranges of removal of CASP over five large Italian urban WWTPs analyzed by the authors.

Table 18.8 Removals of PAHs and BTEXs in conventional full scale urban WWTPs: role of the different treatment sections

	Headworks and primary treatments	Secondary treatments	Total
Removal of PAHs (%)	20–40	20–50	63–90
Removal of BTEXs (%)	40–60	10–50	60–99

Table 18.9 Removal of organic xenobiotics from urban wastewater in CASP and MBR

		In	CASP (Removal %)	MBR (Removal %)[a]
Mineral oils	mg/L	3–4	80–90	82–88
Greases	mg/L	0.1–1.1	80–85	82–99
Anionic surfactants (MBAS)	μg/L	3,400–6,200	85–95	89–97
Non-ionic surfactants (BIAS)	μg/L	1,082–2,050	50–60	75–85
ΣDi-chloro-phenols[b]	μg/L	<0.05	–	
Pentachlorophenol	μg/L	<0.05	–	
Organic halogenated solvents	μg/L	19–40	70–90	65–>99
ΣOrganic aromatic solvents	μg/L	15–30	90–>99	93–>99
Benzene	μg/L	<0.01–1.03	>99	>99
Toluene	μg/L	4–13	95–>99	>99
Xilene	μg/L	10–13	95–98	91–>99
Polycyclic aromatic hydrocarbons[c]	μg/L	0.1–2.0	95–97	75–>99
Dioxins	pgTE/L	1.1–15.1	>99	>99
Organo-chlorine pesticides	μg/L	<0.01	–	
Tri-butyl-tin	μg/L	<0.03	–	
Hexachlorobenzene	ng/L	26–32	81	94–97
Poly-chlorinated bi-phenyls	ng/L	4–8	95	>99

[a] Range over 4 experimental runs detailed in Table 18.4

[b] Sum of 2,4- 2,3- 2,5- 2,6- dichlorophenols

[c] Sum of benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenzo[a,h]anthracene, Indeno[1,2,3-c,d]pyrene

As far as the effect of SRTs is concerned, which was supposed to play a major role in enhancing the xenobiotic removal, the results from the investigation Pilot 1 are shown in Table 18.9.

One can observe that the performances of CASP and MBR were almost comparable.

Although the scale of the experimentation did not allow the finding of the volatilized fraction (which is considered relevant only for compounds with Henry constants comprised in the range 10^{-3}–10^{-2} [Joss et al. 2008]), measures of organic xenobiotics in the WAS allowed us to calculate the mass balances and find out the compounds sorbed and/or bioconverted, and to distinguish between apparent and actual removal (bioconversion). Except for dioxins, HCB and PCBs, whose biodegradation seemed to be significantly enhanced by high sludge age (hundreds of days), generally the other industrial xenobiotics did not seem to be highly SRT-dependent. This may demonstrate that the xenobiotics contents and characteristics in the

Table 18.10 Energy consumption in the Viareggio MBR and comparison to literature data (Judd 2006; Fatone et al. 2007; Montagnoli 2006)

Section	(kWh/m^3)	Potentiality	Membrane
Pumping and pretreatments	0.13	–	–
Alternate cycles process	0.13–0.15	–	–
Ultrafiltration section	0.16–0.25	–	–
Total EE requirement	0.42–0.53	6,000 m^3/day	Zenon
Brescia – Verziano	0.85	12,000 m^3/day	Zenon
Nordkanal – Kaarst	0.9	48,000 m^3/day	Zenon
Park Place US	1.1	700 m^3/day	Memcor
Knautnaundorf	1.3	430 m^3/day	Huber

analyzed urban wastewater were not sufficient to involve the enrichment of slowly growing bacteria and/or the establishment of a more diverse biocoenosis able to degrade a large number of xenobiotics. Moreover, the analysis on the waste activated sludge showed that most of the organics from Table 18.10 were under the detection limit both in the CASP and in the MBR, and demonstrated that the SRT of about 15 days was sufficient to achieve significant biodegradation.

Of course, this consideration cannot be applied to industrial wastewater treatment where the target xenobiotics are less numerous and their content is expected to be much higher, so to potentially allow for biomass speciation.

18.3.3 Upgrading of Full Scale CASPs by MBR Technology: Considerations on Costs and Power Requirements

MBRs investments costs are rapidly decreasing thanks to the continued technical improvements and the economies of scale deriving from a growing demand for membrane production (Judd 2006). Costs of both membranes and processes appear to have decreased exponentially over the past 10–15 years, with the whole life cost decreasing from \$ 400/m^2 to below \$ 50/m^2 in 2005 (Judd 2006), while recent data (source: www.MBR-Network.eu) reported investment costs of € 50–80/m^2. Cotè et al. (2004) reported that capital costs are 10–15% higher for MBRs in respect to CASP. Recent data from STOWA (in Evenblij 2006) reported that assuming SWF (Storm Weather Flow) = 4*DWF (Dry Weather Flow) the MBRs are convenient up to 50,000 PE. Finally, the cost of the Nordkanal MBR (Engelhardt and Linder 2006) was reported to be 21.5 Mil€ for 84,500 m^2 membrane area installed. However, the MBRs capital costs are still higher than the CASPs. In this scenario, the main driver for MBRs application still seems to be the land costs, while the high quality of the effluent, likely suitable for reuse with high quality standard, is an important added value. Moreover, the legislative evolution is still an unknown, but could be a fundamental driver for MBRs widespread implementation and, in this concern, the behaviour and fate of xenobiotics may play a major role in addressing the law-makers.

Whilst the investment feasibility may depend on several factors, the operation and maintenance (O&M) costs are still higher with respect to the CASP. Cotè et al. (2004) reported that in MBRs the O&M costs about \$ 0.1/m^3 compared to \$ 0.7/m^3 of the CASP and that the energy consumptions count for about 30%. Even adopting the more convenient submerged configuration, operating municipal MBRs still requires more energy than the conventional activated sludge plants.

In the Viareggio full scale MBR, the energy-saving policy was pursued by three main choices (Fatone et al. 2007): (1) the low aeration demand for membrane scouring, suggested by the membrane producer; (2) the choice of the AC technology, a biological process able to save up to 20–30% energy with respect to traditional multi-zone scheme; and (3) the plant operation according to MLSS as low as possible, which allows one to optimize the oxygen transfer to the biomass. Moreover, frequency regulators for pumps and blowers were installed along the treatment line. As a result, the energy consumptions were as reported in Table 18.10, where also literature values are reported for comparison.

18.4 Conclusions

Conventional activated sludge processes remove xenobiotics from urban wastewaters up to a limited extent which may be not suitable for sensitive aquatic environment and/or hazardous for human health. Except for the environmental conditions (T, pH, etc), the limited removal performances are mainly related to (1) the low operation flexibility of the operating parameters, restricted by the necessity to guarantee good sludge sedimentation properties, and (2) the non perfect final solid/liquid separation, which leads to discharge a fraction of sorbed xenobiotics with the secondary effluent. MBR technology modifies the conventional activated sludge process allowing one to improve, on one hand, the retention of sorbed contaminants and, on the other, the flexibility of the operation of the biological processes, so to potentially enhance their effectiveness. Also, several more practical advantages are achievable with MBRs, such as small plant footprint and compactness. Although membrane bioreactors are rapidly growing in number and in terms of scale, to date the benefits in terms of xenobiotics removal are not well quantified as far as the urban wastewater treatment is concerned. The results hereby discussed demonstrated that the MBRs may cover the gap which allow one to reach the strict environmental standards, such as those required for discharge in the Lagoon of Venice. In particular, as for the metals, with respect to the conventional activated sludge system, the membrane bioreactor enhanced the removal of Cr, Cu, Ni. On the other hand, Hg and Cd were effectively removed also in the conventional system followed by gravitational final secondary clarifiers. Major problems were found for the As removal, while the Pb underwent similar removals both in the conventional and in the membrane system. Operating high SRTs (up to >1,000 days) did not involve significant enhancement of the metals removals from mixed municipal/industrial wastewater. Also, high SRTs did not involve significant removal increase for the major part of the organic micropollutants detected in urban wastewater. Relevant effects were found with highly hydrophobic and partially recalcitrant compounds like PCB, HCB and dioxins whose bioconversion was also enhanced by high SRTs. As for the economics, capital MBR costs are still higher with respect to the CASP, but are rapidly decreasing. To date, land cost seems actually to be one of the main drivers for MBRs application. As for O&M and energy consumptions, recent full scale data reports specific values of 0.4–0.5 kWh/m^3, thanks to the coupling with an adequate biological process.

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Chapter 19
Removal of Xenobiotics from Wastewater in Sequencing Batch Reactors: Conventional and Two-Phase Configurations

M. Concetta Tomei, M. Cristina Annesini, and Andrew J. Daugulis

Abstract Sequencing Batch Reactors (SBRs), characterised by a large variety of potential operating conditions and high operational flexibility, are an effective technological solution to the treatment of xenobiotic compounds, while also being able to generate a versatile micro-organism culture able to develop metabolic pathways required in the degradation of such recalcitrant substances. The main limitation in the operation of SBRs is the high concentrations of xenobiotic substrates that the biomass can experience, leading to a significant reduction in kinetic performance that is often not acceptable in practical applications (i.e. industrial wastewater treatment). The effects of substrate inhibition can be mitigated by a two phase partitioning system that is able to optimize "substrate delivery" to the cells in order to keep the substrate concentration at a level high enough to have reaction rates suitable for application but not inhibitory and/or toxic for the biomass. Immiscible organic solvents or solid polymers can be utilized as partitioning phases. Combining the two phase system with SBRs is a promising area to be investigated as a possible strategy when xenobiotic removal has to be achieved in critical conditions characterized by very high influent substrate concentrations.

In this chapter the principles of operation and an overview of the existing and potential applications for conventional and two phase sequencing batch systems are presented. In addition, the results obtained for the application of both technological approaches to the case study of 4-nitrophenol removal are reported.

M.C. Tomei (✉)
Water Research Institute, C.N.R, Via Salaria km 29,300 C.P. 10, 00015,
Monterotondo Stazione (Rome), Italy
e-mail: tomei@irsa.cnr.it

M.C. Annesini
Department of Chemical Engineering Materials Environment, Sapienza University of Rome,
Via Eudossiana 18, 00184, Rome, Italy

A.J. Daugulis
Department of Chemical Engineering, Queen's University, Kingston Ontario, Canada, K7L 3N6

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19.1 Introduction

The conventional approach to the removal of xenobiotic compounds from industrial wastewater is via chemical–physical processes: adsorption, stripping, chemical oxidation. All these processes can offer high removal efficiencies, but the first two have the main disadvantage that they do not provide actual degradation of the compounds but only transfer them from a dilute to a concentrated stream to be ultimately treated or disposed of. On the other hand, chemical oxidation can produce intermediates characterised by a toxicity level similar to, or worse than, the original substance.

An alternative and promising approach is the application of biological treatments that are able in principle to attain complete mineralization of many compounds and at the same time are characterised by low capital and operating costs. Notwithstanding these advantages, biological processes can be extremely complex ecosystems and often difficult to operate due to the high sensitivity of micro-organisms to the reaction environment conditions. Biodegradation of chemical contaminants has been studied since the 1940s and the potential application of biological wastewater treatment plants for removal of toxic compounds has been proposed, but, at present, research activity is still required both in process and technology innovation in order to make biological industrial wastewater treatment truly competitive and applicable on a larger scale.

Steady state conditions usually assumed in designing conventional wastewater treatment plants are not always the best solution for xenobiotics removal; in fact, the capabilities of biomass in degrading new compounds are determined by the induction of the synthesis of specific enzymes able to metabolize the compounds and there is experimental evidence that the induction process is favoured by dynamic conditions that are typical of periodic systems. The Sequencing Batch Reactor (SBR), characterised by a large variety of operating conditions (easily obtainable by varying the times of the operating cycle) and high operation flexibility, appears to be a promising and suitable technological solution in order to obtain a versatile micro-organism culture able to develop metabolic pathways required in the degradation of recalcitrant substances (Ellis et al. 1996). Moreover, in the specific case of phenolic wastewater treatment, the suitability of SBRs has been investigated and proved effective. The main limitation of SBR operation is the high concentration of xenobiotic substrates that the biomass can experience, leading to a significant reduction in kinetic performance that is often not acceptable in practical applications (i.e. industrial wastewater treatment). The effects of substrate inhibition can be mitigated by a system that is able to optimize "substrate delivery" to the cells in order to keep the substrate concentration at a level high enough to have reaction rates suitable for application but not inhibitory and/or toxic for the biomass. To provide such balanced substrate delivery the use of two phase partitioning bioreactors (TPPBs) has been proposed; these systems are based on the use of a water-immiscible and biocompatible organic phase (an immiscible solvent or a polymeric material) in contact with an aqueous phase containing the micro-organisms. With this configuration, even if the bioreactor is operated with high xenobiotic loads, the micro-organisms are exposed to low levels that in the majority of the cases are sub-inhibitory and the amount of delivered substrate is always the optimal one because the transfer rate is dependent on the biodegradation kinetics.

Combining the two phase process with SBR technology is a promising area to be investigated as a possible strategy when xenobiotic removal has to be achieved in critical conditions characterized by very high influent substrate concentrations. One typical example is the “remediation of stored xenobiotics” that is the removal of toxic compounds stored in containers in large amounts deriving from industrial closures or of the stockpiling of substances no longer usable (Daugulis 2001).

19.2 Conventional Sequencing Batch Reactors (SBRs)

19.2.1 Operating Modes

In the last few years discontinuous sequential reactors have become popular as an innovative solution in applications to biological wastewater treatment. They can operate with suspended mixed cultures (SBR: *Sequencing Batch Reactor*) or with attached biomass where the micro-organisms are developed on biofilm supports (SBBR: *Sequencing Batch Biofilm Reactors*). In comparison to conventional activated sludge plants, characterized by a spatial operation sequence, SBRs are time oriented systems with work phases that are realized consecutively in the same process unit. This feature makes the SBR a typical non steady state system.

SBR applications to both urban and industrial wastewater, which is characterized by high qualitative and quantitative variations often difficult to predict, could be advantageous due to their easy adaptation to influent characteristics. In fact, problems in conventional continuous plants, usually designed as steady state systems, are often caused by unpredicted influent variations. The general tendency to prefer steady state operation is suggested by the common practice that the steady state conditions are necessary to maintain the effluent concentration constant and in the range of regulatory emission targets. To this end, flow equalization tanks are utilized but this practice may not be effective in the presence of substantial influent load variations.

In contrast, for controlled unsteady state systems operating cyclically on a time basis, the pronounced effect of variable operating conditions on the process kinetics and the high operation flexibility can minimize the impact associated with load variations (Irvine and Ketchum 1989). The amplitude and the frequency of the working cycle can be regulated depending on the process objectives (i.e. removal of specific compounds, enrichment of the culture, increase of sludge settleability) so this system, intrinsically operating in unsteady state conditions, is particularly effective in maintaining quasi-steady state performance on a long term basis.

The SBR potential of working with a wide range of operating conditions and control strategies is, for biological processes, a valuable tool to control the culture composition. In the specific case of xenobiotics removal, the dynamic conditions cause a selection pressure favourable to micro-organisms that are both more resistant to inhibition and able to develop specific metabolic pathways required for the degradation of biorefractory compounds (Ellis et al. 1996).

The conventional configuration of an SBR system consists of one or more tanks in series that, after the initial filling phase, are operated in discontinuous mode. The essential difference between an SBR and a conventional continuous-flow activated sludge system is that in each unit of the SBR system the series of operations (equalization, reaction, settling) is realized in a time rather than in space sequence.

The duration of the whole operation sequence (work cycle) is the reference parameter for the design of the system and can be related to the total volume of a conventional continuous-flow facility. The fraction of time devoted to a specific function in the SBR is equivalent to the volume of the corresponding unit in the continuous-flow system.

The work cycle for each tank in a typical SBR is divided into five time phases: Feed, Reaction, Settling, Draw, and Idle, which can be realized under various operating conditions depending on the treatment objectives. Figure 19.1 shows a typical scheme of operation and the possible alternatives for each work-phase.

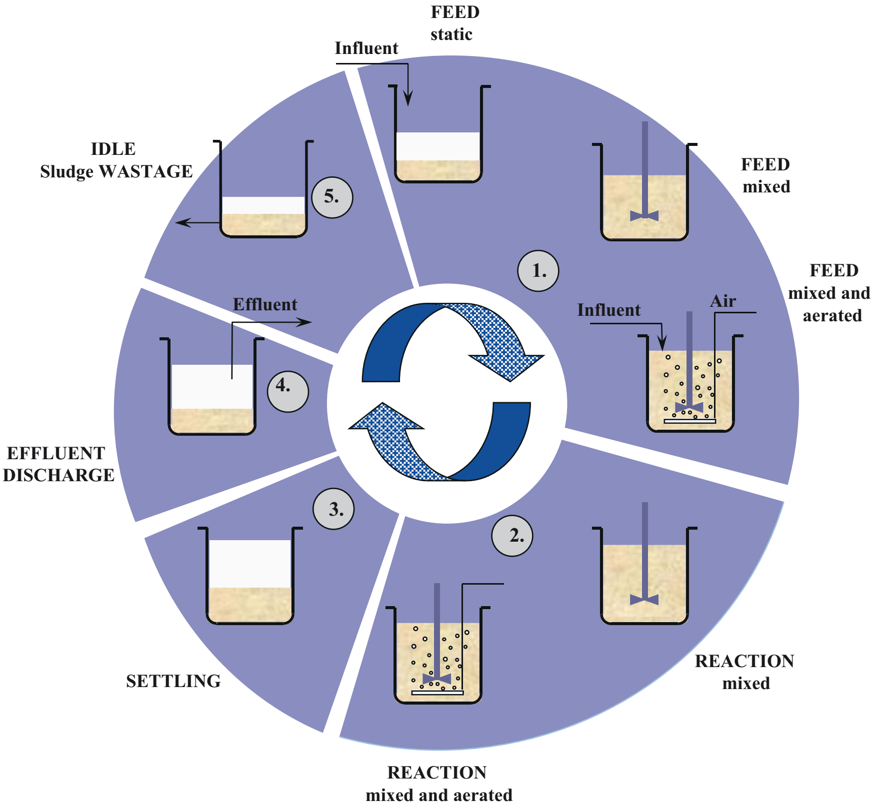

Fig. 19.1 SBR work cycle: phases and possible operating conditions

19.2.2 Advantages of SBRs

The notable advantage of SBR systems is the flexibility associated with working in time rather than in space that allow SBRs to replace conventional continuous-flow system from contact stabilization to extended aeration by properly planning tank volumes and aeration strategies.

The batch configuration allows flow equalization in the whole reactor volume thus avoiding hydraulic and/or organic load peaks. For the same reason the settling phase can be accomplished in favourable conditions without disturbances derived from underflow solid removal or effluent discharge. In addition, the settling area is the whole reactor area and therefore the applied solid flux is generally low.

The advantages of SBRs are strongly dependent on the efficiency and reliability of the instrumentation and control system. In fact, by appropriate control strategies it is possible to act on many variables such as duration and distribution of the work cycle, nutrient availability, mixing and aeration conditions in the different work phases. All of these possibilities extend the flexibility of the system allowing the system to "push and orientate" the microbial selection towards adaptation within the reaction environment. Moreover, of particular interest in the case of xenobiotics removal is also the possibility to easily modify the feed and reaction pattern in terms of length and aeration conditions. This allows optimization of the contact between biomass-xenobiotics and can address the inhibition and toxicity effects on the micro-organisms.

Finally the absence of recycle pumps gives a substantial energy saving considering that in continuous systems the recycle flow rate is of the same order of magnitude of the feed flow rate.

19.3 Two Phase Partitioning Bioreactors (TPPBs)

19.3.1 Two Phase Configuration: Principles and Operation

In the biological treatment of xenobiotic compounds undertaken in SBR reactors one of the critical aspects, essentially related to industrial wastewater, is the high xenobiotics concentration potentially present in the influent. This could generate substrate inhibition and/or toxicity phenomena with consequent serious reduction of the biomass activity. Therefore the challenge is to find a technological solution that will expose the biomass to sub-inhibitory concentrations when concentrated influent streams are treated. This goal can be attained with the optimization of "substrate delivery". High substrate loads, in the specific case of xenobiotics are dangerous for the biomass while, on the other hand, a too low substrate addition can reduce the process kinetics and generate starvation conditions with consequent activity loss of the biomass. In the TPPB configuration the system is operated with two phases, the aqueous one containing the microorganisms and an immiscible phase able to "store", or sequester, the xenobiotic compound(s). The immiscible phase is able to dissolve large amounts of the target compound(s) (due to the hydrophobic nature of most organic contaminants) which then partition into the aqueous phase at a concentration depending on the partition coefficient. The substrate concentration in the aqueous phase is the result of a delivery process completely driven by the cellular metabolic processes: in fact when the substrate is biodegraded in the aqueous phase, the thermodynamic equilibrium has to be restored in the system with consequent xenobiotic transfer from the organic phase to the water phase. In Fig. 19.2 a schematic representation of a TPPB is shown.

The same "substrate storage" effect can be obtained with solid polymers beads that have recently been proposed (Prpich and Daugulis 2005, 2006) as a partitioning phase, and have been shown to be an effective alternative to liquid organic solvents in TPPBs when mixed cultures are used. In previous studies (Prpich and Daugulis 2005; Daugulis and Boudreau 2008; Rehmann and Daugulis 2008a) solid polymer beads have shown partition capabilities similar to those of liquid solvents but, at the same time, have the significant advantage of being biocompatible with the biomass and non biodegradable. These characteristics allow operation with mixed cultures without altering the biomass composition. The reaction environment is always the optimal one in that the biomass is exposed to sub-inhibitory substrate concentrations and this can favour culture adaptation to new compounds. An important parameter to be preliminarily evaluated in the use of polymers in TPPBs is the substrate absorption/desorption rate that may significantly affect the process performance, since the structure of the polymer has to act via absorption and not adsorption in order to ensure the complete release of the compound in the aqueous phase.

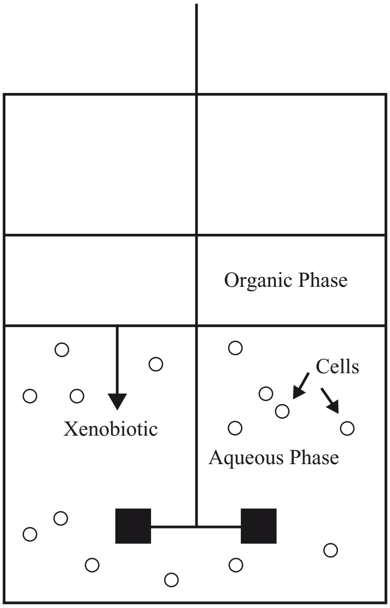

Fig. 19.2 Schematic representation of a TPPB

19.3.2 TPP Bioreactors Operating with Liquid Solvents

The performance of the two-liquid phase systems is critically dependent on the solvent employed, which has to be selected for each specific case; desirable properties for solvents to be tested in the screening phase include:

- Biocompatibility
- Non-biodegradability
- Favourable partition coefficient
- High selectivity
- Water immiscibility or low solubility
- Chemical and thermal stability
- Non-hazardous nature

Considering the wide spectrum of available organic solvents, the chemical–physical properties can be quite easily satisfied; more critical is the testing of biocompatibility and biodegradability. In particular, the solvent biocompatibility (to verify that the organic solvent does not have a negative effect on the biomass activity) is one of the key aspects to be determined experimentally.

In terms of biodegradability it is obviously desirable that the solvent is not utilized by the microorganisms. However, solvent biodegradation could be accepted if the biodegradation kinetics of the target compound is not affected by the parallel solvent biodegradation. This has been seen before in MacLeod and Daugulis (2003) who successfully employed a bioavailable solvent in a TPPB for the biodegradation of polycyclic aromatic hydrocarbons. TPPBs operating with liquid solvents were successfully applied in the removal of important classes of xenobiotics such as phenols, polycyclic aromatic hydrocarbons (PAHs), benzene toluene and xylene (BTX), etc. Table 19.1 summarizes a number of applications since 2001.

19.3.3 TPP Bioreactors Operating with Polymers

Although, as noted, it is possible to use a biodegradable solvent in a two-liquid phase TPPB, long term operation in an industrial setting (which would most certainly be conducted aseptically with mixed microbial populations) with a biodegradable solvent is problematic. Examples of TPPBs employing organic solvents and microbial consortia are rare due to the difficulty of identifying solvents that are non-biodegradable by all members of the microbial community. The choice of the organic phases has therefore essentially been restricted to a few relatively microbial resistant compounds such as silicone oil (Marcoux et al. 2000), ionic liquids (Baumann et al. 2005) or the branched alkane 2,2,4,4,6,8,8-heptamethylnonane (HMN) (Al Aalam 1993).

More recently solid polymers have been used to replace the second liquid phase in TPPBs (Amsden et al. 2003). It has been demonstrated that small organic compounds can partition between an aqueous medium and a variety of thermoplastic polymers

Table 19.1 Applications of TPPB systems for xenobiotics removal (Updated from Daugulis 2001)

Compound	Culture	Solvent	Reference
PAHs	*Sphingomonas aromaticivorans*	Dodecane	Janikowski et al. 2002
PAHs	*Mycobacterium sp.*	bis(2-ethylhexyl) sebacate	MacLeod and Daugulis 2003
Hexahydro-1,3,5-trinitro-1,3,5-s-triazine	*Enterobacter cloacae*	2-Undecanone	Pudge et al. 2003
Benzene, toluene, phenol	*Pseudomonas putida*	2-Undecanone	Hameda et al. 2004
Phenol	*Pseudomonas putida*	Ionic Liquids	Baumann et al. 2005
Phenanthrene	*Pseudomonas migulae/Chlorella sorokiniana*	Silicone Oil	Muñoz et al. 2005
Benzene	*Achromobacter xylosoxidans*	*n*-hexadecane	Nielsen et al. 2005
Toluene	*Achromobacter xylosoxidans*	*n*-hexadecane	Boudreau and Daugulis 2006
1,2-Dichloroethane	*Xanthobacter autotrophicus*	Sunflower Oil	Koutinas et al. 2006
Hexane	*Pseudomonas aeruginosa*	Silicone Oil	Muñoz et al. 2006
Biphenyl	*Burkholderia xenovorans*	bis(2-ethylhexyl) sebacate	Rehmann and Daugulis 2006
Indole	*Sporotrichum thermophile*	Soybean Oil	Katapodis et al. 2007
PCBs	*Burkholderia xenovorans*	Silicone Oil	Rehmann and Daugulis 2008b
PAHs	*Sphingomonas sp.*	Dodecane, Silicone Oil	Vandermeer and Daugulis, 2007
Phenanthrene	*Mycobacterium sp.*	Silicone Oil	Abdelhay et al. 2008
Dichloromethane	*Hyphomicrobium sp.*	Silicone Oil	Bailon et al. 2009
Pyrene	*Mycobacterium frederiksbergense*	Silicone Oil	Mahanty et al. 2008
Pinene	*Pseudomonas fluorescens*	Hexamethylnonane	Muñoz et al. 2008
4-Nitrophenol	Mixed culture	2-Undecanone	Tomei et al. 2008
Pentachlorophenol	*Sphingobium chlorophenolicum*	Dioctyl Sebacate	Zilouei et al. 2008
Toluene	*Acinetobacter sp.*	Silicone Oil	Watanabe et al. 2008

in an identical fashion as between aqueous medium and immiscible organic solvents, and that these polymers can therefore be used to replace organic solvents in TPPBs (Prpich and Daugulis 2004; Daugulis et al. 2003). Importantly, the partitioning between an aqueous phase and a thermoplastic polymer is via *absorption* (rather than the surface phenomenon of adsorption) and, like two-liquid phase partitioning, operates via thermodynamic equilibrium through the establishment of partition coefficients. Additionally, the polymeric phase can readily be moulded into any shape, size and thickness of interest, although to date cylindrical or spherical beads with diameters of between 2 and 5 mm have generally been employed. The significant operational advantages possessed by polymers over organic solvents are largely due to the polymers' resistance to microbial degradation and to their lack of cell toxicity.

Additionally, some organisms capable of degrading hydrophobic compounds can secrete biosurfactants to increase the availability of the hydrophobic substrate (Madigan et al. 2000), which, in liquid–liquid TPPBs, can result in emulsification of the organic phase causing considerable operational challenges (Guieysse et al. 2005). These difficulties do not occur in a solid–liquid TPPB (Morrish and Daugulis 2008). This inherent compatibility of polymers extends the range of possible biocatalysts that can be used in TPPBs, in particular allowing the use of widely mixed microbial consortia, which can be of importance for degrading persistent contaminants and mixtures of contaminants such as PAHs and polychlorinated biphenyls (PCBs), which generally require microbial consortia to achieve complete mineralization.

19.4 Fundamental Modelling

A general model for SBRs is reported in Table 19.2 where mass balances and kinetic equations are summarized for the conventional SBR and TPP-SBR. In the last case both organic solvent and polymer were considered as partitioning phase. The reference system is a biological CSTR (Completely Stirred Tank Reactor) where one substrate is degraded by aerobic micro-organisms.

A more detailed analysis of the model is reported elsewhere (Tomei et al. 2009) and only a few considerations of the kinetics and assumptions for mass-transfer modelling in the two-phase systems are reported here.

In the case of xenobiotics removal to model the substrate inhibited kinetics, the Haldane equation is generally utilized:

$$r_S = v\frac{C}{C + K_s + \frac{C^2}{K_I}} = k^{*}\cdot X\frac{C}{C + K_s + \frac{C^2}{K_I}} \tag{19.1}$$

where X and C are the biomass and substrate concentration, respectively. In order to have an equation with more representative parameters in relation to the process kinetics, the Haldane equation is rearranged in a different form:

$$r_S = k_{max}\cdot X(2+\beta)\frac{C/C^{*}}{1+\beta\left(C/C^{*}\right)+\left(C/C^{*}\right)^2} \tag{19.2}$$

In Eq. 19.2 $C^{*} = \sqrt{K_s \cdot K_I}$ is the substrate concentration where the maximum removal rate occurs, k_{max} is the maximum removal rate observed at C = C* and $\beta = \sqrt{K_I / K_s}$ is a parameter that accounts for the extent of the inhibitory effects (the smaller β the larger the removal rate reduction at high substrate concentration). The effect of β and C* on the kinetics is represented in Fig. 19.3 where the ratio $r_S/(X\cdot k_{max})$ is reported vs. the substrate concentration C: the two plots (a) and (b) display the effects of the parameters C* and β respectively. The procedure to derive Eq. 19.2 from Eq. 19.1 is reported in (Tomei and Annesini 2007).

Table 19.2 Fundamental modeling for conventional and two-phase SBRs

Mass balance – Aqueous phase	
$\frac{dV_w}{dt} = F_{in} - F_{out} - F_{ws}az$	Hydraulic
$\frac{d\left(V_w C_w\right)}{dt} = F_{in}C_{in} - F_{out}C_w - F_{ws}C_w - V_w r_s - N_{wo}$	Substrate
$\frac{d(V_w X)}{dt} = -F_{ws}\cdot X + r_X \cdot V_w$	Biomass
$\frac{d(V_w O_2)}{dt} = -r_{O_2}V_w + F_{in}O_{2,in} - F_{out}O_2 - F_{ws}O_2 + K_L a(O_2^* - O_2)V_w$	Oxygen
Mass balance – Organic solvent	
$N_{wo} = K_{wo}a\left(\frac{C_{org}}{P} - C_w\right)$	
$\frac{d}{dt}(V_{org}C_{org}) = -N_{wo}$	Substrate
Mass balance – Polymer phase	
$N_{wo} = V_w a D \left.\frac{\partial C_P}{\partial r}\right\|_{r=R}$	
$\frac{\partial C_P}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_P}{\partial r}\right)$	Substrate
Boundary conditions: $r = 0 \ \frac{\partial C_p}{\partial r} = 0 \ r = R \ C_P = P \cdot C_w$	
Kinetics	
Haldane Equation $r_S = -k^* X \frac{C_w}{C_w + K_s + \frac{C_w^2}{K_I}}$	

Symbols in table:
V = volume; F = flow rate; C = substrate concentration; X = biomass concentration, O_2 = oxygen concentration, a = specific surface referring to the water phase, K_L = mass transfer coefficient for oxygen, K_{wo} = mass transfer coefficient for substrate, N_{wo} = substrate transferred from the partitioning to the water phase, r = radial coordinate, R = polymer bead radius; P = partition coefficient; D = substrate diffusivity in the polymer phase; r_S = substrate degradation rate; r_X = biomass growth rate; K_s = saturation constant; K_I = inhibition constant; k* = kinetic parameter
Subscripts:
w = aqueous phase; out = outlet; in = inlet; ws = wastage; org = organic solvent phase; P = polymer phase

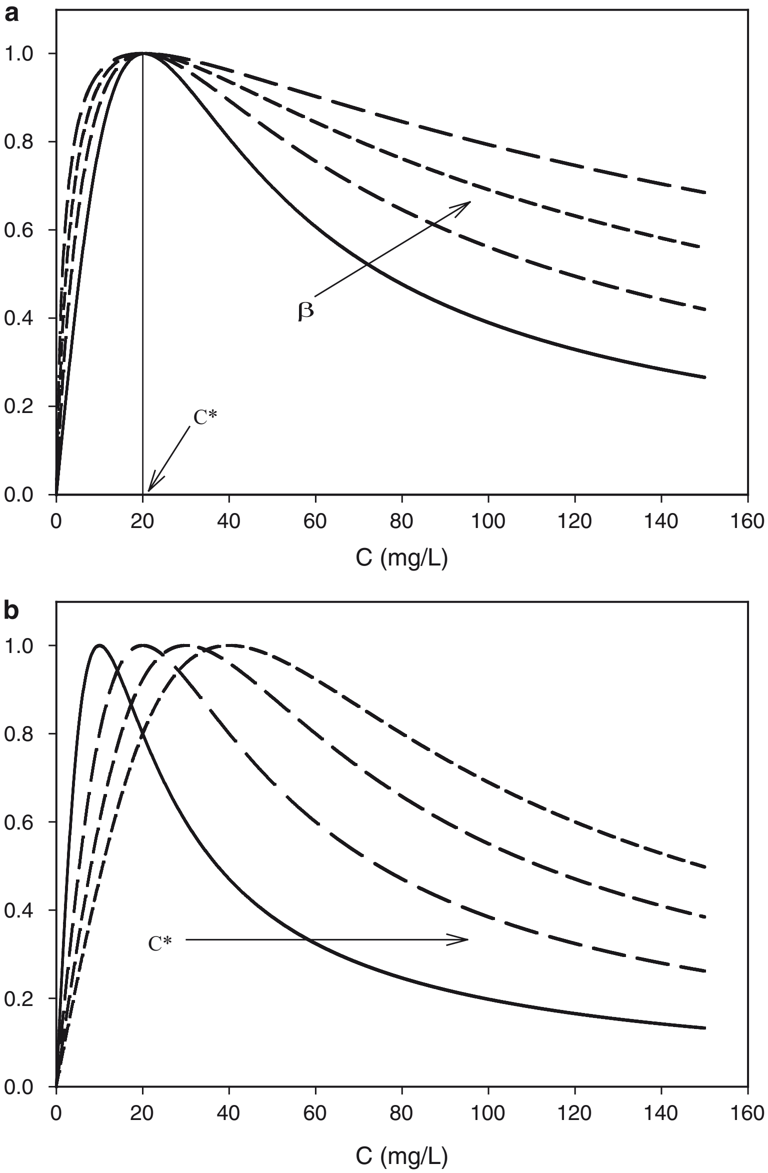

Fig. 19.3 Effect of β and C* on substrate removal kinetics: (**a**) fixed C* = 20 mg/L, increasing β (**b**) fixed β = 0, increasing C*

In the two phase system operating with solvent, depending on the operating conditions (i.e. degree of mixing, characteristics of the micro-organisms, temperature etc.), the formation of a biofilm at the water–solvent interface, foaming, and cell entrapment in the organic layer can be observed. All these phenomena reduce the fraction of the biomass actively participating in the biodegradation process. It is therefore advisable to take this into account in modelling the process. According to Cruickshank et al. (2000), the simplest way is to reduce the biomass growth rate with an “entrainment coefficient” k_e In consequence r_S is modified as:

$$r_s = \frac{\mu(1 - k_e)}{Y} \cdot X \tag{19.3}$$

where μ is the biomass growth rate and Y the growth yield coefficient.

Moreover, in the liquid–liquid system a mean substrate concentration in the organic phase is assumed and the substrate transfer rate is described by an overall mass transfer coefficient K_{wo}. According to K_{wo} values obtained for similar systems, it can be concluded that the overall kinetics is controlled by the biological reaction rate and aqueous and organic phases are at thermodynamic equilibrium conditions.

As for the mass transfer in the polymer-water system the resistance in the external liquid phase is neglected while a radial distribution of the substrate concentration and unsteady diffusion inside the polymer beads are considered. The characteristic time for intraparticle diffusion, being comparable to the reaction time (Tomei et al. 2009), has to be taken into account in the evaluation of the overall process kinetics.

19.5 Case Study: 4-Nitrophenol

The flexibility of SBR systems has been effectively demonstrated in the biodegradation of 4-nitrophenol (4NP), which is a typical representative of substituted phenols. 4NP is a xenobiotic included in the lists of priority pollutants as a toxic compound with EC_{50} = 64 mg/L, evaluated on micro-organisms of activated sludge origin, as reported in (Volskay and Grady 1990). It is a common contaminant of industrial wastewater (Chen et al. 1997), being employed in many industrial processes (the manufacture of explosives, drugs, dyes, phosphororganic insecticides, pesticides, and leather colouring), and can be discharged in aqueous matrices during the production, distribution and application of pesticides (Trapido and Kallas 2000).

Complete removal of this compound requires a sequence of aerobic and anoxic reaction phases. In the first reaction phase 4NP oxidation produces an effluent characterized by a high content of nitrites and nitrates, which must be removed prior to discharge to the receiving water body; this can be easily achieved by introducing an anoxic phase (where the denitrification takes place) into the SBR process cycle.

19.5.1 Conventional SBR

The kinetics of 4NP aerobic biodegradation in a suspended biomass SBR both in the presence of a biogenic substrate (sodium acetate and peptone) (Tomei et al. 2003) and with 4NP as the sole carbon source (Tomei et al. 2004) was extensively investigated. To ensure the presence of required nutrients and microelements, in this second case the feed consisted of a pure compound solution with the addition of the mineral medium MSV (Williams and Unz 1989).

Degradation of the compound (efficiency >99%) with residual 4NP concentration in the effluent lower than 0.5 mg/L and the stoichiometric formation of nitrites/nitrates were obtained for feed concentrations up to 400 mg/L with operating parameters typically applied in full-scale systems.

Complete removal of 4NP with a sequence of aerobic and anoxic reaction phases was also investigated and the effect of different operating parameters (dissolved oxygen, carbon nitrogen ratio, influent 4NP concentration) on the process kinetics was evaluated (Tomei and Annesini 2005). The denitrification was realized with acetate as carbon source after verifying that the internal carbon was not suitable to have appreciable kinetics. Figure 19.4 shows the typical concentration profiles of 4NP, $N\text{-}NO_2$ and $N\text{-}NO_3$ observed during the aerobic-anoxic cycle.

As Fig. 19.4 shows, 4NP was completely removed in the feed and aerobic reaction phases and its degradation was associated with the production of ($N\text{–}NO_2$+$N\text{–}NO_3$). This is consistent with the 4NP degradation mechanism proposed by Spain and Gibson (1991), who state that nitrites are formed by detachment of the nitro-group from the aromatic ring and regard this as the most critical step in the whole process. Low residual COD concentration (about 10 mg/L) in the aerobic effluent (data not shown), reasonably due to the biomass lysis products, suggests that complete 4NP biodegradation occurs in the aerobic phase; a more detailed discussion of 4NP aerobic biodegradation pathways and related experimental results is reported in a previous paper (Tomei and Annesini 2005). Finally, a fast denitrification process takes place in the anoxic phase.

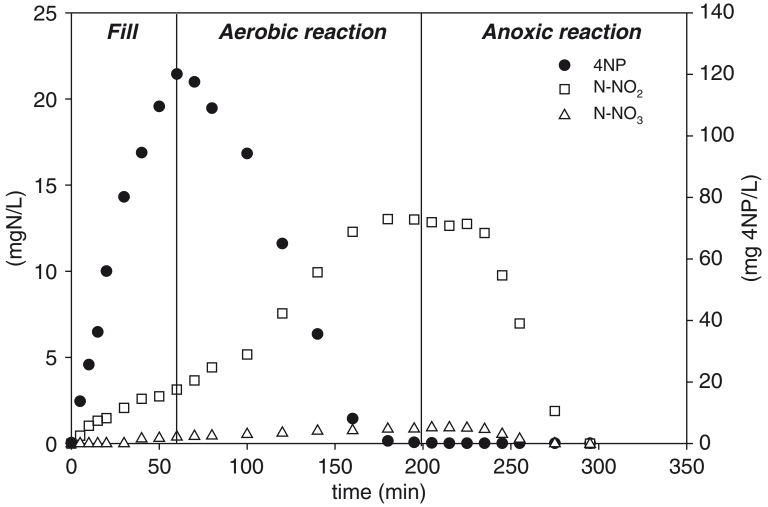

Fig. 19.4 4NP, $N\text{-}NO_2$ and $N\text{-}NO_3$ profiles observed during the integrated SBR aerobic-anoxic cycle

Table 19.3 Summary of the kinetic parameters in the aerobic anoxic cycle (dissolved O_2: 2–3 mg/L) (Tomei and Annesini 2005)

Process	Equation	Parameter	Value
Aerobic degradation	Haldane (Eq. 19.1)	k^* (mg4NP mgVSS^{-1} h^{-1})	0.29
		K_s (mg4NP/L)	55.0
		K_I (mg4NP/L)	15.0
Aerobic degradation	Haldane (Eq. 19.2)	k_{max} (mg4NP mgVSS^{-1} h^{-1})	0.059
		C^* (mg4NP/L)	28.72
		β	0.52
Denitrification	First order with respect to substrate and biomass	k_D (mgN mgVSS^{-1} day^{-1})	0.30

A summary of the kinetic parameters for 4NP degradation in the aerobic and anoxic phases is reported in Table 19.3.

19.5.2 *TPPB-SBR*

19.5.2.1 Undecanone as Liquid Partitioning Phase

The first screening of the solvents to be used with 4NP was done on the basis of literature data reporting organic solvents with satisfactory properties to be applied in TPPBs for phenol and aromatic compound biodegradation. The three compounds tested were 1-undecanol, 2-undecanone and oleyl alcohol. The final choice was 2-undecanone (Partition Coefficient = 150 in distilled water) because of the highest partition coefficient, the low emulsion forming tendency and the very good biocompatibility with the biomass. This last property was assessed by parallel kinetic batch tests carried out to verify the removal rate of 4NP in water and in a solution saturated with the solvent (that is the worse condition to face for the biomass).

The lab scale SBR reactor was operated in conventional and TPPB configurations under the same operating conditions (mixing, aeration, work cycle etc.) at feed concentration in the range of 300–450 mg/L in order to provide a direct comparison of the process performance in the two cases. Figure 19.5 shows the concentration profiles obtained in both cases for 4NP feed concentrations of 350 mg/L.

An initial lag phase was observed in the conventional configuration mode. In contrast, in the two phase system the lag phase was not observed because the biomass is always exposed to lower (certainly sub-inhibitory) substrate concentrations and the substrate/biomass ratio is low enough to allow the complete and rapid degradation of the available substrate that is gradually replaced from the organic phase. Details on the experimental apparatus, methods and results are reported in (Tomei et al. 2008).

Results confirmed the main advantage of the two phase system, that is the possibility of treating high concentrations of the xenobiotic without altering the biomass activity. Moreover, the marked reduction of the reaction time with respect

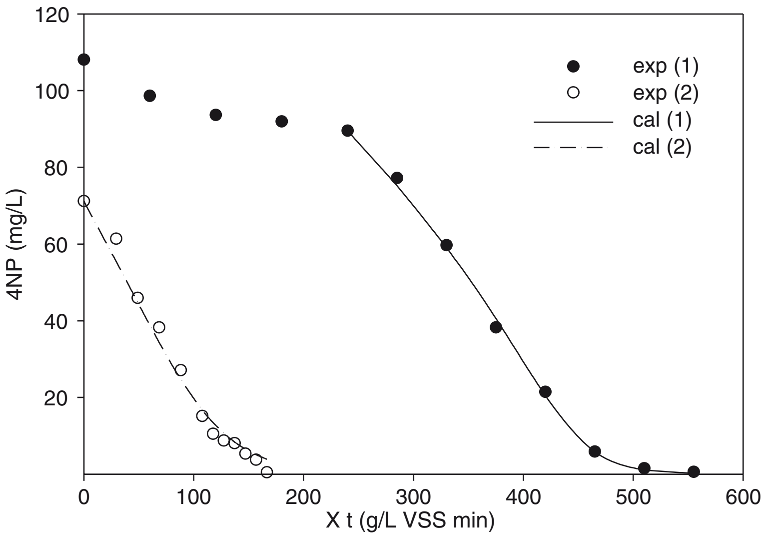

Fig. 19.5 Experimental and predicted concentration profiles for a kinetic test performed in the SBR reactor operated in the conventional and two-phase configurations. 4NP feed concentration 350 mg/L. Exp = experimental data, cal = calculated profile, (1) = one phase system, (2) = two-phase system (From Tomei et al. 2008)

Table 19.4 Best fit parameters values for the series of kinetic tests in the SBR bioreactor working with one phase (1) and two-phase (2) configurations

Test	Influent 4NP (mg/L)	β	C* (mg4NP/L)	k_{max} (mg4NP mgVSS^{-1} h^{-1})
(1)	350	0.6	30	0.052
(2)	350	0.6	50	0.132
(1)	450	0.6	30	0.054
(2)	450	0.6	50	0.125

to the single phase system indicates that the TPPB could be potentially able to treat even higher substrate loadings.

Finally, it is worth noting that for the two phase configuration, besides the reduction of the toxic effect on the biomass deriving from the exposure to sub-inhibitory substrate concentrations, a significant improvement in the process kinetics is also observed. The kinetic analysis was performed with the Haldane equation in the modified form and the data are reported in Table 19.4.

This beneficial effect was detected both in terms of reduced inhibition (increase of C*) and increased maximum removal rate. It is also important to point out that the obtained kinetic parameters for the TPPB/SBR configuration are potentially scaleable for larger applications, since the k_{max} value is of the same order of magnitude as that assumed for heterotrophic bacteria operating in wastewater treatment plants.

Results show that the TPPB/SBR configuration provided improved performance over a single phase system, but some drawbacks were observed that have to be considered in practice. The formation of micro-emulsions was observed causing the entrapment and removal of micro-organisms in the effluent with consequent loss of biomass and increased effluent turbidity. Occasionally at the solvent–water interface, depending on the mixing conditions, biofilm formation was observed. Additionally, with long work cycles indirect evidence for the partial degradation of the selected solvent by the consortium based on a slight increase in oxygen consumption was obtained. All these operational problems in the SBR can be mitigated with an accurate control of the mixing conditions and of the work cycle duration to avoid long starvation periods that can favour the utilization of alternative substrates.

In light of these results, it was deemed appropriate to investigate the potential of solid polymers as alternative partitioning phases that appear to be more promising when mixed cultures are utilized and have recently been shown to be effective with microbial consortia in the degradation of phenol (Prpich and Daugulis 2005; Prpich and Daugulis 2006).

19.5.2.2 Polymers as Solid Partitioning Phase

A preliminary evaluation of the use of polymers beads as alternative partitioning phase in a TPPB reactors applied to the removal of 4NP was performed. The biomass was a mixed culture operating in a conventional Sequencing Batch Reactor (SBR) and acclimatized to the 4NP as the sole carbon source. The first screening was performed to determine the partition coefficient of 4NP between polymers as partitioning phases and an aqueous phase at different initial concentrations of 4NP. The two selected polymers were then utilized in a series of batch kinetic tests carried out in parallel with single and two phase systems, at the same biomass concentration, in order to compare the performance of 4NP removal. The best results for polymers were obtained with a polyether-ester copolymer Hytrel 8206 (DuPont) in the form of oval shape beads (5 mm length, 1.5 mm diameter) and with a polycaprolactone polyester Tone P787 (Dow Chemical) in the form of roughly spherical beads (~4 mm diameter). The two polymers Hytrel and Tone gave a 4NP partition coefficient in distilled water equal to 152 ± 12 and 24 ± 5 respectively.

Typical concentration profiles observed in the batch kinetic tests are reported in Figs. 19.6 and 19.7.

It was observed that in the two phase system the biomass was exposed to 4NP concentrations that are significantly lower when compared to the one-phase system during the entire course of the experiment. As expected from the partition coefficient data, the best results were obtained with Hytrel which, even at the highest initial concentration, reduced the substrate concentration in the water phase to sub-inhibitory values (≤50 mg/L) for the utilized culture. This is certainly an advantage when the system operates with high concentrations of xenobiotics as was also observed in our experiments. In fact in the first test at 440 mg/L the reaction time required for

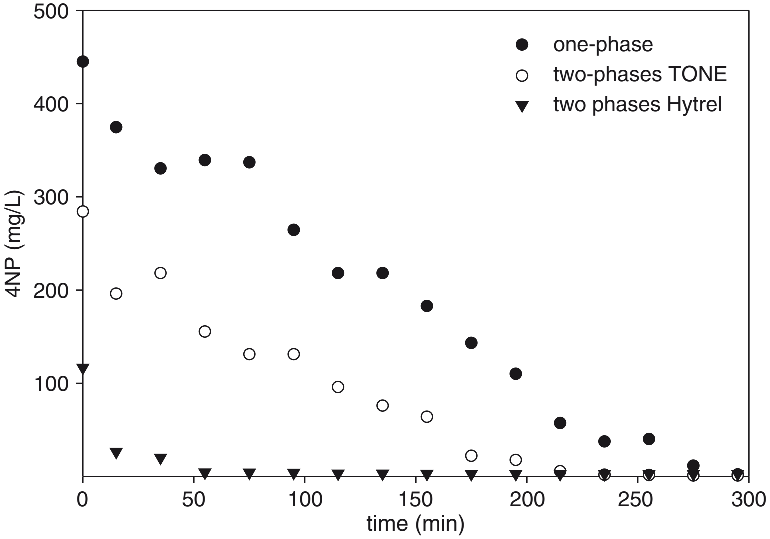

Fig. 19.6 4NP concentration profiles in one and two phase systems vs. time observed in the kinetic test at initial concentration of 440 mg/L

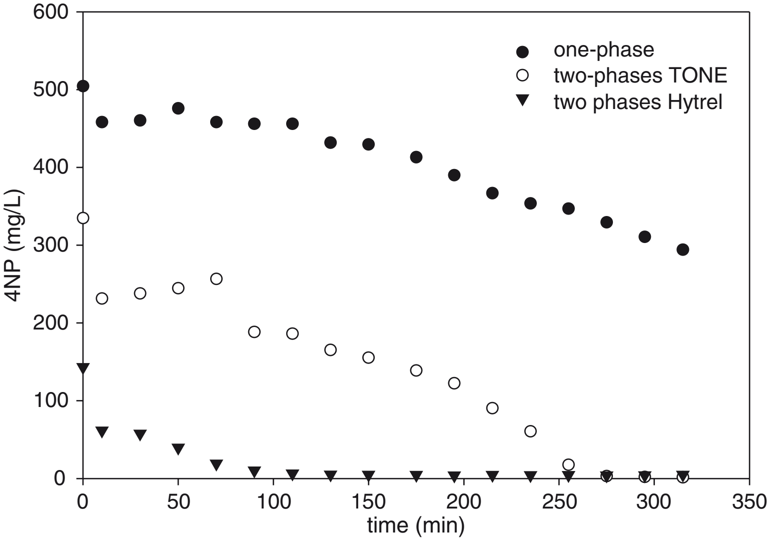

Fig. 19.7 4NP concentration profiles in one and two phase systems vs. time observed in the kinetic test at initial concentration of 500 mg/L

complete removal is reduced by 21% and 43% with Tone and Hytrel, respectively. The positive effect was even more evident at 500 mg/L; in the single phase system the strong inhibitory effect resulting from the higher substrate/biomass ratio caused quite a low 4NP degradation efficiency (about 25%) while complete 4NP removal was obtained in both of the two phase systems.

The two phase configuration working with polymer beads was demonstrated to be effective in degrading nitrophenol and particularly advantageous for concentrations ≥400 mg/L. Better process performance was obtained with Hytrel although both polymers are suitable for use in such applications. The behaviour of the polymers with respect to the biomass was clearly superior compared to immiscible liquid solvents as they are not biodegraded, are easy to separate from the biomass, did not cause emulsions to form and no biofilm formation was observed on the beads.

In the present example the adsorption/desorption rates appeared to be high enough to have satisfactory degradation rates, although this is a critical aspect to be verified in the polymer selection strategy in order to ensure effective process performance.

19.6 Conclusions

Effective biodegradation of 4NP was observed for inlet concentrations of up to 400 mg/L in the single phase SBR. Operation of the SBR in two-phase mode provided significantly improved performance, however, with reduced lag phase, superior kinetics, and the potential to treat much higher influent 4NP concentrations. By replacing the immiscible organic solvent with polymer beads, not only were similar improvements obtained for the combined TPPB-SBR configuration, but improved operability was also achieved since the polymers are non-biodegradable, are very easy to handle and separate from the aqueous phase, do not cause emulsions and biofilm formation at the solid–liquid interface, and are inexpensive. Ongoing work includes the treatment of mixtures of xenobiotic contaminants with multiple types of polymers, and an examination of the impact of polymer diffusivity on the rate of target molecule release and degradation in TPPB-SBR systems.

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Chapter 20
Fate and Occurrence of Surfactants-Derived Alkylphenolic Compounds in Conventional and Membrane Bioreactor (MBR) Wastewater Treatment Plants

Mira Petroviċ and Damià Barceló

Abstract Alkylphenol ethoxylates (APEOs) are produced in huge amounts and used in industrial cleansing processes. After use they are usually discharged into municipal sewer systems and afterward treated in wastewater treatment plants. Their environmental acceptability is strongly disputed because of potentially estrogenic metabolic products (two short ethoxy chain APEO oligomers [APE_1O and APE_2O] and fully de-ethoxylated alkylphenols [APs]) generated during wastewater treatment.

In this chapter the occurrence of APEOs and their metabolites in wastewaters and sludges is reviewed and their removal during wastewater treatment applying conventional activated sludge treatment and membrane bioreactors (MBR) is discussed. Biodegradation of APEO and formation of persistent metabolites is also discussed as a key phenomenon, as well as their removal by sorption onto sewage sludge.

20.1 Introduction

Alkylphenol ethoxylates (APEOs) are one of the most widely used surfactant classes with worldwide production of about 600 kt/year, which comprise 6.5% of the total surfactant (not including soaps) production in the world (data 2003)

M. Petroviċ (✉) and D. Barceló
Department of Environmental Chemistry, IDAEA-CSIC,
Jordi Girona 18-26, 08034 Barcelona, Spain

M. Petroviċ
ICREA – Catalan Institution for Research and Advance Studies,
Passeig Lluis Companys, 23, 08010, Barcelona, Spain
e-mail: address: mpeqam@cid.csic.es

D. Barceló
Catalan Institute for Water Studies, (ICRA),
Pic de Peguera, 15, 17003, Girona, Spain

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(CESIO 2007). They are widely used as cleaning products, detergents, emulsifiers, wetting and dispersing agents in industry and households, and as pesticides adjuvants in agriculture (Knepper and Berna 2003). Consequently, a large quantity of APEOs is continuously discharged to sewer systems and reaches wastewater treatment plants (WWTP). Although parent APEOs are not classified as highly toxic substances (EC_{50}, 48 h, *Daphnia magna* 1.5 mg L^{-1}) (Servos 1999) their environmental acceptability is strongly disputed because of metabolic products (two short ethoxy chain APEO oligomers [APE_1O and APE_2O] and fully de-ethoxylated alkylphenols [APs]) generated during wastewater treatment (Ahel et al. 1994). These compounds are substances perceived to possess estrogenic activity due to their ability to mimic the endogenous hormone 17β-estradiol (Sonnenschein and Soto 1998; Jobling and Sumpter 1993; Jobling et al. 1996). Numerous studies determined that surfactants-derived alkylphenolic compounds accounted for a large portion of the estrogenicity of sewage effluents and receiving surface waters (Nichols et al. 1999; Solé et al. 2000; Petrovic et al. 2002). These findings resulted in an incitement for action against the use of APEOs and inclusion of nonylphenol (NP) and octylphenol (OP) as priority substances in the Water Framework European Directive (WFD) 2000/60/EC (Directive 2000/60/EC), whereas NP is included in the US EPA non-priority pollutant list (US EPA [non]priority pollutant list 2006). The European Directive 2003/53/EC amending the Council Directive 76/769/EEC prohibits the use of NP and NPEOs as a substance or constituent of preparations in concentrations equal or higher than 0.1% by mass for domestic cleaning, cosmetic products, co-formulants in pesticides and biocides, manufacturing of pulp and paper, textiles and leather processing and industrial and institutional cleaning except in controlled closed systems with no release into wastewater or systems with special treatment where the process water is pre-treated prior to biological wastewater treatment or recycled or incinerated. As a result of this restriction, the general trend of declining of concentrations of alkylphenolic compounds is observed in whole Europe. However, mainly because of lower production costs, APEOs are still being used in substantial amounts in institutional and industrial applications and detected in high levels in wastewaters and environmental matrices. Therefore, they still pose a risk and their occurrence and fate in wastewaters and treatment processes should be carefully evaluated.

20.2 Sources of Alkylphenolic Compounds in Wastewaters

Due to a voluntary ban and legal restrictions for use of APEOs in household cleaning products and industrial applications a significant reduction of APEO concentrations in raw wastewater and consequently of concentrations of degradation products found in effluent samples has been observed. For example, in five Norwegian WWTPs nonylphenol (NP) was found in the range of 0.2–7 μg L^{-1} in the influents in the 2002 samples, while concentrations below the detection limit (2 ng L^{-1}) were found in the samples from 2004 (Vogelsang et al. 2006), which is attributed to new restrictions implemented in 2002. In Catalonia (Spain), typical levels of NP measured in WWTPs influents in 1998 and 1999 ranged from 100–200 μg L^{-1}, while 2002–2003 data show almost a 10-fold decrease (Gonzalez et al. 2004). Similarly, a comprehensive study in the region of Western Balkan (Bosnia and Herzegovina, Croatia and Serbia) (Terzić et al. 2008) showed widespread occurrence of surfactant-derived alkylphenolic compounds in raw wastewater entering WWTPs, although the concentration levels were relatively low and suggest a decreasing trend in comparison to some previous campaigns conducted in early 1990s (Kvestak et al. 1994).

In order to determine the sources of APEOs and their metabolites in wastewaters in Stockholm (Sweden), Manson et al. (2008) used substance flow analysis allowing the comparison of 13 groups of goods' emissions to wastewater. In the absence of industry manufacturing APEOs or APs in the area, it was found that the groups of textile and cleaning agents were the major sources to wastewater, while other groups such as personal care products and paint give smaller contributions. The production of textiles and leather includes several steps of washing, where APEOs could be used as detergents, which leaves significant amounts of APEOs that can be released during washes. In the USA a survey of urban sewers suggested that household products still constitute an important source of the APEOs reaching WWTPs (Loyo-Rosales et al. 2007).

20.3 Fate of APEOs in Wastewaters

20.3.1 Removal in Conventional Wastewater Treatment Plants

Wastewater derived alkylphenolic compounds and their elimination in conventional WWTPs (applying activated sludge treatment) have been extensively studied(Petrovic and Barceló 2003). Biodegradation of APEOs starts with the stepwise ω-oxidation of the ethoxy chain leading to progressive shortening of the ethoxy chain (Ahel et al. 1994). The products are short-chain APEOs (mainly di- and mono ethoxylates), which are subsequently transformed via oxidation to corresponding alkylphenoxy carboxylates (APECs) and finally to alkylphenols (APs) (Ahel et al. 1994). It is generally assumed that AP_1EC and AP_2EC are the most persistent metabolites formed under aerobic conditions, while APs are mostly formed under anaerobic conditions. In addition to this generally accepted biodegradation pathways Jonkers et al. (2001) found that the oxidation of the nonyl chain goes hand in hand with the stepwise ω-oxidation of the ethoxy chain and its progressive shortening leads to metabolites carboxylated alkylphenoxy carboxylates (CAPEC) having both a carboxylated ethoxy and alkyl chain of varying lengths.

Several extensive studies were conducted with the objective to determine the concentrations of APEO and their degradation products in raw and treated wastewaters and their removal during sewage treatment. According to Ahel et al.

(1994), approximately 63% of all nonylphenolic compounds introduced to WWTPs are discharged into the environment; 19% in the form of carboxylated derivatives, 11% in the form of lipophilic NP_1EO and NP_2EO, 25% in the form of NP and 8% as untransformed NPEO. Secondary effluents are responsible for 60% of the total input of nonylphenolic compounds into the environment, while digested sewage sludge represents 40% of the total load. González et al. (2008) found that conventional activated sludge (CAS) treatment at WWTP Rubi, that receives mixed municipal and industrial wastewaters and operating at 14 h of hydraulic retention time (HRT) and 3 days of sludge retention time (SRT), was generally inefficient in removing nonylphenolic compounds with overall elimination around 54% and remaining total concentration still in the range of 100 μg/L. $NP_{(1-2)}EC$ were the most abundant component of the CAS effluent accounting for up to 60% of the total pool of nonylphenolic compounds. Neutral metabolites $NP_{(1-2)}EO$ represented approximately 29% of the total pool, the parent $NP_{(3-15)}EO$ 10%, while NP comprised less than 1%. In another WWTP (González et al. 2007) working at similar HRT, but longer SRT (12 days) overall removal of nonlyphenolic compounds was slightly better (69%) with NPECs representing 58% of the nonylphenolic compounds in the effluent. Similarly, Langford et al. (2007) studied the impact of process variables, such as sludge age, influent concentrations, concentrations of co-pollutants and hydraulic retention time on the removal of NPEOs during simulated activated sludge treatments and observed more NPEO removal from influent at higher sludge age, which resulted in greater NP, and short-chain NPEO compound accumulation in sludge. Loyo-Rosales et al. (2007) studied the fate of APEOs and their carboxylated derivatives in three American WWTPs, two of which included chlorination. Although average NP(0–16)EO removal from wastewater was high (99% in summer and 93.7% in winter) the overall removal (degradation) from the WWTP including transformation products and APEOs in sludge was low (12%, 42% and 59% respectively for three WWTP) as shown in Fig. 20.1. The results suggested that advanced treatment does not invariably result in better APEO removal and that both effluent concentrations and the removal efficiency of the APEOs were strongly correlated to water temperature.

Typically, concentrations of NPEOs and their acidic and neutral degradation products found in WWTP effluents rarely exceeded 100 μg L^{-1}. It should be mentioned that NPEO metabolites, NP and NPECs are already detected in WWTP influents, due to in-sewer degradation, in concentrations up to 40 μg L^{-1}. The presence of NP and NPECs in the influents is mainly attributed to the metabolism of NPEOs, but also their entry in WWTP, resulting from application in other fields, has to be taken into account. For example NP is also used as an ingredient of pesticide formulations and NP_1EC as the corrosion inhibiting agent. A comprehensive monitoring of NP in effluents in 40 WWTP in Japan detected maximum concentrations of 1.7 μg L^{-1} (Fujita et al. 2000), while levels in six Spanish WWTPs, NP was found in concentrations from 0.2–18 μg L^{-1} in influent samples and up to 5 μg L^{-1} in the treated water (Gonzalez et al. 2004).

A survey of nonylphenolic compounds in WWTP effluents revealed that NPECs and CAPECs are typically predominant nonylphenolic compounds. Of the NPECs

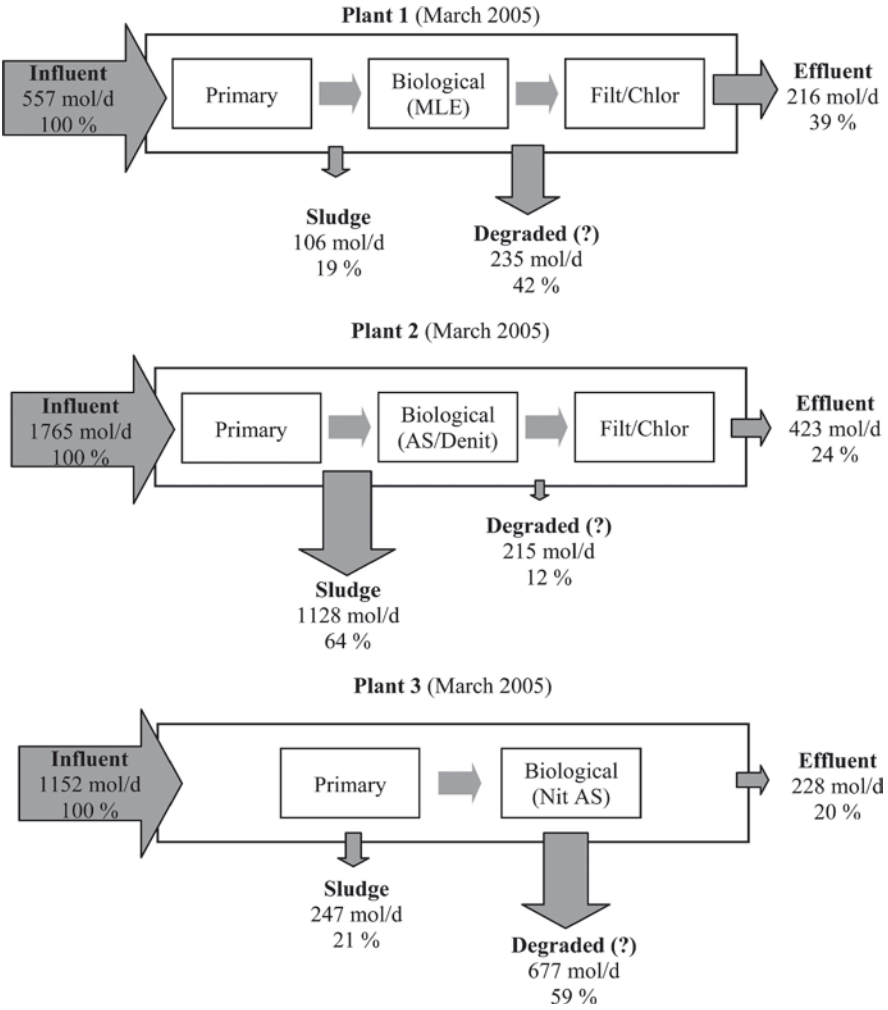

Fig. 20.1 NPE (including NP0-16EO and NP1-2EC) mass balance in three WWTPs. Influent: total mass in influent influent (except for plant 3 in August, where it corresponds to the primary effluent); Sludge: total mass in waste primary and secondary sludge (plant 2 includes tertiary sludge); Effluent: total mass in final effluent; Degraded: estimated from influent − (sludge + effluent) (Reprinted with permission from Loyo-Rosales et al. 2007. © 2007 American Chemical Society)

detected in effluents the most abundant forms are NP_1EC and NP_2EC, often found in concentrations of several hundreds of μg L^{-1}. For example in three American WWTPs, two of which included chlorination as tertiary treatment, NPECs were detected in influents at concentrations ranging from 0.28–25.9 μg L^{-1} and in effluents at levels ranging from 44.9–121 μg L^{-1} (Loyo-Rosales et al. 2007).

However, this study, as well as the majority of the monitoring studies dealing with alkylphenolic compounds did not include the analysis of CAPECs, due to the difficulties in analysis of these compounds and lack of commercial standards. In one of the few studies focusing on dicarboxylated compounds, Di Corcia et al. (2000) showed that CAPECs were the dominant products of the NPEO biotransformation. By averaging data relative to five major activated sludge WWTPs in Rome, Italy, over 4 months, relative abundances of NPEO ($n_{EO} = 1$ and 2), NPECs and CAPECs were found to be respectively 10±2%, 24±5% and 66±7%. The concentrations of CAPECs were as follows: 2.5–24 μg L^{-1} (CA_8PEC), 0.3–2.0 μg L^{-1} (CA_7PEC), 2.3–16 μg L^{-1} (CA_6PEC), 0.3–2.1 μg L^{-1} (CA_5PEC), 0.1–1.4 μg L^{-1} (CA_4PEC) and 0.1–0.6 μg L^{-1} (CA_3PEC).

20.3.1.1 Occurrence in Sewage Sludge

Forty percent of the total output of nonylphenolic compounds is via digested sewage sludge (Ahel et al. 1994). Consequently, nonylphenolic compounds are frequently detected in substantial amounts in digested sludges. From an ecotoxicological point of view, the most important surfactant derived compounds are the weakly estrogenic NP and short ethoxy chain NPEOs.

NPEOs were detected in concentrations ranging from values below mg/kg to over 500 mg/kg (maximum concentration of 2 g/kg was reported for sludge from a WWTP receiving industrial wastewaters) with $NPEO_1$ and $NPEO_2$ being the predominant species (Petrovic and Barceló 2003). Generally, higher contamination is found in WWTPs using anaerobic digestion. NP was found in concentrations ranging from the lower mg/kg range to the lower g/kg range. Adsorption of NP onto primary and secondary sewage sludge, and its formation from NPEOs during anaerobic stabilisation of sludge, results in extremely high concentration of NP in anaerobically digested sludge. The high levels of NP (more than 1 g/kg) are consistently found in anaerobically stabilised sludge. An increase of NP concentration during anaerobic digestion has been reported (Giger et al. 1984) resulting in extremely high concentrations of NP in an anaerobically digested sewage sludge (450 to 2,530 mg/kg, mean 1,010 mg/kg). The concentrations in activated sewage sludge, in mixed primary and secondary sludge, and in aerobically stabilized sludge were substantially lower, suggesting that the formation of NP is favoured under mesophilic anaerobic conditions. Hydrophillic NPECs were also detected, at significantly lower concentration levels. Field and Reed (1999) studied the occurrence of NPECs in anaerobically digested municipal and industrial sludges. $NPE_{1-4}C$ concentrations ranged from 27–113 mg/kg with NP_2EC as the most abundant oligomer and *ortho*-to-*para* isomer rations ≥1, which indicated the depletion of *para* NPEC isomers relative to *ortho* isomers during anaerobic sludge treatment. In contrast, sludge that had not undergone anaerobic treatment contained only *para* isomers.

20.3.2 Removal Using Membrane Bioreactors (MBR)

Membrane bioreactor (MBR) technology is considered as one of the most promising development in wastewater treatment. Now, when economic reasons do no longer limit the application of MBR to industrial and municipal wastewater treatment and that new requirements are being set for the treatment of wastewaters, MBR treatment may become one of the key techniques in all future scenarios that consider the direct or indirect reuse of wastewaters. This is due to two characteristics of MBRs; (a) the low sludge load in terms of BOD that can be expected to force bacteria to mineralise also poorly degradable organic compounds and (b) the high sludge age that gives the bacteria time to adapt to these substances.

However, although many papers (Van Nieuwenhuijzen et al. 2008) have reported the application of MBR for the treatment of urban and industrial wastewaters, up to our knowledge there are only few papers reporting on the behaviour of alkylphenolic compounds during the MBR treatment.

Several studies reported that the elimination of long chain NPEO was improved by the usage of MBRs treatment (Li et al. 2000; Lubello and Gori 2005; Terzic et al. 2005) but only in few cases the degradation products were studied.

Using a laboratory scale MBR, González et al. (2007) found significantly improved elimination of NPEOs and their degradation products short NPEO and nonylphenol carboxylates (NPEC) (98% elimination of total nonylphenolic compounds in a MBR vs 54% elimination in a CAS treatment), while such improvement was not significant in a study using two pilot scale MBR (González et al. 2008). The overall elimination of total nonylphenolic compounds for conventional activated sludge treatment was 75% while it was 91% for the MBR1 (using flat sheet membranes) and 82% for the MBR2 (using hollow fiber membranes) (see Fig. 20.2). Similarly, comparable elimination of NPEOs in CAS and pilot MBR, operated at different solid retention times (SRTs), was observed by Clara et al. (2005).

Li et al. (2000) assessed the elimination efficiency of NPEO in membrane-assisted biological WWTP. The results showed that compared to conventional WWTP, membrane assisted biological treatment with biomass concentrations of about 20 g L^{-1} exhibit improved elimination efficiency for NPEO, AEO and LAS. The elimination rate for NPEO in the conventional WWTP reached a maximum of only 86%, while 91–97% was eliminated under membrane treatment with different types of membranes.

Cirja et al. (2006) performed a study aimed at giving a better insight into the possible fate of NP during wastewater treatment by using a lab-scale MBR designed and optimized for fate studies carried out with radiolabeled compounds. The mass balance of NP residues at the end of the study showed that 42% of the applied radioactivity was recovered in the effluent as degradation products of NP, 21% was removed with the daily excess sludge from the MBR, and 34% was recovered as adsorbed in the component parts of the MBR. A high amount of NP was associated to the sludge during the test period, while degradation compounds were mainly found in the effluent.

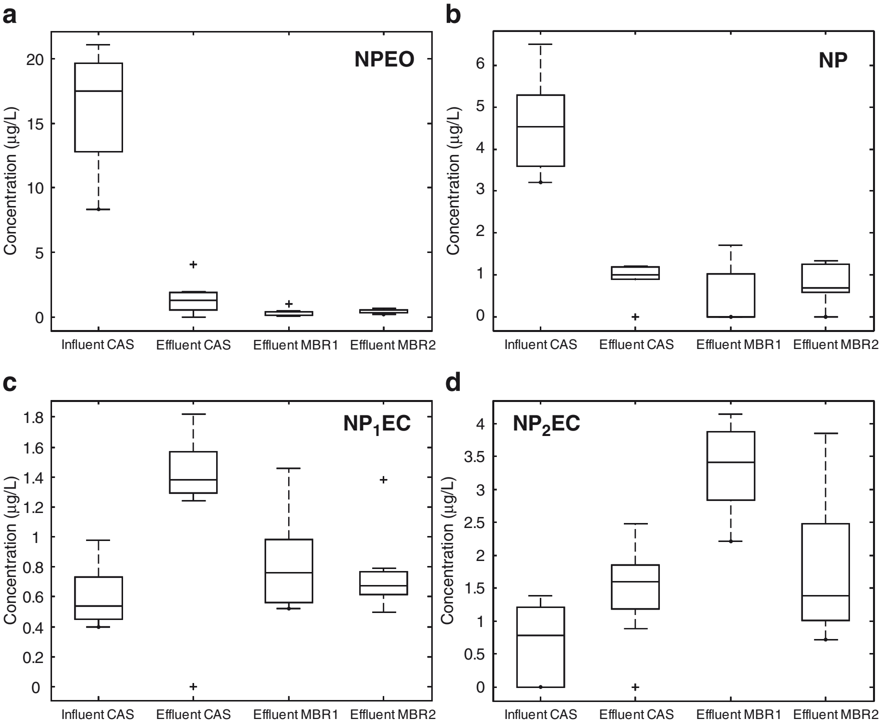

Fig. 20.2 Boxplots of concentrations found in influent samples and effluents of two pilot-plant MBRs (flat sheet and hollow fiber membranes, respectively) working in parallel with a CAS treatment at WWTP Terrassa, Spain. (**a**) Concentrations of parent long chain NPEOs, (**b**) concentrations of NP, (**c**) concentrations of NP1EC, (**d**) concentrations of NP2EC (Modified from González et al. 2008)

20.4 Conclusions

Surfactant derived alkylphenolic compounds are widespread pollutants characterized with very high potential to enter the environment through treated wastewaters and sludge. In WWTPs, generally high removal rates have been found for parent APEOs. However the main environmental concern is the formation of recalcitrant metabolites such as NP1EO, NP2EO and NP. These metabolites being partially very resistant against further degradation are of special interest since they enter the receiving surface waters at μg L^{-1} concentrations where subsequently interactions with aquatic organisms may lead to adverse effects (i.e. endocrine disruption). Additionally of particular interest are polar intermediates (e.g. NPEC) which are believed to possess high mobility and persistence and therefore their migration into soil and groundwater aquifers may deteriorate the quality of drinking water. Therefore, an improved treatment and strict control of the treatment process have to be employed so that the removal of these micro-contaminants is as high as possible.

The comparative study on removal of alkyphenolic compounds by conventional activated treatment technology and MBR process has shown generally better removal of parent compounds and less polar metabolites such as NP and short ethoxy chain NPEOs in an MBR than in the conventional WWTP. However, in the case of the acidic degradation products both MBRs and CAS system showed their formation, with significant concentrations still released in the treated water. However, membrane technology gives room for expectation that with this alternative wastewater treatment the ecological risk associated with alkylphenolic compounds can be reduced. In addition, further improvement of the MBR process will increase its cost-effectiveness and MBR technology is expected to play an important role for wastewater treatment in the next years, in Europe as well as worldwide.

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Chapter 21

Removal of Xenobiotic Compounds from Water and Wastewater by Advanced Oxidation Processes[1]

Despo Fatta-Kassinos, Evroula Hapeshi, Sixto Malato, Dionisis Mantzavinos, Luigi Rizzo, and Nikos P. Xekoukoulotakis

Abstract Advanced oxidation processes (AOPs) constitute a family of redox technologies that have been involved in various environmental applications, including, amongst others, the treatment of municipal and industrial wastewater contaminated by various organic and inorganic compounds.

This chapter focuses on the science and engineering of water and wastewater treatment in relation to AOPs applications. The chapter gives a short but necessary description of the key AOPs employed in water treatment and then discusses process fundamentals, advantages and drawbacks. This is done providing recent paradigms from the literature on process integration aiming to improve degradation rates or separate pollutants, catalysts and chemicals prior to or after advanced oxidation.

The chapter includes also information on solar-driven applications (homogeneous and heterogeneous photocatalysis) as an excellent example of sustainable treatment technologies. This part discusses technological advances (development of non-concentrating collectors and scaling-up of photocatalytic reactors) and summarizes most of the recent research related to the degradation of water contaminants.

D. Fatta-Kassinos (✉) and E. Hapeshi
Department of Civil and Environmental Engineering, School of Engineering,
University of Cyprus, 75 Kallipoleos Str. 1678, Nicosia, Cyprus
Tel: 0035722892275, Fax: 0035722892295 e-mail: dfatta@ucy.ac.cy

S. Malato
Plataforma Solar de Almería (CIEMAT), Carretera Senés, km 4. 04200 Tabernas (Almería), Spain

D. Mantzavinos and N.P. Xekoukoulotakis
Department of Environmental Engineering, Technical University of Crete, Polytechneioupolis,
GR 73100 Chania, Greece

L. Rizzo
Department of Civil Engineering, University of Salerno, Via Ponte don Melillo, 84084-Fisciano
(SA), Italy

[1] All authors have contributed equally to this chapter.

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The approach is exemplified through a combined solar photocatalysis and bio-treatment unit capable of destroying very persistent toxic compounds.

Finally, in this chapter, the use of AOPs in drinking water treatment is discussed with respect to both disinfection by-products control and micro-pollutants removal and compared to the efficiency of conventional treatment technologies.

21.1 Fundamentals of Advanced Oxidation Processes

Advanced oxidation processes (AOPs) can be broadly defined as redox methods which are based on the intermediacy of reactive oxygen species, such as hydroxyl radicals, $HO^{\bullet}$, superoxide radical anions, $O_2^{\bullet-}$, and perhydroxyl radicals $HO_2^{\bullet}$, to convert harmful organic and inorganic pollutants found in air, water and soil to less hazardous compounds. The most widely used AOPs include ozonation, electrochemical oxidation, Fenton's and photo-Fenton's reagent, heterogeneous semiconductor photocatalysis, wet air oxidation, and sonolysis, among others (Tarr 2003; Parsons 2004). A brief description of these technologies is given below.

Ozone, O_3, is a strong oxidant that is able to react through two different reaction mechanisms, called direct and indirect ozonation (Gottschalk et al. 2000; Beltran 2003). Thus, ozone can directly react with certain functional groups of organic compounds found in water and wastewaters, such as unsaturated and aromatic hydrocarbons with substituents such as hydroxyl, methyl and amine groups, through 1,3 dipolar cycloaddition and electrophilic reactions, giving rise to degradation products (Beltran 2003). On the other hand, ozone decomposes in water to form $HO^{\bullet}$, which are stronger oxidizing agents than ozone itself, thus inducing the so-called indirect ozonation. Ozone decomposition in water can be initiated by the hydroxyl anion, HO^-, and thus indirect ozone oxidation is favored at alkaline pH conditions. Treatment performance is enhanced if ozone is combined with ultraviolet irradiation, hydrogen peroxide or with iron or copper complexes that act as catalysts, thus generating additional $HO^{\bullet}$. Ozonation has been traditionally employed in drinking water treatment for odor and taste control and disinfection, as well as (in some cases) for wastewater disinfection.

Homogeneous oxidation with the Fenton's reagent involves the use of ferrous, Fe(II) or ferric, Fe(III) ions in the presence of hydrogen peroxide via a free radical chain reaction mechanism, which produces $HO^{\bullet}$ (Pignatello et al. 2006; Bautista et al. 2008). It is considered to be a metal-catalyzed oxidation reaction, in which iron ions act as the catalyst. Process efficiency is closely related to the solution pH, whose optimal values are between 2 and 4, as well as the COD:H_2O_2:catalyst ratio in the feed. Moreover, efficiency may be enhanced in the presence of UV irradiation as more $HO^{\bullet}$ are produced in the so-called photo-Fenton reaction. Optimization of the catalyst and oxidant concentrations relative to the effluent's polluting load renders the process suitable to treat strongly polluted hospital effluents or effluents from pharmaceuticals manufacturing. In most cases, Fenton oxidation is capable of mineralizing a substantial fraction of the polluting load yielding effluents that are less toxic and more readily amenable to biological post-treatment.

Heterogeneous semiconductor photocatalysis using TiO_2 as photocatalyst involves the illumination of an aqueous TiO_2 suspension with irradiation with energy equal to or greater than the band gap energy of the semiconductor, thus generating valence band holes and conduction band electrons (Hoffmann et al. 1995; Mills and Le Hunte 1997; Kaneko and Okura 2002). Holes and electrons may either undesirably recombine liberating heat or make their separate ways to the surface of TiO_2, where they can react with species adsorbed on the catalyst surface. Valence band holes can react with water and the hydroxide ion (i.e. under alkaline conditions) to generate $HO^{\bullet}$, while electrons can react with adsorbed molecular oxygen reducing it to $O_2^{\bullet-}$, which, in turn, reacts with protons to form peroxide radicals. TiO_2 photocatalysis is an emerging water and wastewater treatment technology with key advantages including the lack of mass transfer limitations, operation at ambient conditions and the possible use of solar irradiation. The catalyst itself is inexpensive, commercially available in various crystalline forms and particle characteristics, non-toxic and photochemically stable.

Electrochemical oxidation over anodes made of graphite, Pt, TiO_2, IrO_2, PbO_2, several Ti-based alloys and, more recently, boron-doped diamond (BDD) electrodes in the presence of a suitable electrolyte has been employed for the decontamination of various organic-containing effluents, including pharmaceutical and endocrine disrupting compounds (Chen 2004; Martinez-Huitle and Ferro 2006; Menapace et al. 2008; Yoshihara and Murugananthan 2009). Two mechanisms are responsible for organic matter electrochemical oxidation, namely: (a) direct anodic oxidation where the pollutants are adsorbed on the anode surface and destroyed by the anodic electron transfer reactions and (b) indirect oxidation in the liquid bulk which is mediated by the oxidants that are formed electrochemically; such oxidants include chlorine, hypochlorite, ozone and hydrogen peroxide, among others.

Sonolysis is a relatively new AOP in water treatment based on the use of low to medium frequency (typically in the range 20–1,000 kHz) and high-energy ultrasound irradiation to catalyze the destruction of organic pollutants in water (Mason and Lorimer 2002; Gogate and Pandit 2004; Adewuyi 2005). The chemical effects of ultrasound irradiation are the result of the phenomenon of acoustic cavitation, which is the formation and subsequent collapse of micro-bubbles in a liquid medium upon ultrasound irradiation. At the extreme conditions generated inside the cavitation bubbles during collapse, vapor is homolytically cleaved leading to the formation of $HO^{\bullet}$ that can oxidize the organic pollutants found in water. There are three potential sites for sonochemical reactions, namely: the cavitation bubble itself, the interfacial region between the bubble and the surrounding liquid and the solution bulk. Pyrolytic reactions inside or near the bubble as well as solution radical chemistry are the two major pathways of sonochemical degradation. Organics of low solubility and/or high volatility are likely to undergo fast sonochemical degradation as they tend to accumulate inside or around the gas-liquid interface; in this respect, the process may be well suited to tackle pharmaceutical micro-pollutants. Sonochemical treatment typically operates at ambient conditions and does not require the addition of extra chemicals or catalysts.

Sub-critical wet air oxidation (WAO) or hydrothermal treatment can be defined as the oxidation of organic and inorganic compounds in an aqueous solution by means of molecular oxygen or air as oxidants at elevated temperatures (in the range 100°C–372°C) and pressures (in the range 2–20 MPa) (Bhargava et al. 2006). Elevated temperatures accelerate reaction rates while elevated pressures are required to increase oxygen solubility in water, as well as to maintain water in the liquid phase. In order to reduce the high temperature and pressure required for the process and at the same time increase its efficiency, various catalysts are used in the so-called catalytic wet air oxidation (CWAO) (Bhargava et al. 2006; Levec and Pintar 2007). CWAO has lower energy requirements and due to the presence of the catalyst, much higher oxidation rates are achieved. The processes have great potential for the treatment of wastewaters with moderate to high organic content (i.e. 10–100 g/L COD). In both processes reactive oxygen species, such as $HO^{\bullet}$ are generated, thus converting dissolved organic pollutants into highly oxidized intermediates and eventually to carbon dioxide and water. The process is extremely clean, since it does not involve the use of any harmful chemical reagents and leads to harmful mineral end products. Both WAO and CWAO have been reported to completely eliminate a wide range of refractory organic pollutants from the aqueous phase. At temperatures and pressures above the critical point of water (374°C, 22 MPa), the process is referred to as supercritical water oxidation (SCWO) with its main feature being that gas and liquid phases form a homogeneous single phase. In this respect, organics and oxygen become completely miscible, thus eliminating mass transfer limitations, which, in conjunction with increased reaction temperatures, lead to very high reaction rates.

AOPs have a wide range of applications, mainly for the oxidation of refractory compounds, TOC (Total Organic Carbon) and COD (Chemical Oxygen Demand) reduction in wastewater reclaim/reuse/recycling, industrial and municipal wastewater. Industrial effluents treated by AOPs include among others distillery, pulp and paper, textile, olive mill, metal-plating, agrochemical, while other hazardous effluents treated by such technologies include hospital and slaughterhouse flows. Municipal effluents are treated by AOPs in order to remove various organic micropollutants such as pharmaceutical active ingredients, personal care products and endocrine disrupting compounds, among others. Depending on (a) the properties of the wastewater stream (i.e. matrix, composition and concentration) to be treated, (b) the treatment objective itself and (c) the treatment technology available, AOPs can be either employed alone or coupled with other physicochemical and biological processes. The treatment objectives may span from decreasing the concentration of certain pollutants to values below the discharge limit, to partially converting polluting fractions to less toxic and/or more biogenic compounds and finally to mineralizing the stream (breaking the organics down to CO_2 and inorganic salts).

Coupling is often beneficial, most frequently leading to higher removal efficiencies. AOPs can be applied as a pre-treatment step to convert compounds initially resistant to bio-treatment to more labile intermediates followed by biological treatment. The concept of coupling AOPs and bio-treatments is related to the fact that a chemical oxidation method aiming at complete mineralization might become extremely cost-intensive if applied as the main process for treating a wastewater stream containing high loads of organic pollution. The concept is schematically illustrated in Fig. 21.1 (Mantzavinos and Psillakis 2004). The objective is to firstly decompose the organic compound into smaller ones e.g. short-chain organic acids, that can enter cells and may be more readily biodegradable than the original molecule, since it is generally accepted that the rate of biological oxidation increases with decreasing molecular size. Conversely, total chemical oxidation of the intermediates to carbon dioxide, water and inorganic ions may be difficult and require severe oxidative conditions, since the rate of chemical C-C bond scission seems to decrease with decreasing molecular size. As seen in Fig. 21.1, there is a break point where the two rates become equal; i.e. this is the optimum location to switch from chemical to biological treatment.

Alternatively, in cases of wastewaters that contain substantial quantities of biodegradable fractions, a biological process may precede chemical oxidation that can eventually be employed as a final polishing step. In this case, biodegradable species are removed first and consequently do not compete with the recalcitrant ones for the costly chemical oxidants.

21.2 Recent Applications of Advanced Oxidation Processes in Wastewater Treatment

Over the last several years, numerous studies have dealt with the removal by AOPs of various single compounds spiked in aqueous matrices, while relatively fewer studies have focused on real wastewater matrices. Recent reviews summarize the progress achieved so far in the particular field and highlight the remarkable

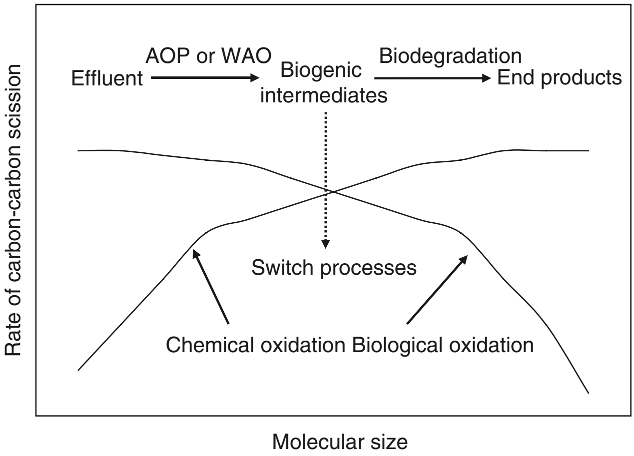

Fig. 21.1 Coupling chemical and biological treatment

efficiencies of these technologies. Mantzavinos and Psillakis (2004) present the studies performed in the field of industrial wastewaters by chemical oxidation as a pre-treatment step, Belgiorno et al. (2007) discuss the various studies performed by photocatalysis and ultrasound, Esplugas et al. (2007) present studies carried out for the degradation of endocrine disrupting compounds, pharmaceuticals and personal care products by ozonation and other AOPs, and Klavarioti et al. (2009) present the progress made in the field of AOPs for the removal of residual pharmaceuticals.

In this section, an effort was put to present the work accomplished so far in the field of process integration, i.e. combining various AOPs together or coupling AOPs to other technologies. Although the term "xenobiotics" includes an endless catalogue of chemicals, emphasis was given on those compounds that are found in environmentally relevant water and wastewater matrices. AOPs can be employed simultaneously to induce faster oxidation rates of the organic compounds by increasing the rate of the formation of reactive moieties. The most popular AOPs that are applied in combination are H_2O_2/UV, O_3/UV, H_2O_2/O_3, H_2O_2/O_3/UV, UV/TiO_2/H_2O_2, ultrasound/Fenton's reagent, UV/Fenton's reagent, wet air oxidation/H_2O_2 and electrolysis/Fenton's reagent. What is important here to note is the fact that the simultaneous application of these processes can lead to removal efficiencies that are higher than the sum of the efficiencies that could be achieved by the individual processes applied alone (Comninellis et al. 2008). As shown in Berberidou et al. (2007), although the photocatalytic degradation of biocide malachite green is considerably faster (by about an order of magnitude) than sonolytic degradation, efficiency can be improved during the so-called sonophotocatalysis (coupled ultrasound irradiation with TiO_2 photocatalysis). The beneficial synergy of this process integration may be attributed to the increased production of reactive free radicals via water sonolysis as well as an increase in the catalyst surface area. In addition, the ultrasound may accelerate mass transfer of reagents onto the surface of the catalyst and remove impurities from its surface as well. Another example is the simultaneous application of TiO_2 photocatalysis and ozonation for the treatment of textile effluents (Gomes de Moraes et al. 2000). The investigation was focused on the reduction of TOC and color. For a reaction time of 60 min, the photocatalytic process yielded color and TOC reduction of about 90% and 50% respectively. Meanwhile, ozonation gave about 60% decolorization but negligible TOC reduction. When the processes were applied simultaneously, decolorization was almost complete and TOC reduction was higher than 60%. Iordache et al. (2007) compared the Fenton and sono-Fenton degradation of bisphenol-A and they found out that the ultrasound irradiation of wastewater improved oxidation rates due to the higher efficiency for the production of $HO^\bullet$ as well as to the ultrasonic physical (bubble collapse and mixing) effects.

Methyl orange present usually in textile wastewaters has been removed from aqueous solution by nano-TiO_2/exfoliated graphite composites with the combination of ultrasound/adsorption/photocatalysis (Li et al. 2008). The experimental results showed that nano-TiO_2/exfoliated graphite composites provided the adsorptive capacity of exfoliated graphite and the photocatalytic capability of nano-TiO_2 simultaneously. It was shown that the removal ratios (up to 95.5%) were related to the adsorption and photocatalysis capability of the composites and were influenced by ultrasound and UV irradiation, the reaction time, the reaction temperature, the initial pH value and the initial substrate concentration. The adsorption capability was the smallest, and the adsorption and photocatalysis capability in the presence of US irradiation was smaller than the one in the presence of US and UV irradiation.

A study performed by Wang et al. (2008) focused on the treatment of wastewater from a surfactant detergent plant, containing linear alkylbenzene sulfonate (LAS) and abundant sulfate by Fenton oxidation and aerobic biological processes. Working at an initial pH value of 8, a Fe^{2+} dosage of 600 mg/L and a H_2O_2 dosage of 120 mg/L, the COD and LAS concentration were decreased from 1,500 and 490 mg/L to 230 and 23 mg/L after 40 min of Fenton oxidation, respectively. Fenton reagent was very effective at enhancing the biodegradability of this kind of wastewater as assessed in an immobilized biomass reactor with a hydraulic detention time of 20 h. It was found that the COD and LAS contents of the final effluent were less than 100 and 5 mg/L, corresponding to an overall removal efficiency of over 94% and 99%, respectively.

Cellulose and paper pulp factories utilize a large amount of water generating several undesirable contaminants. Boroski et al. (2008) investigated the efficiency of electrocoagulation-flotation (EC) method followed by photocatalysis to treat such wastewater. By applying 30 min of EC/Fe^0, 153 A m^{-2} and pH 6, the COD values, UV-Vis absorbance and turbidity decreased considerably. The duration of electrochemical treatment could be reduced for 30–10 min achieving comparable efficiency if 5 g/L of NaCl were added. The subsequent photocatalytic treatment was performed with 0.25 g/L TiO_2, 50 mmol/L hydrogen peroxide at pH 3 and gave after 4 hours of treatment 84% COD reduction compared to that of the initial effluents collected after the pulp bleaching process unit stage which applied ozone treatment and 64% compared to that of the EC treated samples showing that the proposed sequence is very helpful to improve effluent quality.

Ma and Xia (2009) examined the efficiency of Fenton process followed by coagulation for the treatment of wastewater from a water-based printing ink plant. Eighty six percent of color and 92% of COD could be removed at pH 4, 50 mg/L H_2O_2, 25 mg/L $FeSO_4$ and 30 min settling time, but this was accompanied by only 46% suspended solids removal. Therefore, the Fenton-treated effluent was further subjected to coagulation using a mixture of polyaluminium chloride and ferrous sulfate, thus leading to overall removal values of 100%, 93% and 87% for color, COD and solids respectively.

The performance of a full-scale treatment plant, for the wastewater produced at jean clothes wash processes, at a textile production plant, was investigated by Wang et al. (2008). The combined process consisted of chemical coagulation, hydrolysis/acidification and Fenton oxidation. Chemical coagulation treatment with polymeric ferric sulfate/lime alone proved to be effective in removing COD by 70% and color by 50% from the effluent. However, when coagulation was coupled to subsequent acidification and Fenton oxidation, average removal efficiencies for COD, BOD, SS, color and aromatic compounds were between 90% and 97%, with the average effluent having 58 mg COD/L, 19 mg BOD_5/L, 4 mg SS/L and 15 color units (standard dilution multiple method), consistent with the set discharge limits for textile wastewater.

The applicability of Fenton's oxidation to improve the biodegradability of a pharmaceutical wastewater was investigated by Tekin et al. (2006). The wastewater was originated from a factory producing a variety of pharmaceutical chemicals. Laboratory-scale studies were conducted first to evaluate the treatability of the various pharmaceutical chemicals produced in the factory. At an H_2O_2/Fe^{2+} ratio of 155 (0.3 M H_2O_2 and 0.002 M Fe^{2+}), initial COD in the range 900–7,000 mg/L and acidic conditions, COD removal by Fenton oxidation was 45–65% for the various chemicals studied. Following these preliminary studies, a full-scale plant was built comprising Fenton pre-treatment and biological post-treatment in two sequencing batch reactors of 8 m^3 each operating at a total cycle time of 1 day. The overall COD removal for the combined process was 98%, in compliance with local discharge limits and the BOD_5/COD ratio of the wastewater was increased by about 3–5 times.

Three different wastewater samples from a pharmaceutical plant formulating medical ointments were treated onsite by adsorption/flocculation/filtration processes yielding effluents with poor characteristics that could not meet environmental standards for discharge to the local sewerage (Kulik et al. 2008). The main components of the effluents such as active agents and formulation additives were: adder's venom, camphor, oil of turpentine, salicylic acid, petroleum jelly, cetostearyl alcohol, and paraffin for effluent I, camphor, dimethyl sulfoxide, oil of turpentine, benzyl nicotinate, vanillyl nonamide, cetostearyl alcohol and bronopol for effluent II and benzyl benzoate, carbomer, bronopol and methylparaben for effluent III. The pre-treated samples were then subjected to Fenton oxidation with optimal conditions including a H_2O_2/COD mass ratio of 2:1, a H_2O_2/Fe^{2+} molar ratio of 10:1 and 2 h of treatment time. Fenton-treated samples were then added alkali to precipitate iron from the liquid phase, as well as facilitate the subsequent lime coagulation. Combination of Fenton oxidation and lime coagulation proved capable of improving considerably COD removal, as well as enhancing the aerobic biodegradability of the effluent as assessed by the BOD_7/COD ratio. Under the most favourable treatment conditions for example, the residual COD was 535, 325 and 610 mg/L starting from 4,000, 5,400 and 13,130 mg/L for the pre-treated samples for effluent I, II and III respectively.

The TOC removal from the wastewater from the secondary clarifier of an industrial and domestic wastewater treatment plant was studied by means of ozone oxidation in alkaline conditions (pH~8) and ozonation coupled with hydrogen peroxide. In the absence of hydrogen peroxide, a TOC decay of about 15% was obtained after 1 h, 80% of which took place during the first 5 min of reaction. On the other hand, by injecting pulses of hydrogen peroxide (0.15 mL of H_2O_2 30% w/v in a 5-L reactor every 5 min), the degree of mineralization reached an average value of over 90% (Rosal et al. 2008). A kinetic model based on TOC and ozone concentration profiles was developed and accounted for both mechanisms of ozone oxidation, i.e. indirect oxidation through $HO^•$ and direct attack. A group of 33 organic compounds, mainly pharmaceuticals and some relevant metabolites present in the wastewater effluents, were analyzed before and after the treatment. Alkaline ozonation and O_3/H_2O_2 treatments yielded high removal efficiencies for pharmaceuticals whose concentrations in wastewater ranged between 3 and 2,100 ng/L with a total concentration of 10 mg/L. After 5 min, removal efficiencies were over 99% for most compounds irrespective of the use or not of hydrogen peroxide. Only fluoroquinolones and fluoxetine were relatively resistant to ozonation with removal in the 90–95% range. The total concentration of the analyzed pharmaceuticals after 10 min reached, for the most unfavorable conditions less than 0.5% of the initial load.

In a similar fashion, Benner et al. (2008) demonstrated that ozonation was capable of destroying several pharmaceuticals found in the feed and the concentrate from a reverse osmosis unit treating effluents destined for drinking water production.

21.2.1 Advantages and Disadvantages of the Application of Advanced Oxidation Processes

AOPs demonstrate a number of advantages in comparison to conventional physical, chemical and biological treatments including fast reaction rates, possible elimination of toxicity and other adverse effects, ability to achieve very high removal of total organic carbon and ability to tackle several different pollutants at the same time due to their non-selective character. Unlike separation processes typically employed in wastewater treatment (e.g. adsorption, coagulation, filtration, sedimentation, etc.), AOPs are destructive techniques and do not simply transfer pollution from one phase to another. Although they may generate sludge (due to e.g. precipitation of homogeneous catalysts), the amount is considerably lower than that produced by conventional biological processes. On the other hand, AOPs may be energy-intensive technologies and sometimes their complex chemistry must be tailored to the needs of the specific application. Other drawbacks include the need to remove extra chemicals like oxidants and catalysts that are employed to enhance process efficiency prior to effluent disposal. The latter is one of the major drawbacks of TiO_2 photocatalysis in real-scale applications.

In recent years, several publications have dealt with TiO_2 separation from slurry photocatalytic processes. Kagaya et al. (1999) employed aluminium chloride as a coagulant to remove catalyst particles from a photocatalytic suspension at 1 g/L TiO_2 concentration. Coagulation at alkaline conditions led to 93% solids removal after 60 min of settling time. However, the remaining suspended fraction is still high enough and has to be removed from the treated effluent. Geissen et al. (2001) showed that a sludge blanket type clarifier could efficiently separate the catalyst from the slurry, at a relatively low surface loading rate and high catalyst concentration. Nonetheless, they concluded that only membrane filtration could guarantee the complete retention of the TiO_2, as well as rejection of microorganisms and high molecular weight compounds.

Microfiltration offers high separation performance and operational simplicity, thus lends itself to resolve the slurry separation problem. Microfiltration can act as a barrier to confine the catalyst in the system, increase the residence time of pollutants, or if coated with catalyst, simultaneously provide treatment and separation. Sopajaree et al. (1999) presented a hybrid batch-recirculating photoreactor in combination with cross-flow ultrafiltration that achieved efficient catalyst retention and recycling. Xi and Geissen (2001) evaluated a bench-scale cross-flow microfiltration system to separate TiO_2 from clean water. They found that system performance was strongly affected by the operational parameters and the process was extremely sensitive to pH and to electrolyte concentration. The authors also discussed the importance of membrane material selection, since erosion could pose problems at higher cross-flow velocities. Immersed (or submerged) membrane systems have much smaller (by an order of magnitude) pumping energy requirements than cross-flow systems and have become increasingly affordable in recent years. The use of immersed hollow fiber microfiltration membranes for TiO_2 separation was examined by Thiruvenkatachari et al. (2005). They used a pilot-scale photocatalytic reactor to remove bisphenol-A from water. The effluent suspension had 1 g/L TiO_2 concentration and it was treated with a multi-step process. The process train comprised gravity settling after pH adjustment, clarification with ferric chloride, and finally microfiltration of the clarified effluent. Erdei et al. (2008) proposed a hybrid process comprising continuous slurry TiO_2 photocatalysis and an immersed hollow fiber membrane micro-ultrafiltration unit. The photocatalytic reactor charged with 1 g/L TiO_2 removed 63% of dissolved organic carbon from a synthetic wastewater (representing biologically treated sewage effluent). The addition of 0.05 g/L of powdered activated carbon increased removal to 76%. The immersed membrane module was then employed to retain the catalyst in the reactor, thus yielding a solids-free effluent. Membrane feed pre-treatment with pH adjustment and particle charge neutralization with aluminium chloride improved critical membrane fluxes and organic carbon removal. The complete treatment train achieved up to 92% dissolved carbon reduction with 12 mg/L of aluminium chloride using in-line coagulation conditions, thus demonstrating an effective hybrid system for advanced water and wastewater treatment.

In slurry photocatalytic reactors, the need for a filtration unit to remove catalyst particles seems unavoidable, thus complicating the engineering of the process. Moreover, it is often difficult, in practice, to filter the finest catalyst particles from the effluent, thus causing downstream turbidity. In this respect, an alternative to slurry reactors is the use of immobilized TiO_2 in photocatalytic reactors. The advantage of such systems is obvious, i.e. the catalyst remains fixed in the reactor; however, this set-up may suffer other drawbacks such as (a) decreased performance due to serious external mass transfer limitations (that do not usually exist in slurry reactors) and (b) progressive abrasion of the catalyst (Balasubramanian et al. 2004).

21.3 Introduction to Solar-Driven Advanced Oxidation Processes

The use of AOPs for wastewater treatment has been studied extensively, but generation of UV radiation by lamps or ozone production is expensive. So, future applications of these processes could be improved through the use of catalysis and solar energy. Therefore, research is focusing more and more on those AOPs which can be driven by solar irradiation, photo-Fenton and heterogeneous catalysis with UV/$TiO_{2.}$

The heterogeneous solar photocatalytic detoxification process consists of making use of the near-ultraviolet (UV) band of the solar spectrum (wavelength shorter than 400 nm), to photo-excite a semiconductor catalyst in contact with water and in the presence of oxygen. Under these circumstances, oxidizing species, either bound $HO^{\bullet}$ or free holes, react with oxidizable contaminants. With a typical UV-flux near the surface of the earth of 20–30 W/m^2 the sun puts 0.2–0.3 mol photons m^{-2} h^{-1} in the 300–400 nm range at the process disposal. Although there are many different sources of TiO_2, Degussa P25 TiO_2 has effectively become a standard (Serpone et al. 1996) because it has (a) a reasonably well defined nature (i.e. typically a 70:30 anatase:rutile mixture, non-porous, BET surface area 55 ± 15 m^2/g, average particle size 30 nm) and (b) a substantially higher photocatalytic activity than most other readily available (commercial) TiO_2. Other semiconductor particles, e.g., CdS or GaP absorb larger fractions of the solar spectrum and can form chemically activated surface-bond intermediates, but unfortunately, these photocatalysts are degraded during the repeated catalytic cycles involved in heterogeneous photocatalysis generating toxic dissolved heavy metals in water.

For the treatment of industrial wastewater Fenton and Fenton-like processes are probably among the since longest and most applied advanced oxidation processes (Legrini et al. 1993; Suty et al. 2004; Pignatello et al. 2006) and first proposals for wastewater treatment applications were reported in the 1960s of the past century (Neyens and Baeyens 2003). Several classical works report on the chemistry of the Fenton process (Haber and Weiss 1934; Walling 1975) and a radical mechanism is generally accepted today, whereas the exact mechanism and the nature of the actual oxidizing species are still under discussion (Bossmann et al. 1998; Pignatello et al. 1999). Quite recent reviews give good overviews of the Fenton chemistry (Neyens and Baeyens 2003; Pignatello et al. 2006).

Yet, it was not until the early 1990s of the last century, when the discoveries of scientists working in the field of environmental sciences published results on the role of iron in atmospheric chemistry (Zepp et al. 1992), which called the attention of scientists and engineers working in the wastewater treatment field. Soon afterwards, the first reports of the application of the photo-Fenton process (or photoassisted/light enhanced Fenton process) in wastewater treatment were published by the groups of Pignatello, Lipcznska-Kochany, Kiwi, Pulgarín and Bauer (Pignatello et al. 2006). The primary step of the photoreduction of dissolved ferric iron is a ligand-to-metal charge-transfer reaction. Subsequently, intermediate complexes dissociate by means of irradiation forming Fe^{+2}. The ligand can be any Lewis base able to form a complex with ferric iron (HO^-, H_2O, R-COO-, R-OH, $R\text{-}NH_2$ etc.). Depending on the reacting ligand, the product may be a hydroxyl radical such as in Eq. 21.1 or another radical derived from the ligand. The direct oxidation of an organic ligand is possible as shown for carboxylic acids in Eq. 21.2.

$$[Fe(OH)]^{2+} + hv \longrightarrow Fe^{2+} + HO^{\bullet} \tag{21.1}$$

$$[Fe(OOC-\ R)]^{2+} + hv \rightarrow Fe^{2+} + CO_2 + R^{\bullet} \tag{21.2}$$

Depending on the ligand the ferric iron complex has different light absorption properties and consequently, the pH plays a crucial role in the efficiency of the photo-Fenton reaction, because it strongly influences which complexes are formed. Thus, pH 2.8 was frequently postulated as an optimum pH for photo-Fenton treatment (e.g. Pignatello 1992; Safarzadeh-Amiri et al. 1996), because at this pH precipitation does not take place yet and the dominant iron species in solution is $[Fe(OH)]^{2+}$, the most photoactive ferric iron – water complex.

21.3.1 Solar Devices

Since 1990 there has been a clarification of the kind of solar technology, which should be involved, in solar AOPs. The question was if it is necessary to concentrate the radiation for the photocatalysis technology and if a non-concentrating collector can be as efficient as concentrating ones. The reason of using one-sun systems for water treatment is firmly based on two factors, first the high percentage of UV photons in the diffuse component of solar radiation and second the low order dependence of rates on light intensity. For many of the solar detoxification system components (Blanco-Gálvez and Malato-Rodríguez 2003), the equipment is identical to that used for other types of water treatment and construction materials are commercially available. Most piping may be made of polyethylene or polypropylene, avoiding the use of metallic or composite materials that could be degraded by the oxidant conditions of the process. Neither must materials be reactive, interfering with the photocatalytic process. All materials used must be inert to degradation by UV solar light. Photocatalytic reactors must transmit UV light efficiently because of the process requirements. The choice of materials that are both transmissive to UV light and resistant to its destructive effects is limited. Common materials that meet these requirements are fluoropolymers, acrylic polymers and several types of glass. Borosilicate glass has good transmissive properties in the solar range with a cut-off of about 285 nm. Therefore, such a low-iron-content glass would seem to be the most adequate. With regard to the reflecting/concentrating materials, aluminium is the best option due to its low cost and high reflectivity in the solar UV spectrum on earth surface.

The original solar photoreactor designs for photochemical applications were based on line-focus parabolic-trough concentrators (PTCs) (Dillert et al. 1999). But there is a category of low concentration collectors, called Compound Parabolic Concentrators (CPCs), that are a good option for solar photochemical applications (Ajona and Vidal 2000). If the CPC is designed for an acceptance angle of +90° to −90°, all incident solar diffuse radiation can be collected (Fig. 21.2). The light reflected by the CPC is distributed all around the tubular receiver so that almost the entire circumference of the receiver tube is illuminated.

21.3.2 Target Compounds and Applications

In general, the types of compounds that have been degraded by solar photocatalysis include any type of organics (Malato et al. 2007a). Special attention has recently been given the so called ‘emerging contaminants’, mostly unregulated compounds that may be candidates for future regulation depending on research on their potential effects on health and monitoring data regarding their occurrence. Particularly relevant examples of such emerging compounds are those which do not need to persist in the environment to cause a negative effect, because their high transformation/removal rates can be compensated by their continuous introduction into the environment (Petrović et al. 2003). The solar photocatalytic degradation of these

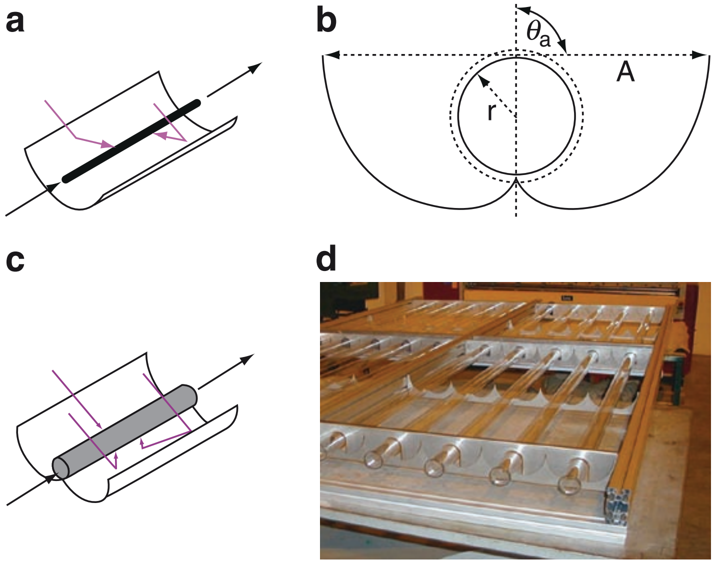

Fig. 21.2 Design concepts for solar water photocatalytic reactors: (**a**) concentrating (parabolic trough), (**b**) compound parabolic collector, (**c**) schematic drawing of CPC with a semi-angle of acceptance of 90°, (**d**) photographs of compound parabolic collector during fabrication

new environmental contaminants (pharmaceuticals, antibiotics, analgesics, steroids, hormones, MTBE, etc; and their hydrolysis/photolysis metabolites) many until recently unknown, is the focus of much research (Dalrymple et al. 2007).

Until now, the absence of total mineralization has been observed only in s-triazine herbicides, for which the final product obtained was essentially 1,3,5-triazine-2,4,6, trihydroxy (cyanuric acid), which is, fortunately, nontoxic. This is because the triazine nucleus is so highly stable that it resists most methods of oxidation. Cl^- ions are easily released into the solution from chlorinated molecules. Nitrogen-containing molecules are mineralized mostly into NO_3^- and NH_4^+. Ammonium ions are difficult to oxidize, and the proportion depends mainly on the oxidation stage of organic nitrogen and irradiation time (Calza et al. 2005). Organophosphorous contaminants produce phosphate ions. However, in the pH range used (usually < 4), phosphate ions remain adsorbed on TiO_2. This strong adsorption somewhat inhibits the reaction rate, though it is still acceptable. In photo-Fenton, phosphate sequestrates iron forming the corresponding non-soluble salt and retarding the reaction rate. Therefore, more iron is necessary when water-containing phosphates is treated by photo-Fenton. Until now, the analyses of fragments resulting from the degradation of the aromatic ring have revealed formation of aliphatics (organic acids and other hydroxylated compounds), which explains why total mineralization takes much longer than dearomatization, as mineralisation of aliphatics is the slowest step (Agüera et al. 2005) Special attention has recently been given to the ‘emerging contaminants’ (Kosjek and Heath 2008).

21.3.3 Solar Heterogeneous Applications

The first outdoor engineering-scale reactor (2 m^3) developed (in 1990) related with solar driven AOPs was a converted solar thermal parabolic-trough collector in which the absorber/glazing-tube combination had been replaced by a simple Pyrex glass tube through which contaminated water could flow (Goswami 1997). Since that time, research all over the world has advanced a number of reactor concepts and designs, including CPCs and non-concentrating reactors (Malato et al. 2007b), as parabolic-trough concentrators are not the best option.

Biologically pretreated industrial wastewaters have been treated from the car factories at Wolfsburg (Germany) and Taubaté (Brazil) of the Volkswagen AG in laboratory and bench-scale experiments. The initial values of the COD and the TOC were determined to vary between 69.5 and 21.1 mg L^{-1} and 26.9 and 7.3 mg L^{-1}, respectively. The results of the experiments were so promising, that a pilot plant was installed in the Wolfsburg factory during the summer 1998. The flowsheet of a more recent version of this pilot plant, which was installed in 2000, has been recently published (Bahnemann 2004). Another pilot plant, financed by the European Commission, has been built at the site of a textile factory in Tunisia (Menzel Temime). The TFFBR (Thin Film Fixed Bed Reactor) was chosen because previous studies showed sufficient degradation rates with the selected textile wastewater in combination with its simple, low cost construction and the low energy consumption (Bousselmi et al. 2004). Under the 'SOLARDETOX' project (financed by the EC-DGXII through the Brite Euram III Program, 1997–2000) a full-size demonstration plant was erected based on CPCs, with a concentration ratio = 1 (Malato et al. 2002). This plant was designed to treat 1 m^3 of water contaminated with 100 m^2 of collector aperture area.

21.3.4 Solar Homogeneous Applications

Recently (2004) a new CPC-based plant has been installed. In the area of El Ejido, a town in the province of Almería in southern Spain, intensive agriculture in 400 km^2 of greenhouses consumes approximately 2.0 million plastic bottles of pesticide per year. So far, these empty plastic bottles have simply been disposed as normal waste, being a toxic residue. The solution is to selectively collect these containers for recycling. Before the plastic can be recycled, it must be washed and the water used for that process becomes polluted by the pesticides. This water must be treated before it is discharged or re-used. It is in the detoxification of this water that Solar Photocatalysis intervenes (Malato et al. 2007a). The plant has been constructed to treat 1.6 m^3 of contaminated water with 150 m^2 of collector aperture area. Treatment time is around 3 h. Operation is fully automatic and maintenance requirements are minimum.

Fig. 21.3 Views of the solar collector field of the hybrid solar photocatalytic-biological plant developed in CADOX Project (http://www.psa.es/webeng/projects/cadox)

The last step in solar photocatalytic treatment plants has been a hybrid solar photocatalytic-biological plant with a 4 m^3 daily treatment capacity. It consists of a solar photo-Fenton reactor with 100 m^2 of Compound Parabolic Concentrators, and an aerobic biological treatment plant based on an immobilised-biomass activated-sludge reactor (1 m^3). This plant treats a highly saline industrial wastewater containing around 600 mg/L of a non-biodegradable compound (α-methylphenylglycine) and 400–700 mg/L total organic carbon (Fig. 21.3). The purpose of this treatment strategy was to achieve sufficient biodegradability of the photo-oxidized effluent to allow its discharge into the biotreatment.

21.4 Applications of Advanced Oxidation Processes in Drinking Water Treatment

Conventional drinking water treatments such as coagulation, sedimentation, filtration and adsorption, typically used for the treatment of surface water, may not be effective enough for the complete removal of certain classes of xenobiotics (Westerhoff et al. 2005; Hua et al. 2006; Stackelberg et al. 2007; Vieno et al. 2007). Moreover, chlorine, the most widely used oxidant/disinfectant in the treatment of groundwater and surface water, may not improve significantly the removal of these pollutants. Results from a recent study showed that 52 out of 98 xenobiotic compounds spiked in drinking water would remain nearly unchanged for as long as 10 days after chlorination at 1.2 mg/L free chlorine (Gibs et al. 2007).

In light of the inefficiency of conventional drinking water treatments in regards to the removal of xenobiotics, different AOPs were investigated over the past years aiming to (a) decrease natural organic matter (NOM) typically found in waters, thus consequently preventing or reducing the formation of disinfection by-products (DBPs) and (b) remove xenobiotics associated with micro-pollution. It should be noticed here that although AOPs may also be employed for disinfection purposes, this topic falls outside the scope of this chapter and will be not dealt with.

21.4.1 Natural Organic Matter Removal and Control of Disinfection by-Products

The formation of DBPs can be controlled by reducing NOM, which occurs in natural waters. NOM, particularly humic acids, can react with disinfectants (chlorine gas and hypochlorites) to form chlorination by-products (Nikolaou et al. 2007). Different AOPs have been investigated in regards to NOM removal and DBPs control.

The removal of humic acids by TiO_2 photocatalysis was investigated at bench scale in synthetic aqueous solutions as well as in natural waters. The effects of light intensity, photocatalyst type and loading, origin of humic substances, presence of anions, cations and metals on the removal of humic acids by TiO_2 photocatalysis have all been addressed in a recent review by Uyguner et al. (2007). Process efficiency was investigated in terms of UV absorbance (typically measured at the wavelength of 254 nm, UV_{254}), TOC and trihalomethanes formation potential (THMFP). Bekbölet and Özkösemen (1996) reported that after a 60 min irradiation time, THMFP of humic acid solutions (5–50 mg/L) can be decreased below 100 μg/L. THMFP was further decreased to about 10 μg/L during Fenton, photo-Fenton and photocatalytic processes applied to real water samples (Murray and Parsons 2004). The potential for chlorination by-products' formation in natural water samples during treatment by various oxidative and physico-chemical methods was recently investigated (Bekbolet et al. 2005) and the formation of individual trihalomethanes (THMs) and haloacetic acids was found to be NOM-site specific. TiO_2 photocatalysis was found to be effective as post-treatment of heterotrophic-autotrophic denitrification (HAD) to reduce organic matter as well as bacteria, which are the main drawbacks of the HAD process (Rizzo et al. 2008). The highest removal efficiency was obtained for photocatalyst loading of 1.5 g TiO_2/L for both the bacteria inactivation and organic matter removal while the THMFP was very low as well (<2.5 μg $CHCl_3$/L after 10 min irradiation and no THMs were detected after 30 min). Different AOPs (UV-C photolysis, UV/H_2O_2, Fenton and photo-Fenton) were investigated by Goslan et al. (2006) to reduce NOM in reservoir water. Photo-Fenton process was found to be the most effective in the removal of dissolved organic carbon (DOC) (88% removal after 1 min). Although pH 3 is reported to be the optimal pH for oxidation with Fenton and photo-Fenton processes, no significant differences were detected in terms of DOC and UV_{254} in the pH range 3–7.

Adsorption on granular activated carbon (GAC) is a conventional process for drinking water treatment, which can naturally support the growth of bacterial population. It is well known that the presence of pre-treatment by AOPs (particularly ozonation) can increase the formation of biodegradable organic matter, thus GAC unit can work as biological activated carbon (BAC) reactor which can selectively remove biodegradable organic matter and, consequently, decrease biological regrowth potential (Van der Kooij et al. 1989). UV-H_2O_2 process followed by biodegradation has been shown to have significant impact on the reduction of THMs (Speitel et al. 2000). In light of the advantages of the combined AOP-BAC treatment, Toor and Mohseni (2007) focused their subsequent work exclusively on the investigation of the synergistic benefits of combining AOPs with downstream biotreatment at reducing THM and HAA formation potentials (FP). The UV/H_2O_2 process alone was found to be effective at reducing DBPs only at UV fluencies higher than 1,000 mJ/cm^2 and initial H_2O_2 concentration of about or greater than 23 mg/L. However, the combined AOP-BAC treatment was found to significantly decrease DBPs' formation (43%), and NOM concentration (52% and 59% removal in terms of TOC and UV_{254} respectively).

The oxidative removal of NOM from waters was also investigated using hydrogen peroxide and iron-coated pumice particles as heterogeneous catalysts (Kitis and Kaplan 2007). Original pumice and peroxide dosed together provided UV absorbance reductions as high as 49%, mainly due to the presence of metal oxides including Al_2O_3, Fe_2O_3 and TiO_2 in the natural pumice. The best removals of NOM in both natural water and humic acids solution were observed when pumice was coated with iron oxides and combined with peroxide. Maximum DOC reductions obtained for humic acid solution and the natural water were 73% and 35%, respectively. The authors suggest that surface reactions between iron oxides and peroxide occurred (Fenton-like reactions), thus resulting in the formation of strong oxidants, probably $HO^{\bullet}$.

21.4.2 Removal of Xenobiotics

A lot of contaminants have been detected in surface and ground waters destined for drinking water production because of uncontrolled wastewater disposal as well as agricultural, industrial or urban activities (Sacher et al. 2001; Kolpin et al. 2002). Since a wide literature is available about the treatment of xenobiotic compounds in aqueous solutions by AOPs, the effort herein was to review the application of AOPs for the decontamination of natural waters (surface and ground waters) as well as model aqueous solutions specifically prepared to reproduce natural waters for drinking use.

As already stated, humic substances are the main constituents occurring in natural waters. Since they can interfere with AOPs when applied to remove xenobiotics from water (Ma and Graham 1999; Song et al. 2008), the investigation of the effect of humic substances is very important for evaluating the treatment efficiency of these processes. Accordingly, Ma and Graham (1999) investigated the effect of humic substances in the manganese-catalyzed ozonation of atrazine. Atrazine, a herbicide used as selective pre- and post-emergent agent to control annual grasses and broadleaved weeds in major crops, is not readily biodegradable, persists in soil and can contaminate groundwater (Guzzella et al. 2006; Barth et al. 2007; Hildebrandt et al. 2008). Ma and Graham (1999) observed that the removal of atrazine improves when the content of humic substances is quite low (e.g. 1 mg/L as DOC). However, as humic substances concentration increased, a negative effect on the catalytic oxidation of atrazine was observed. Song et al. (2008) investigated the influence of NOM on the degradation of the carbamate pesticide alachlor by UV/H_2O_2. The effects of water quality and process parameters on the oxidation kinetics were investigated as well. The UV/H_2O_2 process was found to be effective in destroying alachlor in NOM-containing water although its decomposition was significantly hindered by the presence of NOM due to high hydroxyl radical reactivity with alachlor.

Gasoline is the most common source of groundwater contamination in the USA and its most toxic components, such as benzene, toluene, ethylbenzene, and xylene

(BTEX) are among the most frequently detected contaminants in US public drinking-water systems that rely on groundwater sources (USEPA 2003). The application of AOPs for the removal of gasoline components from aqueous solutions has been reported in the literature. The removal of methyl tert-butyl ether (MTBE), aromatic and aliphatic hydrocarbons by UV-based AOPs was investigated in both synthetic solution and polluted groundwater of a petrochemical industrial site in Italy (Mascolo et al. 2008). The results showed a different order of efficiency according to the water matrix: the UV/TiO_2 treatment was the best option for the synthetic solution, while the UV/H_2O_2 process provided higher efficiency when polluted groundwater was investigated. The authors inferred that the much lower performance of UV/TiO_2 compared to UV/H_2O_2 depends on groundwater characteristics; particularly, salt content and organic dissolved matter can quench $HO^\bullet$. Finally, a preliminary operation cost evaluation was carried out (1.7 €/m^3) using, as effluent quality target, the current Italian limit for MTBE (0.01 mg/L) in groundwater remediation.

Garoma et al. (2008) investigated the removal of gasoline components, such as BTEX (initial concentration 5–10,000 μg/L), MTBE (3,000–5,500 μg/L), tert-butyl alcohol (TBA) (80–1,400 μg/L), and total petroleum hydrocarbons as gasoline (2,400–20,000 μg/L) from contaminated groundwater samples by an ozone/UV process at different ozone dosage and UV light intensity. It was found out that ozone/UV process can remove more than 99% of the initial concentration of the investigated pollutants with a net ozone consumption per mol of organic carbon (from BTEX, MTBE, and TBA) oxidized in the range of 5–60 depending on the different types of groundwater samples treated.

A conventional process for drinking water treatment such as adsorption on granular activated carbon (GAC) was compared to resin column techniques (XAD-4 and Ambersorb-563) and ozone based AOPs (UV/O_3 and UV/O_3/H_2O_2) to evaluate their effectiveness in the removal of toxic and mutagenic organic micro-pollutants from Como Lake waters (Italy) used for human consumption (Guzzella et al. 2002). The results showed a decrease of the mutagenic and toxic activities of the lake water after adsorption on GAC and resins, while AOPs were generally found out to increase these parameters. The authors did not detect any mutagenic activity only when a GAC adsorption step was performed in addition to the AOPs. Moreover, they observed a similar behavior when toxicity tests where performed.

In order to establish a database with second-order rate constants for the reactions of the selected pharmaceuticals with ozone and $HO^\bullet$, Huber et al. (2003) assessed the potential of ozonation and AOPs (at a bench scale) for the oxidation of nine pharmaceuticals, selected on the basis of consumption and environmental relevance. The experiments were performed with surface waters and ground waters under realistic treatment conditions. It was found out that, compared to other important micro-pollutants such as MTBE and atrazine, the selected pharmaceuticals reacted about two to three times faster with $HO^\bullet$. According to the authors' opinion, the second-order rate constants determined in pure aqueous solution in ozonation experiments could be applied to predict the behavior of pharmaceuticals dissolved in natural waters.

The oxidation of nine chemicals from the USEPA Drinking Water Contaminant Candidate List (CCL) by ozonation and ozone/hydrogen peroxide advanced oxidation process (O_3/H_2O_2) was investigated using batch reactors (Chen et al. 2008). Except for the thiocarbamate herbicides, all other CCL chemicals (linuron, diuron, prometon, RDX, 2,4 dinitrotoluene, 2,6-dinitrotoluene and nitrobenzene) were found to have a low reactivity towards ozone. On the opposite, all the investigated CCL chemicals but RDX were found to have a high reactivity towards $HO^{\bullet}$. What was observed is that the removal of a contaminant does not indicate that complete mineralization occurred and thus reaction intermediates may constitute a problem.

21.5 Conclusions and Perspectives

Although it is still common perception that the sustainability of AOPs to treat waters and wastewaters is eventually dictated by process economics, the water industry and policy makers may have to reconsider given the growing problem of high quality water shortage in arid and semi-arid areas in developing and developed countries, which is expected to worsen due to global climate changes. In other words, wastewater treatment plant effluents have to be considered as a resource, permitting water reuse for different purposes. The treatment of wastewaters which have been generated without application of the “cleaner production” and “waste minimization” principles is a losing game, ultimately costing all parties materials and energy resources. Therefore, drastic solutions capable of cleaning up water polluted by persistent organic and other matter and/or contaminated by infectious microorganisms may be needed. AOPs, either alone or in conjunction with other processes, can provide technically sound options to achieve this goal.

In general, solar AOPs are easy to install but still expensive to operate, i.e. due to the usage of costly chemicals like hydrogen peroxide and increased energy consumption. Moreover, it should be noted that solar AOPs are suitable for areas which are characterized by intense sunlight during the year. Cutting down treatment costs will make AOPs attractive to the water industry; a step in this direction would be the use of AOPs only as a pre-treatment to improve the biodegradability of biorecalcitrant streams, thus permitting their disposal in a conventional municipal wastewater treatment plant. In this respect, chemical oxidation for a short period of time would suffice to alter the biological and toxicological properties of the polluted stream. Avoiding severe treatment conditions can also reduce operational (and capital) costs and this is where environmental catalysis and materials science play an important role through the development of inexpensive, active, stable and recyclable catalytic materials. With the continuous increase in polluted water flows, the challenge arises to develop appropriate, innovative and integrated solutions, such that the produced effluent not only meets requirements but can also be considered as a resource. In general, solar AOPs could be applied to treat industrial wastewater containing biorecalcitrant compounds in the range of hundreds of mg/L with treatment costs ranging between €1/m^3 and €5/m^3. In the case of treating municipal wastewater effluents for eliminating small quantities (<1 mg/L) of biorecalcitrant "emerging" contaminants and disinfecting, the treatment costs could be as low as €0.1–0.3/m^3, depending on the inorganic content (CO_3^{2-}/HCO_3^-, Cl^-, SO_4^{2-}). This would permit the subsequent reuse of these effluents for irrigation. The studies discussed in this review show also the high potential of AOPs to prevent the formation of harmful DBPs as well as to remove xenobiotics from waters. In any way though, care should be taken in the use of AOPs for xenobiotics removal with regard to the formation of oxidation intermediates, which may be more toxic than the parent compounds.

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Chapter 22
Biological, Chemical and Photochemical Treatment of Commercially Important Naphthalene Sulphonates

Idil Arslan-Alaton and Tugba Olmez-Hanci

Abstract In the present work, the rather limited data available regarding the sources, concentrations and treatability of naphthalene sulphonates in biological and chemical treatment systems is discussed and reviewed. Due to the refractory nature of most commercial naphthalene sulphonates, this review focused on the application of advanced oxidation processes for their efficient degradation by providing a deeper insight into the reaction mechanisms involved and products formed in advanced chemical and photochemical oxidation of important naphthalene sulphonates.

22.1 Introduction

The main environmental problems associated with organic industrial chemicals found in wastewater discharges are strongly related to their polarity and hydrophilic nature, which enables them to travel through natural, as well as man-made concentration-elimination steps without any serious structural alteration. Due to the fact that most of these pollutants are rather resistant to biodegradation, they appear in natural waters at significant concentrations, even in the μg/L range. In this chapter, available information regarding the fate and degradability of a diverse and large group of polar organic pollutants mainly originating from industrial activities, namely naphthalene sulphonates, thereby focusing on biological and chemical treatment methods currently being applied for their elimination from water and wastewater, is comprehensively reviewed. Information about the degradation pathway and reaction products formed during application of biological, chemical and photochemical treatment processes are important to assess the fate and ecotoxicological effect of commercial naphthalene sulphonates in the environment after treatment and ultimate discharge in the environment.

I. Arslan-Alaton (✉) and T. Olmez-Hanci
Faculty of Civil Engineering, Department of Environmental Engineering,
Istanbul Technical University, 34469, Maslak Istanbul, Turkey
e-mail: arslanid@itu.edu.tr

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22.2 Industrial Significance, Sources and Fate in Natural Waters

Naphthalene sulphonates are used as precursers for sulphonated azo dyes, wetting agents, leveling agents, dispersants, optical brighteners, pesticides, ion exchange resins, pharmaceuticals and concrete plasticizers, etc. at considerably high amounts (Tan et al. 2005). In particular, their use in the production of textile industry dyes is of utmost economic importance; nowadays India and China are the main providers of azo dye synthesis raw materials (http://www.indiastat.com) and the global dye industry practically solely depends on the production rate of naphthalene sulphonates in these two countries (Arslan-Alaton et al. 2009). Recently, the production of commercially important naphthalene sulphonates such as H-acid has been limited since their discharge into receiving water bodies has led to serious environmental pollution problems in the main providing countries (Reife and Freeman 1996). This development resulted in a significant increase in the azo dye raw materials prices (http://www.chemweek.com) revealing that environmental concerns can have serious effects on industrial production and economy. Sulphonated aromatic amines can be formed during the reduction of sulphonated azo dyes under anaerobic/anoxic conditions (Lange et al. 1998). One of the main sources of sulphonated aromatic amines are sulphonated azo dye formulations used in the tannery and textile industry. It is estimated that during the dyeing process, although fixation techniques and dyeing properties have been appreciably improved recently, sulphonated dyes are fixed onto the dyed fabric at a rate of 70–90% and the remaining 10–30% end up in the exhausted dyebath (Cooper 1995). The discharge of sulphonated azo dyes does not only create aesthetic (effluent color) problems, but since their anoxic degradation products, namely aromatic amines, are potentially toxic and/or carcinogenic (Oh et al. 1997) they also impose a serious environmental risk. Besides, due to their poor lipophilicity, sulphonatd aromatic amines are considered to be less dangerous than their unsulphonated analogues (Jandera et al. 2001; Alonso et al. 2005). The fate of naphthalene sulphonates and their degradation products in the aquatic ecosystem as well as in biological treatment facilities is still not very clear since until now only limited attention has been paid towards their occurrence and degradability in treatment systems as well as in the natural environment (Jandera et al. 2001; Song et al. 2003).

It is known that the presence of at least one sulphonated group makes these compounds highly water soluble and mobile (Altenbach and Giger 1995; Jandera et al. 2004; Tan et al. 2005). Hence, after production and use in different industrial processes, naphthalene sulphonates are easily discarded into the aquatic environment and do not significantly sorb on biosludge or sediments (Zerbinati et al. 1997). It has been deduced that their concentration in European river and surface waters is detectable at ng/L to μg/L levels, whereas their concentration is relatively lower in U.S. water bodies (Tan et al. 2005). However, their actual concentrations in industrial wastewater treatment plants are much higher, in the μg/L to mg/L range (Tan et al. 2005). The major source of naphthalene sulphonates in publicly owned sewage treatment works receiving industrial wastewater is from the textile manufacturing facilities due to their intense use in textile processing activities at high concentrations. For instance, in the polyester dyeing process, the concentration of dispersing agents that are made of naphthalene sulphonate blends is in the range of 500–1,500 mg/L, leading to an ultimate concentration of these compounds of around 50–150 mg/L in the combined, total dyehouse effluent. Considering that naphthalene sulphonates are also used as wetting agents in different textile fabric preparation (cleaning, scouring and wetting) stages, the total concentration of practically nonbiodegradable and/or slowly biodegradable naphthalene sulphonates is sometimes as high as 500–1,000 mg/L (Private Communication 2008). On the other hand, the concentration of residual (unfixed) dyes that are also bearing sulphonates functional groups is much lower; typically not more than 10–50 mg/L (Private Communication 2008). Hence, the main source of naphthalene sulphonates are effluents bearing azo dye precursors (azo dye synthesis effluent) as well as fabric preparation and dye assisting chemicals (textile industry effluent).

Although naphthalene sulphonates themselves impart a low acute biotoxicity and have neither mutagenic nor carcinogenic effects, their persistence and mobility in the environment as a result of their physicochemical properties such as their high solubility in water and low octanol-water partition coefficient (Lange et al. 1998; Li et al. 2006) may cause ecological problems. Due to the deactivating nature of their sulphonated functional groupings (R-SO_3H), naphthalene sulphonates have an extremely low reactivity against electrophilic addition reactions including microbial degradation (Rieger et al. 2002). Recent studies have demonstrated that particularly their polysulphonated forms remain in the discharged effluent and receiving water bodies without undergoing any structural changes and conventional methods such as activated sludge treatment are not effective in their elimination (Lange et al. 1998; Tan et al. 2005). Their reduced forms are in most cases an even more serious environmental concern than their original forms (Chung and Cerniglia 1992). Sulphonated aromatic amines are formed from azo dyes and naphthalene sulphonates under anaerobic conditions (Oh et al. 1997). Considering that some of these sulphonated aromatic amines are toxic, mutagenic and/or even carcinogenic (Chung and Cerniglia 1992), the discharge of sulphonated azo dyes, naphthalene sulphonates and their anaerobic degradation products to receiving water bodies can have serious ecotoxicological consequences (Tan et al. 1999).

22.3 Biological Treatment of Naphthalene Sulphonates

Concerning the biodegradability of sulphonated aromatic amines, only limited data is available in the literature indicating that most of these compounds tested are not readily biodegradable, and only partial degradation can be achieved (Razo-Flores et al. 1996; Rieger et al. 2002). Depending on either their molecular structure or other physicochemical properties, naphthalene sulphonates may be degradable in biological treatment systems at very slow rates and upon acclimation (O'Neill et al. 1999;

Tan et al. 1999). For instance, the biodegradation of 3-nitrobenzenesulphonate (3-NBS) and 3-aminobenzenesulphonate (3-ABS) was examined in a laboratory-scale trickling filter by Kölbener et al. (1994). None of the sewage samples obtained from four municipal wastewater treatment plants could degrade 3-NBS or 3-ABS. In contrast, both of the sludge samples taken from two textile industry wastewater treatment plants were able to completely biodegrade 3-NBS and 3-ABS. Under certain conditions, 3-NBS biodegradation took place, even though inoculation of the biofilm with adopted sludge resulted in higher degradation efficiencies. In the absence of a readily degradable carbon source, the performance of the trickling filter was significantly inhibited for at least 1 week; thereafter, an adaptation phase was required for rapid and extensive 3-NBS degradation. Biodegradation was monitored by global environmental parameters (DOC abatement and CO_2 release) and abatement of the selected model pollutants via HPLC. The global environmental parameters indicated incomplete 3-NBS degradation, that was attributed to the presence of a biologically inert impurity (5% by weight), namely 4-NBS, found in most commercial preparations of 3-NBS.

A laboratory-scale biofilm airlift suspension (BAS) reactor was employed to treat infiltration water (COD = 700–1,300 mg/L) samples collected from the drainage wells at an industrial site highly contaminated with aromatic sulfonates (Panizza et al. 2006). The degradation of naphthalene sulphonates (3–77 mg/L) was performed with a mixed bioculture obtained from the treatment works at the factory site where the leachate originated. The biomass was adapted to the leachate for 3 months prior to the biodegradation experiments. The BAS reactor principally consists of two connected sections (riser and downcomer). Air is sparged at the bottom of the riser section and the density difference between riser and downcomer drives the liquid to circulate between the two sections due to the difference in gas hold-up. When the liquid velocity is high enough, carrier particles are suspended and re-circulated with the liquid. A three-phase separator is located at the top of the reactor. Complete degradation was obtained for most of the studied naphthalene sulfonates, whereas relatively low biodegradation efficiencies (9–42%) were obtained for those bearing two- and mainly trisulphonated naphthale functional groups.

An improvement in the degradation performance of biological processes can be achieved by increasing the sludge age and hence sludge concentration in the bioreactors. High sludge concentrations and long biomass retention times are more readily achieved in membrane bioreactors (MBRs), biofilm reactors as well as sequencing batch reactors (SBRs) than in conventional activated sludge units and these systems have been used to treat wastewater containing aromatic sulphonates. In a related study, significantly higher 1,6- and 2,7-naphthalene disulphonate (5–10 μg/L) and benzothiazole-2-sulphonate (2.5–5 μg/L) removals could be demonstrated in MBRs than in conventional activated sludge systems (De Wever et al. 2007). In the same study, 1,5-naphthalene disulphonate (5–10 μg/L) could not be degraded at all in either the MBRs (HRT = 13 h; STR < 115 days and < 623 days; VSS = 5 and 8 g/L; initial CODs = 346 and 206 mg/L) or the conventional activated sludge systems (HRT = 13 h; STR < 115 days and < 623 days; VSS = 3 g/L;

initial CODs = 346 and 206 mg/L; technical naphthalene sulphonate mixture = 300–1,000 μg/L), even upon increasing the sludge age to infinite (running the process without sludge wastage), whereas partial degradation was obtained for 1,3-naphthalene disulphonate (5–10 μg/L) in MBRs. Although MBRs could not always make a difference in the overall pollutant removal efficiencies achieved, they showed reduced lag phases of biodegradation kinetics and a stronger memory effect than conventional activated sludge systems. Finally, naphthalene sulphonate removal in MBRs also turned out to be less sensitive towards system operational variables.

Under aerobic conditions, some naphthalene sulphonates can be degraded and used as carbon and/or energy sources by specific strains. However, these bacterial isolates have a very narrow substrate range, therefore only a limited number of different sulphonates compounds were found to be degradable (Stolz 1999; Stolz et al. 2001). Steinitz (1981) demonstrated that several bacteria and fungi isolated from soils exhibited naphthalene sulfatase activity in presence of lignosulphonate and an inherent ability to release SO_4^{2-} from ester sulphate compounds. It has also been postulated in former studies (Zürrer et al. 1987) that sulphonated aromatic amines can only be used as the sulfur source if no other sulfur compound is present in the reaction medium; a quite unrealistic situation for natural and wastewater treatment systems. In addition, a non-biological removal alternative for sulphonated aromatic compounds is “autoxidation”, resulting in the formation of aesthetically undesired colored polymers (Zerbinati et al. 1997). The most important studies reporting microbial degradation of naphthalene sulphonates using specific biocultures are devoted to naphthalene-2-sulphonic acid (2-NS) and 3-nitrobenzene sulphonic acid (3-NBS). These have been comparatively provided in Table 22.1.

22.4 Chemical and Photochemical Treatment of Naphthalene Sulphonates Including Advanced Oxidation Processes

Ozonation and AOPs have recently emerged as an important class of technologies for the destructive treatment of a wide range of recalcitrant organic pollutants such as naphthalene sulphonates in water and wastewater (Legrini et al. 1993; Alvares et al. 2001; Zhou and Smith 2001; Oppenländer 2003). These treatment processes can either eliminate such pollutants completely through mineralization or convert them to the intermediates that are less harmful to human health and the aquatic environment. Methods employed in studying the treatability of naphthalene sulphonates are (a) ozonation, (b) Fenton (Fe^{2+}/H_2O_2), photo- and electro-Fenton processes, (c) electrochemical (EC) and photoelectrochemical processes, (d) ionizing radiation, (e) microwave-assisted catalytic wet air oxidation and (f) heterogeneous photocatalysis using titanium dioxide (TiO_2/UV-A). Table 22.2 presents a comprehensive summary of the studies conducted on the degradation of naphthalene sulphonates by employing ozonation and different AOPs. As is evident in Table 22.2, the discrepancies in the observed experimental data obtained in different studies

Table 22.1 Microbial degradation of naphthalene-2-sulphonic acid (2-NS) and 3-nitrobenzene sulphonic acid (3-NBS) by specific bacterial strains

Bacterial isolate	Experimental conditionsc	Main results	References
Pseudomonas sp. A3 and *Pseudomonas sp. C22*	1 mM naphthalene-2-sulphonic acid (2-NS) (208 mg/L)	Complete degradation was achieved	Brilon et al. 1981
Sphingomonas sp. BN6	1 mM 2-NS (208 mg/L)	Accumulation of toxic metabolites such as salicylaldehyde and hydroxybenzalpyruvate at 2-NS > 1 mM	Stolz 1999
Pseudomonas putida S-313	<4,500 mg/L 2-NS	2-NS is desulphurized by a monooxygenase system which incorporates molecular oxygen into phenol or naphthol products releasing the sulphur moiety as sulphite	Kahnert et al. 2000
Axenic batch cultures of the strain RMNT and mixed culture (*Bacillus-Kingella-Corynebacterium)*	100 mg/L 2-NS	2-naphthol formation varied with medium pH, dark incubation, glucose concentration and oxygenation; microbial strains desulphonated the aromatic compound, but did not utilize it as a carbon source	Ercole et al. 2005
Arthrobacter globiformis sp. 2AC and *Comamonas testosteroni sp. 4BC*	100–500 mg/L 2-NS	2-NS functioned as the sole C and energy source	Song et al. 2005
Arthrobacter globiformis and *Comamonas testosterone*	100 mg/L 2-NS; microbial support medium = GAC; empty bed contact time = 22 min; t = 120 d	A microbially conditioned GAC fixed-bed reactor containing 15 g GAC removed 100% 2-NSA from tannery wastewater without need for GAC reconditioning or replacement	Song et al. 2006
Pseudomonas sp. N-l	3-Nitrobenzene sulphonic acid (3-NBS) (3 mM) used as the sole carbon and sulphur source	Isolation of a medium with complete 3-NBS-desulphurizing and degradation capability	Locher et al. 1989
Six different inocula obtained from soils	Laboratory trickling filter with six different activated sludges	3-NBS was degraded completely. Difficulty was encountered in the acclimation period	Kölbener et al. 1994
Alculigenes sp. isolate (GA-l)	Substrate: 3-NBS (3 mM) and 500 mg/L yeast extract	Desulphonization and mineralization of 3-NBS with concomitant sulfite ion release, which was thereafter oxidized immediately to sulphate; Nitrite and nitrate ions were also detected from the early growth phase	Takeo et al. 1997

Table 22.2 Ozonation and advanced oxidation of arylsulphonates: treatment performances and reaction conditions

Ozonation			
Reference		Sánchez-Polo et al. 2002	Calderara et al. 2001, 2002
		1,3,6-Naphthalenetrisulphonic acid (NTS)	1-Napthalene sulphonic acid (1-NS) 1,5-Naphthalene sulphonic acid (1,5-NDS) 3-Nitrobenzene sulphonic acid (3-NBS)
Reaction conditions	Initial concentration	Sulphonic acid = 5.75×10^{-5}–1.73×10^{-4} M	1–10 mg/L
	pH	2, 7 and 9	3, 5, 7 and 9
	Ozone dosage	Ozone generation rate = 76 mg O_3/min	Ozone generation rate = 1 g O_3/h
	Temperature	15–35°C	20°C
Most important findings		Bimolecular ozone reaction rate constant = 6.72 M^{-1} s^{-1} at pH 2 Free radical reaction rate constant = 3.7×10^9 M^{-1} s^{-1} at pH 9	Bimolecular ozone reaction rate constants at pH 3 1-NS = 252 M^{-1} s^{-1} 1,5-NDS = 41 M^{-1} s^{-1} 3-NBS = 22 M^{-1} s^{-1}
Reference		Shiyun et al. 2002	Chen et al. (2002)
		2-Amino-1- naphthalene sulphonic acid 1-Hydroxy-7-amino-5- naphthalene sulphonic acid 6-Hydroxy-1- naphthalene sulphonic acid 6-Amino-1,4-naphthalene disulphonic acid 1-Hydroxy-6-amino-3- naphthalene sulphonic acid	2-Naphthalenesulphonate (2-NS)
Reaction conditions	Initial concentration	TOC = 100 mg/L	2-NS = 200 mg/L
	pH	Acidic pH	5.2
	Applied ozone dose	5.56 mg min^{-1} L^{-1} (aqueous phase)	11–44 mg/L
	Temperature	31°C	Ambient
Most important findings		Complete parent compound removal after 2 h	Complete removal after 30 min at an ozone dose of 11 mg/L Complete removal after 10 min at an ozone dose of 44 mg/L

(continued)

Table 22.2 (continued)

Ozonation			
Reference		Gehringer et al. 2006	
		Naphthalene-1,5-disulphonic acid (1,5-NDSA)	
Reaction conditions	Initial concentration	30 mg/L	
	pH	7.5	
	Ozone dose	55 mg/L	
	Temperature	–	
Most important findings		99% 1,5-NDSA removal	
Direct UV-C photolysis			
Reference		Sánchez-Polo and Rivera-Utrilla 2006	
		1-Naphthalenesulphonic (NS)	
		1,5-Naphthalenedisulphonic (NDS)	
		1,3,6-Naphthalenetrisulphonic (NTS)	
Reaction conditions	Initial concentration	25 mM	
	pH	7	
	UV source	Medium-pressure mercury lamp	
	Temperature	25°C	
Most important findings		Quantum yield (F) values	
		NS = 0.019	
		NDS = 0.008	
		NTS = 0.002	
Fenton and electro-fenton processes			
Reference		Swaminathan et al. 2003	Panizza and Cerisola 2001
		1-Amino-8-naphthol-3,6-disulphonic acid (H-acid)	Regeneration wastewater of ion-exchange resin towers by a chemical industry containing naphthalene- and anthraquinone-sulphonic acids
Reaction conditions	Initial concentration	250 mg/L	COD = 1,361 mg/L

	pH	3	4
	Fe^{2+} concentration	10–25 mg/L	3 mM
	H_2O_2 concentration	400–500 mg/L	
	Electrode type	–	Graphite cathodes
Most important findings		Complete COD removal after 2h	87% and 89% COD and color removal, respectively
Heterogeneous photocatalysis (TiO_2/UV-A)			
Reference		Yu et al. 1998	Mohanty et al. 2005
		1-Amino-8-naphthol-3,6-disulphonic acid (H-acid)	1-Amino-8-naphthol-3,6-disulphonic acid (H-acid)
Reaction conditions	Initial concentration	50 mg/L	50–150 mg/L
	pH	4–8	6.8
	Catalyst concentration	3 g/L	1 g/L
	Catalyst type	TiO_2	TiO_2
	UV source	30 W low-pressure mercury vapor lamp	400 W medium-pressure mercury vapor lamp
Most Important Findings		90% removal after 5h	70–90% reduction in COD after 5 h
Heterogeneous photocatalysis (TiO_2/UV-A)			
Reference		Sánchez-Polo and Rivera-Utrilla 2006	Fabri et al. 2005
		1,3,6-Naphthalenetrisulphonic (NTS)	3-Hydroxy-2-naphthoic acid (2,3-BON)
			1,5-Naphthalenedisulfonic acid disodium salt (1,5-NDS)
			1,3,6-Naphthalenetrisulfonic acid trisodium salt hydrate (1,3,6-NTS)
			6-Amino-4-hydroxy-2-naphthalenesulfonic acid (6-A-4-H-2-NS)
			2,6-Naphthalenedisulfonic acid disodium salt (2,6-NDS)
Reaction conditions	Initial concentration	25 mM	0.3 mM

(continued)

Table 22.2 (continued)

Ozonation			
	pH	7	–
	Catalyst concentration	10 mg/L	1 g/L
	Catalyst type	Carbon aerogels doped with transition metals (Co(II), Mn(II) and Ti(IV))	TiO_2
	UV source	Medium-pressure lamp	1,500 W Xenon arc lamp equipped with a 340 nm cut-off filter
Most important findings		Complete NTS removal after 21 min	Complete mineralization after 2,3-BON = 40 min 1,5-NDS = 60 min 1,3,6-NTS = 40 min 6-A-4-H-2-NS = 60 min 2,6-NDS = 120 min
Reference		Noorjahan et al. 2003	
		1-Amino-8-naphthol-3,6-disulphonic acid (H-acid)	
Reaction conditions	Initial concentration	0.1 mM	
	pH	5	
	Catalyst concentration	3 g/L	
	Catalyst type	TiO_2	
	UV source	250 W mercury arc lamp	
Most important findings		100% and 41% removals for H-acid and COD after 5h, respectively	
Electrochemical methods			
Reference		Panizza et al. 2006[a]	Socha et al. 2005
		Naphthalene-1,5-disulfonic acid (1–5 NDS) 2-Aminonaphthalene-5,7-disulfonic acid (2-NH_2-5,7-NDS) 2-Hydroxynaphthalene-3,6,8-trisulfonic acid (2-OH-3,6, 8-NTS)	1-Amino-8-naphthol-3,6-disulphonic acid (H-acid)

Reaction conditions	Initial concentration	1–5 NDS = 5.3 mg/L 2-NH_2-5,7-NDS = 2.9 mg/L 2-OH-3,6,8-NTS = 8.3 mg/L	1×10^{-3} to 8×10^{-3} M
	pH	–	0.6, 7.0, 12.5
	Electrode types	Boron-doped diamond (anode) Stainless-steel (cathode)	Platinum or titanium covered with TiO_2/RuO_2 (anode) platinum (cathode)
	Current density	200 A/m^2	2.0×10^{-2} A/cm^2
Most important findings		Complete parent compound removal	18% and 36% removals for TOC and COD, respectively
Photoelectrochemical oxidation			
Reference		Socha et al. 2005	Socha et al. 2006
		1-Amino-8-naphthol-3,6-disulphonic acid (H-acid)	1-Amino-8-naphthol-3,6-disulphonic acid (H-acid)
Reaction conditions	Initial concentration	1×10^{-3} to 8×10^{-3} M	1×10^{-3}–8 to 10^{-3} M
	pH	0.6, 7.0, 12.5	3
	Electrode type	Platinum or titanium covered with TiO_2/RuO_2 (anode) Platinum (cathode)	Platinum or titanium covered with TiO_2/RuO_2 (anode) platinum (cathode)
	Current density	2.0×10^{-2} A/cm^2	1.0×10^{-3} A/cm^2
	UV source	8 × 35 W lamps	8 × 35 W lamps
Most important findings		40% and 58% removals for TOC and COD, respectively	49% and 68% removals for TOC and COD after 4 h, respectively
H_2O_2/UV-C			
Reference		Our own study[b]	
		1-Amino-8-naphthol-3,6-disulphonic acid (H-acid) 1-Amino-8-naphthol-4,6- disulphonic acid (K-acid) 2-Amino-5-naphthol-7-sulphonic acid (J-acid)	
Reaction conditions	Initial concentration	COD equivalent of 450 mg O_2/L for H-acid and K-acid COD equivalent of 400 mg O_2/L for J-acid	

(continued)

Table 22.2 (continued)

Ozonation		
	pH	5.9
	Initial H_2O_2 concentration	60 mM
	Incident photon flux	1.6×10^{-5} Einstein L^{-1} s^{-1}
	UV source	40 W low-pressure, mercury vapor sterilization lamp
Most important findings		Parent compound degradation rates in decreasing order: H-acid = 0.017 min^{-1} J-acid = 0.014 min^{-1} K-acid = 0.006 min^{-1}

[a] The experiments were performed on the infiltration water collected at an industrial site

[b] Arslan-Alaton et al. 2009

for the same treatment process are due to differences in the applied experimental (reaction) conditions and the analyzed parameters. A large variation in the initial naphthalene sulphonate concentration, which is one of the main process parameters affecting advanced oxidation efficiency and kinetics, is also obvious. In a large majority of the reviewed articles the degradation of naphthalene sulphonates at much higher concentrations than detected in the natural waters was studied. However, much higher values are encountered in industrial process effluent streams. The difficulty of working with ng/L – μg/L concentration levels to simulate natural waters is due to the application conditions convenient for AOPs (recommended application range: mg/L levels) and the limitations in available analytical instrumentation because of detection limits.

22.5 Identification of Advanced Oxidation Products and Degradation Pathway

One of the major concerns of organic matter degradation by AOPs are the advanced oxidation intermediates and end-products. Only few of the published research dealing with the advanced oxidation of naphthalene sulphonates was coupled with a qualitative and/or quantitative byproduct analysis. In our own study (Arslan-Alaton et al. 2009) H_2O_2/UV-C treatment of three commercially important naphthalene sulphonates (namely H-acid, K-acid and J-acid) was investigated at varying initial H_2O_2 concentrations. Parent compound (naphthalene sulphonate) abatement during photochemical treatment was followed via HPLC, whereas organic carbon removals were measured as changes brought about in the collective parameters COD and TOC. The efficiency of H_2O_2/UV-C treatment was also evaluated by following specific H_2O_2 consumption rates throughout the experiments, and photodegradation products were qualitatively traced by HPLC/MS. It could be established that all studied naphthalene sulphonates were rather resistant to photochemical degradation and the progress of advanced oxidation was rather slow. A positive correlation existed between TOC abatement and H_2O_2 consumption rates. HPLC/MS analysis revealed that H_2O_2/UV-C treatment of the selected naphthalene sulphonates followed a $HO^{\bullet}$-addition mechanism as mainly hydroxylated photodegradation products could be qualitatively identified. A detailed list of the scientific literature devoted to the identification of advanced oxidation products of naphthalene sulphonates including our own experimental findings is given in Table 22.3. On the other hand, the toxicity of the advanced oxidation intermediates or end-products of naphthalene sulphonates has not been investigated so far. However, a few case studies reported an increase in the BOD values as well as BOD/COD ratios (accepted as a rough indicator of biodegradability) of chemically pre-treated naphthalene sulphonates (Breithaupt et al. 2003; Noorjahan et al. 2003). From the above mentioned experimental results it can speculatively be concluded that no biotoxic/inhibitory degradation intermediates were formed during the treatment of naphthalene sulphonates with AOPs.

Table 22.3 Identified oxidation byproducts of naphthalene sulphonic acids

Applied treatment process	Model naphthalene sulphonate	Oxidation products	References
Ozonation	1-Naphthalene sulphonic acid 1,5Naphthalene disulphonic acid 3-Nitrobenzene sulphonic acid	Fumaric acid; maleic acid; oxalic acid; formic acid	Calderara et al. 2001
Ozonation	Naphthalene-1,5-disulphonic acid	$C_8H_5O_5S$; oxipine; sulphophthalic acid	Breithaupt et al. 2003
Ozonation	2-Naphthalenesulfonate	4-Sulfo-o-phthalaldehyde Peroxycyclic benzenesulfonic acid 4-Sulfo-ophthalaldehydic acid	Chen et al. 2002
Heterogeneous photocatalysis (TiO_2/UV-A)	1-Amino-8-naphthol-3,6-disulphonic acid (H-acid)	Hydroxylated intermediates; Phenol; Benzoquinone Benzoic acid	Noorjahan et al. 2003
Photoelectrochemical treatment (electrode covered with TiO_2/RuO_2)	1-Amino-8-naphthol-3,6-disulphonic acid (H-acid)	4-Hydro-4,8-dihydroxy-1-iminonaphthalene-3,6-disulphonic acid 8-Hydroxy-1-imino-4-oxynaphthalene-3,6-disulphonic acid or 4-Hydro-4,8-dihydroxy-1-oxynaphthalene-3,6-disulphonic acid	Socha et al. 2006
Combined photocatalysis and ozonation processes ($TiO_2/UV/O_3$)	1-Amino-8-naphthol-3,6-disulphonic acid (H-acid)	1-Amino-5,7,8-trihydroxynaphthalene-3,6-disulfonic acid 1-Amino-2,4,5,8-tetrahydroxynaphthalene-3,6-disulfonic acid 8-Hydroxy-1,2-naphthoquinone-3,6-disulfonic acid 8-Hydroxy-1,4-naphthoquinone-3,6-disulfonic acid	Sun et al. 2008
H_2O_2/UV-C	1-Amino-8-naphthol-3,6-disulphonic acid (H-acid)	1-Amino-5,8-dihydroxy-naphthalene-3,6-disulfonic acid	Our own study[a]
H_2O_2/UV-C	1-Amino-8-naphthol-4,6-disulphonic acid (K-acid)	2-Amino-naphthol-3,6,8- trisulphonic acid 2-Amino-1,4-dihydroxy naphthalene-3,6,8- tri sulphonic acid	Our own study[a]
H_2O_2/UV-C	2-Amino-5-naphthol-7-sulphonic acid (J-acid)	3,7-Dihydroxy-naphthalene-sulfonic acid 1-Amino-2,6-dihydroxy-naphthalene-4-sulfonic acid 1,4-Naphthaquinone	Our own study[a]

[a] Arslan-Alaton et al. 2009

22.6 Conclusions and Recommendations

The work presented herein indicates that naphthalene sulphonates can be treated at high removal efficiencies and rates by employing biochemical, chemical and photochemical treatment processes. However, regardless of the high treatment efficiencies obtained for different naphthalene sulphonates in laboratory-scale applications and specific case studies, their complete elimination from real effluent discharges and receiving water bodies by employing different end-of-pipe treatment methods seems to be economically and technically rather difficult to realize mainly due to the fact that their actual concentration in natural water and wastewater is by far lower than in the reviewed experimental studies. Since the problem of effective naphthalene sulphonate abatement has not been solved so far, efforts in this area should continue because of their potential negative impacts on the environment. From the above findings it can be concluded that the efficient control and treatment of napthalene sulphonates at source would be more effective and realistic than abatement from natural water after undergoing significant dilution. In addition, more information is urgently needed to effectively treat water as well as wastewater already heavily contaminated with naphthalene sulphonates in industrialized as well as developing countries. It is also very beneficial for industries that are interested in improving their knowledge on the fate, toxicity and treatability of polar industrial organic chemicals and their degradation products. The following issues should be addressed in the future; the development and improvement of analytical techniques for the accurate detection of naphthalene sulphonates and their degradation products in receiving water bodies; minimization of their production rate, their replacement with more environmentally friendly/biodegradable chemicals, their conversion to non-toxic, non-inhibitory, readily and completely biodegradable compounds.

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Chapter 23
Uptake of Xenobiotics from Polluted Waters by Plants

Tomas Vanek, Radka Podlipna, Zuzana Fialova, Sarka Petrova, and Petr Soudek

Abstract An overview on phytoremediation is presented, which includes basic definitions, advantages and potential drawbacks as well as information about recent developments in this field of research and applications, especially in the area of decontamination and cleaning of organic xenobiotics containing industrial and agricultural wastewaters.

23.1 Introduction

Plants are thought to be primarily as a source of food, fuels and fibers. However, it has been realised recently that plants may serve potentially as environmental counterbalance to industrialisation processes, and not only as a sink for the increased atmospheric CO_2. Indeed, over the last century, the content of xenobiotic compounds in ecosystems has increased considerably. Many organic synthetic substances, which include pesticides, solvents, dyes and by-products of chemical and petrochemical industries, are eventually transported to natural vegetation and cultivated crops, where they can either be harmful to the plant itself, totally or partially degraded, metabolised, or accumulated in plant tissues and organs. In the latter case, xenobiotics are concentrated in food chains and finally in man, with possible detrimental effects on his health. Such a situation also occurs with heavy metals. Actually, anthropogenic sources of toxic metals in environment are numerous: metalliferous mining and smelting, electroplating, energy and fuel production, gas exhausts, agriculture and waste disposal.

Reports on plants growing in polluted areas without being seriously harmed indicate that it may be possible to detoxify contaminants using agricultural and biotechnological approaches. Higher plants possess a pronounced ability to

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T. Vanek (✉), R. Podlipna, Z. Fialova, S. Petrova and P. Soudek
Joint Laboratory of Institute of Experimental Botany AS CR, v.v.i. and Research Institute of Crop Production, v.v.i, Rozvojová 263, 165 02 Prague 6, Czech Republic
e-mail: vanek@ueb.cas.cz

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metabolise and degrade many recalcitrant xenobiotics and may be considered as "green livers", acting as an important sink for environmentally damaging chemicals. On the other hand, different plant species are able to hyperaccumulate toxic metals in their tissues. It thus appears that crops and cultivated plants could be developed and used for the removal of hazardous persistent organic compounds and toxic metals from industrial wastewaters and for phytoremediation purposes.

23.2 Phytoremediation

Phytoremediation has been defined as the use of green plants and their associated microorganisms, soil amendments and agronomic techniques to remove, contain or render harmless environmental contaminants (Chappell 1997). These plants can be herbs, shrubs or trees, and they may be able to accumulate organics and heavy metals high above the levels found in nature (Brown 1995; Ma et al. 2000; EPA 2000).

Based on the decontamination approaches potentially available, phytoremediation represents typical in situ biological treatment, the main advantage of which is that it allows soil to be treated without being excavated and transported, resulting in potentially significant cost savings. However, in situ treatment generally requires longer time periods, and there is also less certainty about the uniformity of treatment due to the variability in soil and aquifer characteristics and because the efficacy of the process is more difficult to verify.

Phytoremediation is expected to be complementary to classical bioremediation techniques, based on the use of microorganisms. It could be particularly useful for the extraction of toxic metals from contaminated sites and the treatment of recalcitrant organic pollutants, like trinitrotoluene and nitroglycerin. Plant biomass could also be used efficiently for the removal of volatile organic pollutants or different priority pollutants, like pentachlorophenol, other polychlorophenols and anilines.

At present, phytoremediation is still a nascent technology that seeks to exploit the metabolic capabilities and growth habits of higher plants: delivering a cheap, soft and safe biological treatment that is applicable to specific contaminated sites and wastewaters. In such a context, there is still a significant need to pursue both fundamental and applied research to provide low-cost, low-impact, visually benign and environmentally sound depollution strategies (Schwitzguebel and Vaněk 2003).

One of the greatest forces driving increased emphasis on research in this area is the potential economic benefit of an agronomy-based technology. Growing a crop can be accomplished at a cost ranging from two to four orders of magnitude less than the current engineering cost of excavation and reburial. Expected applications will be in the decontamination of polluted soils and groundwater (phytoremediation) or in the clean-up of industrial effluents (plant cells, tissues or biomass immobilised in appropriate containers; whole plants cultivated in constructed wetlands or under hydroponic conditions).

Five different technologies for phytoremediation (*phytoextraction*, *phytodegradation*, *rhizofiltration*, *phytostabilization* and *phytovolatization*) are usually recognized in literature (e.g. Chappell 1997; Salt et al. 1998; Phytoremediation Decision Tree 1999; ITRC 2001).

23.2.1 General Advantages and Limitations of Phytoremediation

Based on the research during the recent years, phytoremediation technology is a promising cleanup solution for a wide variety of pollutants and sites, but it has its limitations too. The following list reflect that many of phytoremediation advantages and disadvantages are consequences of the biological nature of the system which depends mainly on the season and climatic conditions. Plant-based remediation systems can function with minimal maintenance once they are established, but they are not always the best solution to a contamination problem, mainly from the point of view of contaminant nature, concentration and desired time (Chappell 1997).

The pollutant must be bioavailable to a plant and its root system. If a pollutant is located in a deep aquifer, then plant roots cannot reach it. If a soil pollutant is tightly bound to the organic portion of a soil, then it may not be available to plants or to microorganisms in the rhizosphere. On the other hand, if a pollutant is highly hydrophilic, it will pass by the root system without any retention (and following accumulation and/or degradation).

23.2.1.1 Advantages of Phytoremediation

From the potential advantages of this methodology, the following are usually highlighted (Vaněk and Schwitzguébel 2003b). Phytoremediation is in situ, passive and solar driven technology. Application cost is only 10–20% of the mechanical treatments, less secondary wastes are generated and soils remain in place and are usable for the following treatment. Because of “green” nature, this approach is usually highly accepted by the general public.

23.2.1.2 Limitations to Phytoremediation

Because of utilization of plants, the cleaning process take parts in the root zone only, so effectivity is limited to shallow soils, streams, and ground water. Due to the same reasons, phytoremediation is limited by concentration of xenobiotics, because high concentrations of hazardous materials can be toxic to plants and this involves the same mass transfer limitations as other biotreatments.

Additionally, plants can transfer contamination across media, e.g., from soil to air (phytovolatization) and the toxicity and bioavailability of biodegradation products is not always known (Schwitzguebel and Vaněk 2003).

Phytoremediation can be utilized for cleaning and decontamination of soil, water, sediments, air and other media. From the point of view of xenobiotics, there are two main categories – metals and organic pollutants.

The main difference is in its fate in the plant organism – organic compounds can be degradated or even completely mineralized, on the contrary to metals.

Examples on the utilization of phytoremediation techniques to the cleaning of waters contaminated by organics xenobiotics are described below.

23.2.2 Organic Xenobiotics

Organic contaminants are common environmental pollutants. There are several ways which may be used by plants for the phytoremediation of the contaminants: *phytodegradation*, *rhizodegradation*, and *phytovolatilization*. The main difference, in comparison to metals and radionuclides, is based on the fact that organic pollutants can be degradated and finally totally mineralised (Gianfreda and Nannipieri 2001; Susarla et al. 2002; Singh and Jain 2003; Campos et al. 2008).

23.2.2.1 Phytodegradation

Phytodegradation, also called *phytotransformation*, is the breakdown of contaminants taken up by plants through metabolic processes within the plant, or the breakdown of contaminants external to the plant through the effect of compounds produced by the plants (Schröder and Collins 2002; Nepovím et al. 2004b), including extracellular enzymes (Gianfreda and Rao 2004). Pollutants (complex organic molecules) are degraded into simpler molecules and are incorporated into the plant tissues (Coleman et al. 2002; Collins et al. 2002; Hannink et al. 2002; Harvey et al. 2002; Susarla et al. 2002; Dominguez-Rosado and Pichtel 2004; Ji et al. 2004; Nepovím et al. 2004a; b; Newman and Reynolds 2004; Schoenmuth and Pestemer 2004; Nepovim et al. 2005).

23.2.2.2 Rhizodegradation

Rhizodegradation, also called *enhanced rhizosphere biodegradation*, *phytostimulation*, or *plant-assisted bioremediation/degradation*, is the breakdown of contaminants in the soil through microbial activity that is enhanced by the presence of the root zone (the *rhizosphere*) (Chaudhry et al. 2005). It is a much slower process than phytodegradation. Microorganisms (yeast, fungi, or bacteria) consume and digest organic substances for nutrition and energy. Certain microorganisms can digest organic substances such as fuels or solvents that are hazardous to human beings and break them down into harmless products in a process called biodegradation. Natural substances released by the plant roots (plant exudates) contain organic carbon that provides food for soil microorganisms and the additional nutrients which enhance their activity (Miya and Firestone 2001; Kuiper et al. 2004; Barea et al. 2005).

23.2.2.3 Phytovolatilization

Phytovolatilization is the uptake and transpiration of a contaminant by a plant, with release of the contaminant or a modified form of the contaminant to the atmosphere from the plant. Phytovolatilization occurs when growing trees and other plants take up water and the organic contaminants. Some of these contaminants may be transported through the plants to the leaves and evaporated, or *volatilized*, into the atmosphere (Orchard et al. 2000).

The same approaches were described for selected metals, e.g. mercury (Heaton et al. 1998; Rugh 2001; Heaton et al. 2005) and selenium (Berken et al. 2002; Tagmount et al. 2002).

From the general point of view, this methodology is not real cleaning, but dilution and transport of pollution to atmosphere.

23.3 Utilization of Phytoremediation for Water Cleaning

23.3.1 General Approach

Conventional treatment systems that are based on submerged biomass are not that robust regarding shock loads compared to natural like treatment systems such as constructed wetlands (CWs). CWs are artificial wetlands designed to improve water quality. They are effective in treating organic matter, nutrients and pathogens and are worldwide used to treat different qualities of water. Compared to conventional technical solutions for water treatment CWs are relatively easy to maintain and operate resulting in low operating costs (Horne et al. 2000; Kadlec et al. 2000; Langergraber and Haberl 2001; Haberl et al. 2003; Langergraber and Haberl 2004).

Using CWs the pollution load can be reduced significantly due to the high removal efficiencies (e.g. Kadlec et al. 2000). The very low energy requirement of CWs (Brix 1999) saves energy resources. CWs perform quite favourably with other treatment technologies according to their sustainability when using life-cycle assessment tools (Dixon et al. 2003). Besides water quality improvement and energy savings CWs have other features related to the environmental protection such as biodiversity, habitat for wetland organisms and wildlife (including birds and reptiles in large systems), climatic functions (e.g. less CO_2 production, Dixon et al. 2003) and hydrological functions (Brix 1999).

A overview of the potential utilization of these systems in Europe is provided in Schröder et al. (2007). Concerning constructions, there are generally two types of such systems – vertical and horizontal flow, its combinations (Seo et al. 2008; Cui et al. 2006) and some special arrangements like conveyor production system (Adler et al. 2003).

23.3.2 Industrial Contaminants

Utilization of plants for industrial wastewater cleaning can be more simple, than utilization of this methodology for other contamination.

The reason is that industrial wastewaters e.g. from chemical industry, are well characterised both from the point of xenobiotics' type and concentration, which give better possibilities to tailor the system according to the exact requirements.

There are some examples in the literature for this approach, mainly in laboratory and/or small scale application – textile effluents (Davies et al. 2005), sulfonated antraquinones (Aubert and Schwitzguebel 2004), distillery effluents (Singhal et al. 2003), chlorinated hydrocarbons (Strand et al. 2000), TNT (Best et al. 1999; Vanek et al. 2006; 2007), phenol (Singh et al. 2008), cyanide (Ebel et al. 2007), nitroesters (Podlipna et al. 2008). The effectivity of this approach can be illustrated in Fig. 23.1, which describe uptake of TNT from water solution by poplar. Starting concentration of 50 mg/L of TNT was totally removed during 4 days and some degradation products (2-amino 4,6 dinitrotoluene, and 4-amino 2,6 dinitrotoluene) were isolated and identified (Vanek 2008).

23.3.3 Agricultural Contaminants

Agricultural contaminants can be defined as a contaminants released to the environment as a results of agricultural activities – e.g. agrochemicals and wastes. Phytoremediation approach can be efficient in agricultural countries, with the aim

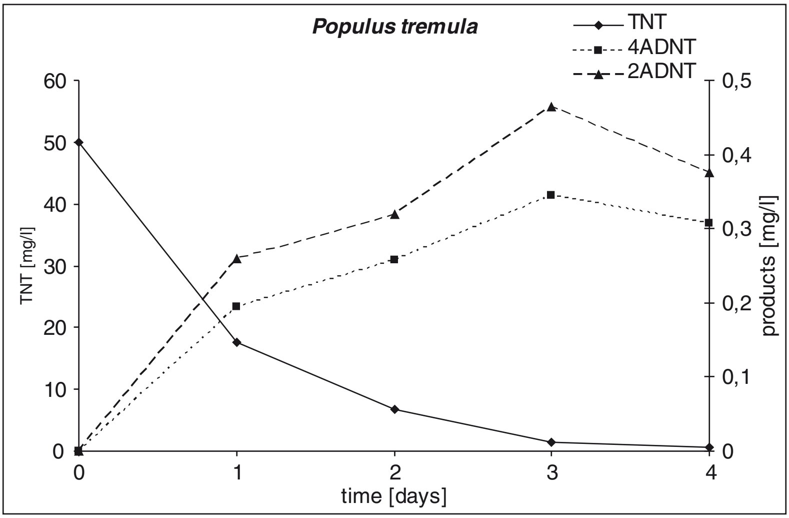

Fig. 23.1 Accumulation of TNT from liquid media using *Populus tremula*. TNT – trinitrotoluene, 2ADNT – 2-amino 4,6 dinitrotoluene, 4ADNT – 4-amino 2,6 dinitrotoluene

to avoid contamination of aquatic environment. Examples include utilization of *Salvia minima* for pig farm wastewaters in Mexico (Olguin et al. 2007), livestock wastewaters in China (Chen et al. 2007), dairy wastewater (Healy et al. 2007; Munoz et al. 2006), fluorinated agrochemicals (Reinhold and Saunders 2006), pesticides (Xia and Ma 2006), herbicides (Schröder et al. 2005), diazinon (Moore et al. 2007) and DDT (Chu et al. 2006).

In a laboratory study *Azolla filiculoides* Lam., an aquatic fern known to absorb pollutants has been exposed to an environmental persistent antibiotic commonly used in intensive farming sulphadimethoxine, to test its bioremediation capability (Forni et al. 2002). All concentrations of tested drug (50, 150, 300 and 450 mg/L) was actively removed from the medium to the plant biomass. These results demonstrated that *Azolla* can be taken into consideration as a tool for sulphonamides environmental monitoring and decontamination.

23.3.4 Pharmaceuticals and Personal Care Products (PPCPs)

This type of contaminants are now detected both in wastewaters and drinking waters too, because of poor efficiency of conventional treatment system. In recently published US study, the drinking water for more than 28 million people was screened for a diverse group of pharmaceuticals, potential endocrine disrupting compounds (EDCs), and other unregulated organic contaminants. Source water, finished drinking water, and distribution system (tap) water from 19 U.S. water utilities were analyzed for 51 compounds between 2006 and 2007. The 11 most frequently detected compounds were atenolol, atrazine, carbamazepine, estrone, gemfibrozil, meprobamate, naproxen, phenytoin, sulfamethoxazole, TCEP, and trimethoprim. Median concentrations of these compounds were less than 10 ng/L, except for sulfamethoxazole in source water (12 ng/L), tris(2-chloroethyl) phosphate (TCEP) in source water (120 ng/L). Atenolol, atrazine, N,N-Diethyl-meta-toluamide (DEET), estrone, meprobamate, and trimethoprim can serve as indicator compounds representing potential contamination from other pharmaceuticals and EDCs and can gauge the efficacy of treatment processes (Benotti et al. 2009).

Only recently the first studies on phytoremediation of organic micro-pollutants and pharmaceuticals and its potential utilization for water cleaning have been published (e.g. Lin et al. 2006; Gustavsson et al. 2007; Schröder et al. 2007; Matamoros et al. 2007, 2008; Vanék et al. 2008).

These studies show that utilization of CWs can be generally feasible to remove organic micro-pollutants such as endocrine disrupting chemicals as well as pharmaceuticals and personal care products. However, these studies show as well that there is still an immense need for further research.

For illustration, our recent study of phytoremediation of drugs with largest volume of distribution in Czech Republic in 2007 (diclofenac, ibuprofen and acetaminophen (paracetamol)) is described using *Lupinus albus, Hordeum vulgaris Phragmatis australis* and *Armoracia rusticana* (hydroponic and *in-vitro* culture).

For paracetamol, best results were achieved using *Lupinus albus* (total accumulation/degradation of starting concentration of 30 mg/L during 2 days), and for ibuprofen using *Phragmatis australis,* where 60% accumulation/degradation of starting concentration of 25 mg/L were achieved during 8 days (Fig. 23.2). Diclofenac was, because of its phytotoxicity, removed with only low efficiency (Fig. 23.3). There is necessary to take to the consideration, that in this laboratory experiments very high concentrations were used, to give us possibility to study metabolisms of pharmaceuticals in plants. For field applications, study will be repeated with more real concentrations of pollutants.

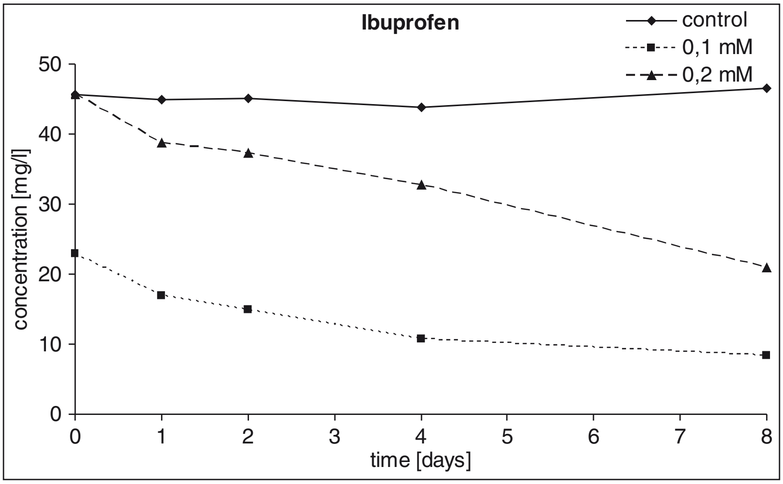

Fig. 23.2 Accumulation of ibuprofen from liquid media using *Phragmites australis*

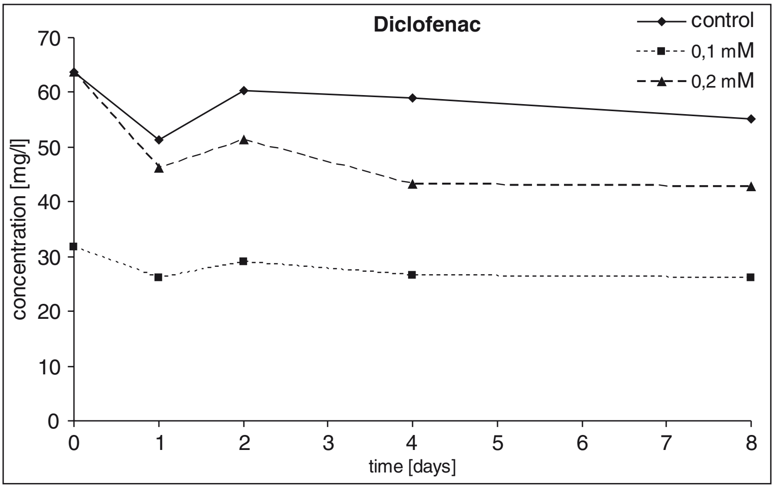

Fig. 23.3 Accumulation of diclofenac from liquid media using *Phragmites australis*

23.3.5 Urban and Storm Waters

This approach can be especially efficient in small isolated communities to avoid environment contamination and permit water re-use for agricultural and other purposes, both in hot (e.g. Puigagut et al. 2007; Masi and Martinuzzi 2007; El Hamouri et al. 2007) and cold climate (Healy et al. 2007; O'Hogain 2008).

Utilization of constructed wetland for the removal of nonylphenol ethoxylate surfactants and their intermediate degradation products such as nonylphenol and nonyphenol mono- and diethoxylate from domestic wastewater was studied in a pilot-scale treatment wetland constructed in the small community of Santa Maria Nativitas in Mexico (Belmont et al. 2006). The treatment wetland removed >75% of compounds of interest from the domestic wastewater, but the greatest proportion of removal occurred in parts of the treatment wetland where sedimentation existed. These data indicate that construction of low-cost and technologically simple treatment wetlands may be one solution to reducing the impacts of contaminants from domestic sewage in developing countries.

23.4 Performance

The most serious problem of new technologies which needs to be overcome is a lack of performance data. Phytoremediation is no exception, despite serious efforts and progress during recent years. One of the current barriers to obtaining performance data is the duration of phytoremediation projects and applications, which are dependent on the rates of plant growth, activity and climatic conditions. Currently, a number of pilot scale projects exist, but they have not resulted in conclusive performance data up to now. These sites are being monitored and will provide results in the next few years. Also, a number of companies have installed phytoremediation systems at polluted sites owned by private clients, so results from those sites are not publicly available. On the other hand, data from basic research are available both from scientific literature and web pages. For the evaluation of CWs efficiency some mathematical models were recently published too (Brasil et al. 2007; Akratos et al. 2008; Sun and Cooper 2008) as well as for size estimation (Stecher et al. 2001).

23.5 Conclusion

For the efficient utilisation of phytoremediation as an effective tool for contaminated water cleaning, there is still necessary to improve the understanding of some aspects, both at the level of basic research and practical applications.

Some of them are mentioned below.

- Delineation of pathways employed in the uptake and metabolism of organic pollutants by plants.
- Identification of metabolites produced and study of their ecotoxicological behaviour.
- Production of a databank of genes/enzymes that will improve the rate and extent of detoxification of organic pollutants.
- Evaluation of the prospect of the use of metabolic engineering tools to enhance the capacity of higher plants for phytoremediation and clean-up of industrial effluents.
- Generation/evaluation of plants adapted to phytoremediation of specifically contaminated waste-waters.
- Execution of pilot studies in the scale-up of selected plants with an increased capacity for biodegradation of xenobiotics.

At this moment, phytoremediation techniques are available for practical applications, provided, that for each site individual optimisation study is performed.

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Chapter 24
Treatment Techniques and Analysis of Stormwater Run-off from Roads in Hamburg, Germany

Burkhard Stachel, Jens-Uwe Holthuis, Wolfgang Schulz, Wolfram Seitz, Walter H. Weber, Klaus-Thorsten Tegge, and Ingo Dobner

Abstract The treatment of stormwater constitutes an integral part of precipitation water management in Germany. This finds its expression in a variety of treatment concepts which in turn form the basis for technological solutions to meet current demands concerning water quality. In this respect the requirements of the Water Framework Directive (2000/60/EU, WFD) continue to play a central role and provide a basis for discussion leading to further innovative solutions. In order to fulfil these requirements, major investments are necessary. In view of the high costs involved in the construction and maintenance of treatment plants, a key factor may be seen in the development of techniques for measuring their clearing efficiency.

Analysis of highway stormwater run-off has revealed the existence of priority substances as defined in Annex X of the WFD. The concentrations of heavy metals, metalloids, PAHs and benzothiazoles were determined in run-off water as well as in seepage water originating from a plant covered soil filter in the vicinity of a nature protection area from Hamburg. In addition, stormwater treatment plants located in a water protection area were investigated. The analysis of soil samples obtained from three of these filters showed a slight accumulation of Cu, Pb, Zn, Pt, and PAHs in each case in the upper soil horizon.

B. Stachel (✉) and K.-T. Tegge
Department of Water Protection, Ministry of Urban Development and Environment, Billstrasse, 84, D-20539, Hamburg, Germany
e-mail: Burkhard.Stachel@bsu.hamburg.de

J.-U. Holthuis
Bremen University of Applied Sciences, Faculty 2 - Institute for Environmental and Bio-Technology, Neustadtswall, 30, D-28199, Bremen, Germany

W. Schulz, W. Seitz and W.H. Weber
Zweckverband Landeswasserversorgung, Betriebs- und Forschungslaboratorium, Am Spitzigen Berg 1, D-89129 Langenau, Germany

I. Dobner
University of Bremen, Center of Environmental Research and Sustainable Development (UFT), Leobener Strasse, D-28359, Bremen, Germany

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A test filter with modified adsorbent composition and mycorrhizal vegetation was installed in the plant stocked filter. The results show a high degree of retardation efficiency for metals and non-polar substances, but less for the polar compounds such as benzothiazoles and benzotriazoles.

24.1 Introduction

Increasing urbanisation is often accompanied by growing environmental problems. One major problem in large cities like Hamburg (1.7 million inhabitants) is generated by urban water run-off, which is a potential contributor to the contamination of receiving waters. The resultant washout contains pollutants and hazardous substances from urban surfaces, streets and courtyards, households, roofs, other urban land use areas as well as sewer overflows. Climate change and an increase in extreme precipitation will lead to an increase in pollution loads in stormwater run-off. After reaching surface waters the pollutants may affect benthic organisms, fish or algae. Dissolved toxic substances and nutrients from urban water run-off, contaminated suspended particulate matter (SPM) and sediments are transported downstream to the mouth of a river and reach coastal zones and their sensitive ecosystems.

As well as heavy metals, a wide spectrum of organic pollutants is emitted from vehicles. Stormwater also represents the main recipient medium for pollutants from traffic accidents involving hazardous substances. It contains substances from vehicular activities such as emissions from tyres, heavy metals from break pads, combustion by-products, de-icers, tyre wear, corrosion inhibitors, oil and grease, particulates from fuel sources, litter and debris, as well as pollutants from dry and wet atmospheric depositions (Umweltbundesamt 2005). Benzothiazoles are used as vulcanisation accelerators in tyre production. Bisphenol A (BPA) is a primary product in manufacturing plastics which in turn may be used to produce chassis components. This chemical is also involved in tyre manufacturing as an antioxidant (Leisewitz 1999). 4-Tert. octylphenol is used as a tackifier in tyre production (Umweltforschungsplan 2006 and data sheet No. 25). On account of their plastifying properties, phthalate esters can be found in plastics such as PVC and therefore may be expected to be present in vehicle components. It may be assumed that pesticides can enter stormwater run-off via both wet and dry deposition.

Initial investigations of highway stormwater run-off from Hamburg have indicated the presence of hazardous and potentially hazardous substances which are specifically mentioned in the Water Framework Directive (Directive 2000/60/EC, Annex X). The Directive requires that pollution through discharge, emission or loss of hazardous substances must cease or at least be phased out. In order to obtain information on a wide spectrum of organic pollutants and metals, investigations of further compounds associated with vehicular activity were necessary. Samples were taken from seven locations on different stretches of the Hamburg motorway network. The chemical analysis was completed by means of ecotoxicity tests. In a comparative study, different treatment technologies for the purification of stormwater run-off water were investigated. The first treatment plant is located in the water protection area Harburger Berge and the second one, named Halenreie, is in northeast Hamburg, situated in the vicinity of a nature protection area. The vertical transport of selected pollutants was determined in the unsaturated zone of the Harburger Berge plant. Water samples from the Halenreie treatment plant were analysed to assess retardation in respect of pollution load reduction. The purified water flows into a small creek.

The use of soil filters has economic advantages as well as ecological ones, but using current technology they require a large amount of space. To optimise the retardation efficiency different filter materials and plant stocks were tested (Dobner and Holthuis 2007). The present chapter presents and discusses the results of initial field trials using a modified filter bed containing quartz sand and silicate-colloid/humus in combination with mycorrhizal plants in the Halenreie treatment facility.

24.2 Highway Stormwater Run-off

Integrated water samples of highway stormwater run-off were taken from seven different motorway sections in the inner metropolitan area of Hamburg (Fig. 24.1). The sampling procedure is described elsewhere (Stachel et al. 2007). Table 24.1 contains more detailed descriptions of the sampled sections as well as the average daily traffic volumes (ADTV). The results obtained form the basis for further studies in which the purification efficiency of soil filters was investigated.

The substances analysed were polycyclic aromatic hydrocarbons (PAHs), alkylphenols, bisphenol A, pesticides, heavy metals, arsenic and antimony. In addition, ecotoxicological tests with the luminescent bacterium *Vibrio fischeri* and *Daphnia magna* water fleas were carried out. The complete range of substances, analysis techniques and results are detailed elsewhere (Stachel et al. 2007). Table 24.2 contains selected results.

Table 24.1 Characterization of sampling sites adjacent to motorways in Hamburg

No	Motorway	Sampling site	ADTV
1	A7	Moorburg	101,000 (18)
2	A255/A252	Motorway intersection Hamburg Sued, Neumann treatment plant	77,000 (16)
3	A24	Oejendorfer See	63,000 (6)
4	A1	Moorfleet Sued	84,000 (26)
5	A7	Harburger Berge	86,000 (20)
6	A1	Affiliation Billstedt	95,000 (21)
7	A255/A252	Motorway intersection Hamburg Sued, before retention basin	77,000 (16)

ADTV = Average daily traffic volume; () = percentage of heavy load vehicle traffic. Map of sampling sites see Fig. 24.1.

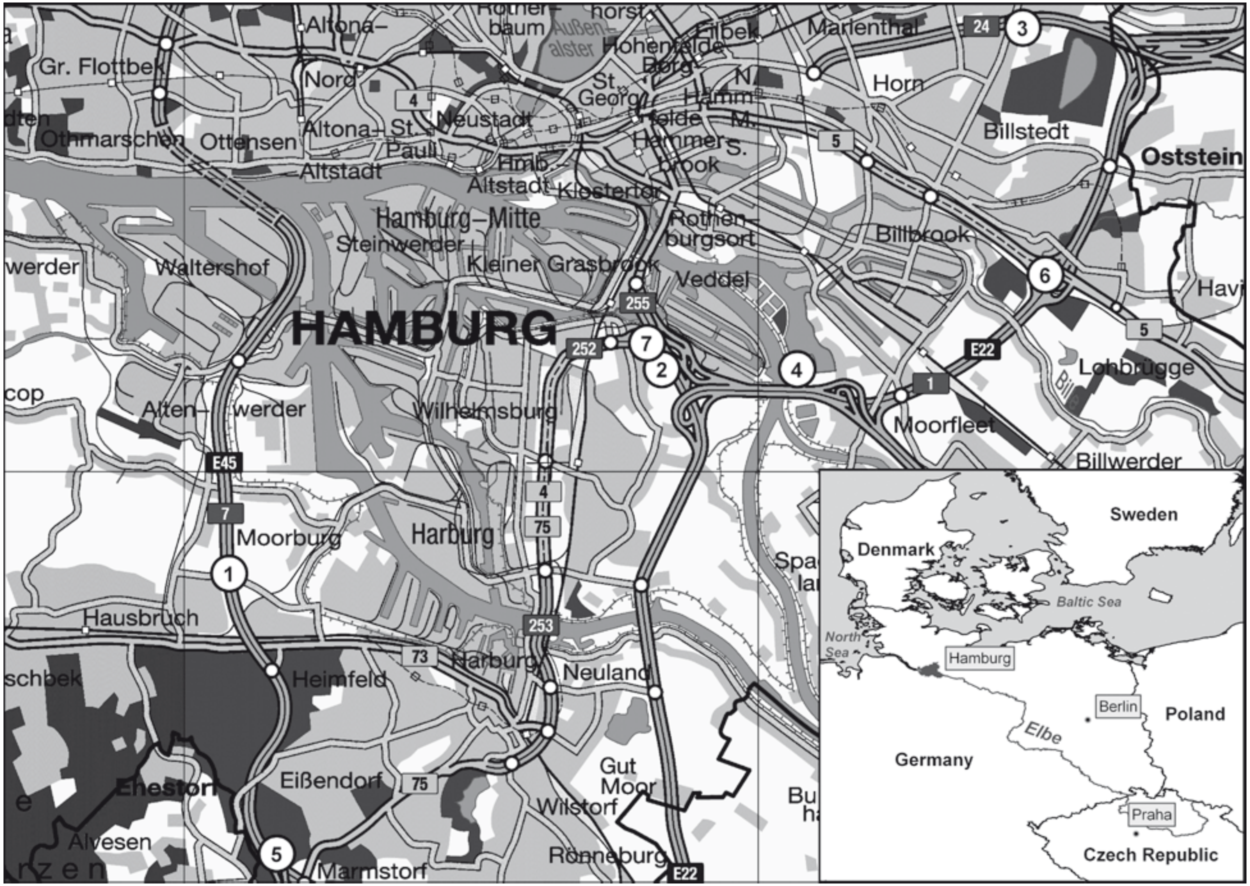

Fig. 24.1 Sampling sites for highway stormwater run-off in Hamburg

Table 24.2 Concentrations of heavy metals, metalloids and organic compounds in stormwater run-off from seven sampling sites from different motorways in Hamburg (Modified from Stachel et al. 2007)

Substance	Cmin-max (µg/L)	Median (µg/L)
Antimony	10–29	16
Arsenic	1–23	1.4
Cadmium	0.16–1.3	0.34
Copper	91–760	180
Chromium	8.6–21	12
Lead	13–99	21
Nickel	4.2–18	8
Mercury	<0.1–0.41	0.2
Zinc	210–1300	450
Anthracene	<0.03–0.11	0.05
Benzo(a)anthracene	0.05–0.18	0.11
Benzo(a)pyrene	0.15–0.65	0.39
Benzo(b)fluoranthene	0.07–0.33	0.22
Benzo(k)fluoranthene	<0.03–0.11	0.07
Benzo(ghi)perylene	0.1–0.33	0.21
Indeno(1.2.3-cd)pyrene	0.04–0.17	0.12
Chrysene	0.11–0.47	0.21
Fluoranthene	0.27–1.1	0.34
Naphthalene	<0.03	–
Phenanthrene	0.11–0.6	0.2
Pyrene	0.21–0.93	0.43
Benzene	<0.1	–
4-tert. Butylphenol	0.77–0.73	0.4
4-tert. Octylphenol	0.15–1.9	0.32
4-iso Nonylphenol	0.17–3.6	0.78
DEHP	6–78	8.6
BPA	0.24–2.5	1.4
2-Methylthiobenzothiazole	0.5–5.4	1.3
Pentabromodiphenylether	<0.005	–
C_{10}-C_{13} Chloroalkanes	<0.05	–
Monobutyltin	0.007–0.03	0.02
Tributyltin	<0.001	–
Chlortoluron	<0.005–0.03	0.015
Diuron	0.02–0.04	0.03
Fenuron	0.01–0.04	0.02
Isoproturon	0.05–0.2	0.09
Simazine	<0.005–0.008	0.007

<[value]: value lies below the limit of quantification; BPA = 2,2′-bis(4-hydroxyphenyl)propane; DEHP=di(2-ethylhexyl)phthalate. For analytical methods see (Stachel et al. 2007).

Compounds in *italics* = substance contained in Annex X, WFD.

The concentrations of heavy metals and metalloids ranged from <0.1 µg/L (Hg) to 1,300 µg/L (Zn). The median values ranged from 0.2 µg/L (Hg) to 450 µg/L (Zn) (Table 24.2). With the exception of Cu, these values are similar to average values obtained in a study involving an inner city road in Switzerland. Based on a considerably lower ADTV of 17,000 vehicles, concentrations (in µg/L) were found there as follows: 0.8 (Cd), 10.2 (Cr), 56.5 (Cu), 7.0 (Ni), 23.1 (Pb) and 299 (Zn), (EAWAG 2006).

On the basis of the distances travelled by different vehicle types on major German highways in 2001, the Federal Environmental Agency performed calculations to estimate annual heavy metal pollution (Umweltbundesamt 2005). The total traffic related emissions for these heavy metals amounted to 81 t Pb, 932 t Cu and 2078 t Zn per annum. These figures show that significant amounts of heavy metals are introduced into the environment via highway run-off waters. High concentrations of Pb, Cu and Zn were found in the Hamburg highway stormwater run-off (Table 24.2).

The concentrations of polycyclic aromatic hydrocarbons (PAHs) ranged from <0.03 µg/L (anthracene, benzo(k)fluoranthene, naphthalene) to 1.1 µg/L (fluoranthene), with median values lying between 0.05 µg/L (anthracene) and 0.43 µg/L (pyrene) (Table 24.2). The main components consist of the three or four condensed rings benzo(a)pyrene, fluoranthene and pyrene, which accounted for about 50% of the total. In comparison, considerably higher concentrations were found in stormwater run-off from four sampling sites in Virginia (Smith et al. 2000). Total PAHs concentrations from discrete samples ranged from non-detectable to 3,500 µg/L with a mean of 44.5 µg/L (sum of 16 PAHs, US-EPA).

PAHs accumulate in sediments and are generally readily adsorbed on solids. Especially the higher condensed aromatic compounds have mutagenic and carcinogenic effects and can cause damage to aquatic organisms (Smith et al. 2000). The anthropogenically triggered introduction of PAHs into the environment results from incomplete combustion of fossil fuels and from domestic heating systems. A further source is represented by natural combustion processes, e.g. forest fires (Naffrechoux et al. 2000). Also, PAHs are used as process oils in tyre manufacture and therefore enter road run-off water in the form of tyre abrasion residue (OECD 2003).

Benzothiazoles have many different applications in industry with the greatest quantities being used as vulcanisation accelerators in tyre production (Christopher and Quinn 1997; Klöpfer et al. 2005). In terms of volume, they can account for 1% of a tyre's constituents. These compounds are polar, sometimes extremely, so they are readily soluble in water and therefore a potential threat to water quality. Benzothiazoles occur in household wastewaters (Klöpfer 2005) and are encountered in municipal wastewater treatment plants. Bacteriological processes which take place in these plants produce transformation products which are more stable and less polar than the original substances (Klöpfer et al. 2005). The 2-methylthiobenzothiazole (MTBT) found in the road run-off water in Hamburg represents such a transformation product. In view of its lipophility, (log $K_{OW} = 3.1$, Klöpfer 2005), this substance may be expected to display a potential for bioaccumulation in respect of aquatic organisms.

Other benzothiazoles were found in run-off water samples from the A24 motorway (sampling site No 3, Table 24.1). Qualitative analysis of benzothiazole, 2-mercaptobenzothiazole (MBT), 2-hydroxybenzothiazole (OHBT) and 2-(4-morpholinyl)benzothiazole showed that these substances should given specific attention. The latter compound, a minor component of a vulcanization accelerator, has recently been evaluated as a possible marker of tyre debris. It was detected in sediment core samples from surface waters located close to a motorway in Tokyo, Japan. The authors of the Japanese study concluded that 2-(4-morpholinyl)benzothiazole is an indicator for substances typically found in connection with traffic emissions (Hidetoshi et al. 2000).

2-Methylbenzothiazole (MTBT) was found in highway stormwater run-off in concentrations ranging from 0.5 to 5.4 μg/L, with a median value of 1.3 μg/L (Table 24.2). The measurement values obtained for run-off water from an inner city highway in Berlin were comparable to this, ranging from 0.2 to 1.5 μg/L (Klöpfer 2005).

The concentrations of the three alkylphenols 4-tert. butylphenol (BP), 4-tert. octylphenol (OP) and 4-iso nonylphenol (NP) lay between 0.15 μg/L (OP) and 3.6 μg/L (NP), with median values between 0.32 μg/L (OP) and 0.78 μg/L (NP) (Table 24.2). OP and NP are included in the list of priority substances in Annex X of the WFD. In comparison, Eriksson et al. 2002 reported data from road run-off samples from Danish and Norwegian studies. The NP concentrations ranged from 0.04 to 23 μg/L, which confirms the data obtained from the Hamburg stormwater run-off (Table 24.2). In a recent paper the authors published a methodology for ranking and hazard identification for xenobiotics in urban stormwater on the basis of large data volumes (Baun et al. 2006). This ranking system could prove to be a helpful tool for planning concepts and for practical investigations of stormwater run-off.

NP is used in the manufacture of adhesives and paints as well as for the production of non-ionised tensides and surfactants (nonylphenol ethoxylates). After chemical treatment, OP is used as a tackifier in tyre manufacturing in the form of phenolic resin. Also, the production techniques for NP or nonylphenol ethoxylates may result in up to 10% OP being present as well (Umweltforschungsplan 2006 and data sheet No. 25, in Umweltforschungsplan). OP is a component of tyres and is to be found in both tyre abrasion residues and stormwater run-off.

Alkylphenols can be found in rivers such as the Elbe and in the North Sea (Bester et al. 2001; Heemken et al. 2001; Stachel et al. 2003), whereby the sources of these pollutants differ widely. Concentrations in the Elbe are about one or two orders of magnitude lower than in the stormwater run-off. These chemicals are persistent and they have a toxic potential, causing estrogenic effects in aquatic organisms (Jobling et al. 1996).

2,2'-Bis(4-hydroxyphenyl)propane (bisphenol A, BPA) was found in concentrations ranging from 0.24 to 2.5 μg/L, with a median value of 1.4 μg/L (Table 24.2). This substance is not contained in the list of priority substances; nevertheless the highway run-off water was analysed for it on account of its estrogenic potential in respect of aquatic organisms (Schulte-Oehlmann et al. 2001; Oehlmann et al. 2008). The study already mentioned above (Eriksson et al. 2002) reports BPA concentrations for highway run-off lying between <0.01 and 0.17 μg/L. Compared with these figures, the corresponding concentrations in the run-off water from Hamburg were significantly higher. It is to be hoped that further investigations can provide an explanation for these differing BPA concentrations. As was the case for the alkylphenols, BPA has been found in the river Elbe and in the North Sea coastal region. BPA is a primary product in manufacturing plastics such as polycarbonates and epoxy resins which in turn may be used to produce chassis components.

The run-off waters were investigated for the presence of 18 individual substances within the plasticiser substance class. The dominant substance here proved to be di(2-ethylhexyl)phthalate (DEHP). Concentrations ranged from 6 to 78 μg/L, with a median value of 8.6 μg/L (Table 24.2). DEHP is included in the priority substance list. In other studies, DEHP have been reported to have occurred in concentrations between 3 and 44 μg/L (Eriksson et al. 2002; Ledin et al. 2002).

Phthalate esters are used as plasticisers in plastics such as PVC, which is probably used in the manufacture of vehicle components. DEHP occurs ubiquitously, and correspondingly it has been found in the river Elbe and its estuary along with the other compounds already mentioned (Stachel et al. 2005). This chemical also has estrogenic effects when aquatic organisms are exposed to it (Oehlmann et al. 2008).

Of the 53 individual pesticides for which analyses were carried out, the herbicides chlortoluron, diuron, fenuron, isoproturon and simazine gave positive findings (Table 24.2). Diuron, isoproturon and simazine are all listed as priority substances. The presence of herbicides in the run-off water may be attributed to atmospheric deposition (Bucheli et al. 1998). It is unlikely that herbicides in Germany are used in motorway maintenance work. Also, sources such as direct input due to agricultural activities probably do not play an important role.

Ecotoxicological investigations involving luminescent bacteria and daphnia tests yielded no findings of any importance. The most remarkable result was that neither test organism displayed more than negligible reactions, although several of the Annex X substances were present. One possible explanation is that the test organisms used are not sensitive in respect to the determined pollution concentrations or that synergetic or antagonistic effects reduce the toxicity of the pollution mixture in the stormwater run-off. The following approach sheds some light on this issue.

A combination of the toxicity test using luminescent bacteria (*Vibrio fischeri*) and thin layer-chromatography may proof to provide a clearer assessment of the toxicity of a substance mixture (Eberz et al. 1996; Weins and Jork 1996; Weber et al. 2005). In contrast to the results obtained using the standard *Vibrio fischeri* test, it could be demonstrated that the sample obtained from the sampling site A24 (drainage ditch) and treatment plant Halenreie (detention pond) contained bioactive substances (narcotic effects), which was indicated by inhibition of the luminescent emissions emanating from the bacteria (Fig. 24.2). In particular, polar to medium-polar substances proved to have inhibitive effects on the luminescent bacteria. In addition, the inhibition of the luminescence from the bacteria as an indicator for bioactivity was compared with the absorption of UV light. The application of this toxicity test as a screening method for bioactivity in water analysis has been described recently (Schulz et al. 2008). The same study also showed how the

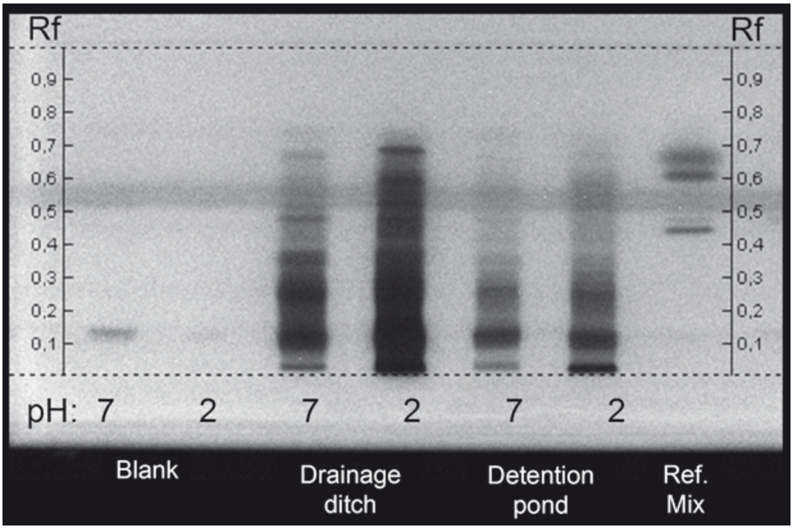

Fig. 24.2 Screening for bioactivity using *Vibrio fischeri* following thin-layer chromatography of water samples obtained by solid-phase extraction (enrichment factor = 500). 'Ref. Mix' refers to a quality control sample to verify chromatography and detection (Modified from Schulz et al. 2008)

images from the luminescence test can be subjected to further evaluation by calculation of inhibition chromatograms.

24.3 Soil Filter Harburger Berge

While traversing the Harburg hills in Hamburg, the A7 motorway intersects the water protection zone III of the water protection area named Harburger Berge. Stormwater run-off is transported from the motorway to the treatment plants via pipelines and purification proceeds in different steps. To deal with the expected volume of highway run-off waters, there are nine treatment plants for the treatment of stormwater run-off located within this protection zone. Their location in this vulnerable region means that extensive technical measures must be taken to provide adequate groundwater protection. The chief components of the treatment plants concerned consist of a light solids separator in combination with a sedimentation pond. A second sedimentation pond is used to separate SPM and initiate microbiological degradation processes. Then the pre-treated water flows into the soil filter in order to retain or degrade the pollutants as effectively as possible. This soil filter consists of a depression in the ground. The layers of the soil filter consist of vegetation, a 5–10 cm thick layer of humus, followed by medium and fine grained sands underneath. The treatment plants, which have been in operation for approximately 25 years, are subjected to inspections at three years intervals. The purpose of the investigations described below was to obtain information on the retardation capacity of the filtration beds in respect of the vertically transported pollutants. Four soil horizons were sampled to a maximum depth of 1 m below the surface in each of three soil filters. Then seven to eight individual samples were extracted from each horizon and combined to form a composite sample. The composite samples were analysed for heavy metals, arsenic, antimony, platinum and PAHs.

Table 24.3 contains results for the composite soil samples from the first horizon of each of the three filters investigated. Table 24.4 shows background values for soils in Hamburg. Comparison between the results of the soil samples and these background values show that pollutants accumulate in the first horizon of the soil filters.

The results in Table 24.3 show the accumulation of heavy metals and arsenic in the first horizon. The concentrations are comparable with those of regional background concentration measurements (Table 24.4, 90th percentile). Only Cu, Pb and Zn display minor peaks. In general, the metal concentrations in the deeper horizons decrease progressively (results not shown). It may be assumed that the accumulation of metals in the upper soil layers is connected with the inflow of highway run-off waters and atmospheric deposition of metals from the nearby motorway.

Platinum is a precious metal which has been used in three-way-catalytic converters for petrol engines since 1986. It has been found to have accumulated in road dust samples obtaind from motorways in Boroughs of Richmond and Kingston, in south-west London, UK. The concentration range for the road dust samples lies between 0.42 and 33 μg/kg. The platinum enters the top soil adjacent to motorways via atmospheric deposition (<0.03–8 μg/kg) (Farago et al. 1996). In top soils next to the A66 motorway between Frankfurt and Wiesbaden, Germany, the concentration range was found to be <2 to 87 μg/kg (Zereini et al. 1993). In the first horizon of the Harburg soil filters Pt-concentrations were found between 17 and 44 μg/kg (Table 24.3), that

Table 24.3 Pollutant concentrations measured in mg/kg dm, for composite soil samples taken from the upper horizons of three soil filter beds in the Harburger Berge (Lichtfuß and Bochert 2006)

Filter	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Pt	PAHs
1	9.2	1	34	204	0.24	17	280	351	0.035	1.5
2	4.2	0.5	18	76	0.07	8	72	222	0.017	1.2
3	8.2	0.8	34	152	0.16	20	120	451	0.044	3.6

PAHs = sum of 16 compounds (US-EPA).

Table 24.4 Background values for soils from the Hamburg region (LABO 2003, cited in Lichtfuß and Bochert 2006). Terrain characteristics: outside inner city and urban concentration areas (type II/III), without further classification of the upper soil usage. Figures given in mg/kg dm

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
n	201	209	228	206	117	173	209	167
50. P.	<1	0.3	26	28	0.2	11	51	48
90. P.	8	0.7	50	47	0.4	18	100	161

P. = percentile, n = number of individual values.

is to say between the extreme values measured on the Frankfurt to Wiesbaden stretch of motorway. On the basis of a background value of 0.4 μg/kg (Wedepohl 1995), this represents an accumulation in the region of 1–2 orders of magnitude.

The summed PAHs concentrations (16 compounds according to US-EPA) in the upper horizons lay between 1.2 and 3.6 mg/kg, which also agrees with background levels of 5.2 mg/kg (in an agricultural topsoil (n = 21), yielded a 90th percentile). It may be concluded that no significant accumulation of PAHs was found in the first horizons of the soil filters.

24.4 Plant-Stocked Soil Filter Halenreie

The Halenreie treatment plant for the purification of road run-off is situated in the northeast of Hamburg. It was constructed as a pilot plant in 1996 and since then, research and monitoring programmes have provided a valuable data pool (Fitschen 2000, Table 24.5). By clearing incoming contaminated road run-off waters, the facility upgrades the quality of the water bodies in the nature protection area 'Volksdorfer Teichwiesen', providing benefits for amphibians and other aquatic organisms.

The facility consists of four separate filter basins (each with an area of about 170 m^2) containing sandy filter beds 1 m in depth. The surface is planted with reeds (*Phragmitis communis*). Two of the basins are pump driven vertical-flow filters, whereas the other two act as horizontal filters. The filters receive run-off water from a detention pond (650 m^3) equipped with an oil separator. The overall catchment area is about 40,000 m^2. The run-off water comes from a main road (15,000 ADTV), an adjacent market place and car parks.

To determine the facility's purification capacity, the effluents of the detention pond as a raw water, the incoming water for the soil filter (influents) and the cleared water (effluents, seepage water) were sampled isochronically between May 2007 and March 2008. The analysis included heavy metals, arsenic, antimony, PAHs, benzothiazole derivates, benzotriazoles, BPA, DEHP and pesticides. The concentrations in the detention pond, the filter inlet and its outlet are detailed in Table 24.5 for 2007 and 2008.

The average SPM concentration at the inlet to the detention pond was measured at 12 mg/L (Table 24.5). The outlet of the pond returned 8.1 mg/L, a level which corresponds to only 10% of the average Hamburg highway run-off water concentrations (Stachel et al. 2007). This low SPM concentration is due to sedimentation of particles in the detention pond. After complete percolation of the plant-covered soil filters, the seepage water had a clear appearance and the SPM concentration was 2.3 mg/L. SPM acts as a powerful adsorbent for heavy metals or hydrophobic organic pollutants. For this reason, effective mechanical filtration of particles through the porous soil system is a prerequisite for successful decontamination of percolating waters. The small amounts of filterable matter to be found in the final effluents are an indication of the good mechanical filtration capacities of both soil filters.

Table 24.5 Concentrations of pollutants in water samples from the detention pond (DP) and sewer pipes of the Halenreie reed-covered soil filter for the treatment of road run-off

Compound	DP influent	Filter influent	Filter effluent
SPM	12,000	8,066	2,320
TOC	7,650	6,700	2,820
DOC	4,650	4,360	2,300
Antimony	0.93	0.70	1.1
Arsenic	0.5	0.45	1.5
Cadmium	<0.05 (0.095*)	<0.05	<0.05
Chromium	1.2	0.61	0.13
Copper	70	21	3.3
Iron	330	315 (1100*)	90 (1200*)
Lead	5.0	2.7	0.36
Mercury	<0.05	<0.05	<0.05
Nickel	0.96	0.90	0.53
Zinc	195	72	<0.05 (1.4*)
Naphthalene	0.031*	<0.05	0.01
2-Methylnaphthalene	0.025*	0.033	0.022
Phenanthrene	0.046*	<0.03	<0.01
Fluoranthene	0.039	0.024	<0.01
Pyrene	0.057*	0.032	<0.01
Chrysene	0.017	0.015	<0.01
Diuron	0.01	0.009	<0.005 (0.009*)
Metobromuron	0.013*	<0.01	<0.01
Azoxystrobin	0.013*	0.006*	<0.005 (0.005*)
Terbutryn	0.009	<0.014	0.008

Mean values in µg/L; sampling period 2007–2008; SPM = suspended particulate matter; TOC = total organic carbon; DOC = dissolved organic carbon; * = single value; <[value]=value lies below the limit of quantification.

Heavy metal analyses of the detention pond water and the filter samples also yielded Hg concentrations below the limit of quantification (LOQ, <0.05 µg/L). With one exception, the same is true of Cd (road run-off: 0.095 µg/L, Table 24.5). High concentrations (in µg/L) were found in the filter inlet for Fe (315), Zn (72) and Cu (21). The remaining metals (As, Cr, Ni, Pb, Sb) were found in concentrations ranging from 0.45 to 2.7 µg/L.

Comparing the actual drainage concentrations with environmental quality standards (EQS, Directive 2008/105/EC) for inland waters (immission concentration, annual mean values), the concentrations specified there were not exceeded in any case (EQS, µg/L: Cd ≤0.08, Ni: 20 and Pb: 7.2).

PAHs (16 PAHs according to US-EPA, as well as 1-methylnaphthalene and 2-methylnaphthalene) results were focused on compounds of two to four rings (naphthalene, methylnaphthalenes, phenanthrene, fluoranthene, pyrene and chrysene). Naphthalene and the methylnaphthalenes are more readily soluble in water than the four ringed PAHs. The analysis results are of importance for the assessment of the purification efficiency in respect of PAHs. Because of their relative low water solubility, 57% of the single species analyses (n = 14) for the detention pond showed concentrations below the LOQ, and where positive identification was possible concentrations for individual PAHs ranged between 0.01 and 0.05 μg/L (Table 24.5). The highest PAHs concentration measured at the filter inlet was 0.033 μg/L (2-methylnaphthalene). Eighty-three percent of the investigated drainage water of the plant-covered soil filters returned PAHs concentrations below the LOQ (results not shown). This means that both soil filters functioned very effectively in respect of PAHs. The only positive findings can be attributed almost entirely to water soluble naphthalene and methylnaphthalene, with concentrations ranging from 0.01 to 0.03 μg/L. It should be mentioned that these low concentrations are close to the LOQs and therefore subject to a considerable degree of uncertainty.

In addition water samples were analysed in respect of 53 pesticides. Low concentrations were found for the compounds diuron, metobromuron, azoxystrobin and terbutryn. The analyses returned low concentrations in the vicinity of the LOQs (Table 24.5). The concentrations measured do not exceed the EQS for diuron (0.2 μg/L).

24.5 Field-Scale Experiments (Halenreie Plant)

As part of a research and development project conducted by the Bremen University of Applied Sciences and the University of Bremen, investigations were carried out at both laboratory and field scales with the aim of developing optimised filter material for plant covered soil filters. For testing the material effectiveness, parameters such as suspended particulate matter, hydrocarbons, low condensed PAHs, Cu, Zn and 2,4-D were selected. The best results were obtained with a filter substrate containing quartz sand and silicate-colloid/humus in combination with mycorrhizal plants such as *Phalaris arundinacea*, *Lythrum salicaria* and *Iris pseudacorus* (Dobner et al. 2008; Holthuis et al. 2008).

For the field-scale experiments, one of the vertical-flow sand filters of the Halenreie plant was replaced by the above mentioned substrate-optimised filter system. The second vertical-flow reed-planted soil filter remained unchanged and acted as an experimental control.

The occurrence of dissolved, polar benzothiazole and benzotriazole species in the run-off water from the detention pond and also from the drainage water is shown in Table 24.6.

Representing the benzotriazole group as compounds, the concentration of 1-H-benzotriazole (1HBTr) in the detention pond was found to be 0.14 μg/L. The same concentration was found in the drainage water emerging from of the newly installed filter material. Concentrations of tolyltriazole (TTr) in the basin amounted to 0.26 μg/L, whereas the effluent of the new filter bed showed slightly higher concentrations (0.35 μg/L). Benzothiazoles (2ABT, MTBT, OHBT and MBT) were found in the detention pond in concentrations ranging from 0.07 μg/L (MTBT) to 1.7 μg/L (OHBT) (abbreviations see Table 24.6). All drainage effluents from the new filter material returned a lower degree of reduction in the concentrations of

Table 24.6 Results obtained from the Halenreie soil filter, sampled in September 2008 (μg/L)

Compound	Filter influent	Efflux Segment I
SPM	5,600	1,400
Cu	<50	<50
Zn	76	<50
BTC	<0.05	<0.05
2ABT	0.14	0.13
MTBT	0.47	0.07
OHBT	1.7	0.24
MBT	0.07	0.07
1HBTr	0.14	0.14
TTr	0.26	0.35
56DMBTr	<0.05	<0.05
BPA	0.054	n. a.

Segment I = modified filter material; SPM = suspended particulate matter; BTC = benzothiazol-6-carbonic acid, 2ABT = 2-aminobenzothiazole; MTBT = 2-(methylthio) benzothiazole; OHBT = 2-hydroxybenzothiazole; MBT = 2-mercaptobenzothiazole; 1HBTr = 1-H-benzotriazole; TTr = Tolyltriazole; 56DMBTr = 5,6-dimethyl-1H-benzotriazole; BPA = bisphenol A; <[value] = value lies below the limit of quantification; n. a. = not analysed.

benzothiazoles and benzotriazoles. Analysis was performed by means of time-of-flight-mass spectrometry after separation by nano-LC (Niñonuevo et al. 2005). The benzothiazoles probably originate from tyre abrasion, whilst benzotriazoles are used as corrosion inhibitors for vehicle components.

BPA is a component of tyres and plastics and is introduced into road run-off through tyre wear and tear. In the Halenreie facility, a sample from the detention pond retuned 0.054 μg/L.

Furthermore, an initial ecotoxicity test using luminescent bacteria (EN ISO 11348-1) indicated a biologically insignificant contamination level in the detention pond. In contrast to these results and the combined screening test provided evidence of varying degrees of inhibition showed the existence of differentiated inhibitions (Fig. 24.2).

24.6 Conclusions

The analysis of samples from highway stormwater run-off has revealed the presence of heavy metals, metalloids, PAHs, benzothiazoles, alkylphenols, BPA and DEHP. Many of these substances are listed in Annex X of the Water Framework Directive as being hazardous or potentially hazardous. They originate mainly through tyre abrasion or from plastic components which are subjected to mechanical wear and tear. Generally, it is necessary to treat such run-off water before it seeps into the groundwater or drain into any surface water body. This is especially the case where major roads transect water protection areas or polluted stormwater run-off threatens to impair the quality of surface waters.

Heavy metals, metalloids and non-polar organic pollutants can generally be retained effectively by treatment plants. When they seep through a soil filter these pollutants tend to accumulate in the upper soil horizon, and the vertical transport of substances through to the groundwater is reduced considerably. Another frequently employed method for the treatment of stormwater run-off involves reed covered soil filters to retain pollutants. This treatment technique also returns good results.

In a field-scale experiment conducted on a plant covered soil filter, part of the original filter material was replaced by a section containing quartz sand and silicate-colloid/humus in combination with mycorrhizal plants. The results show a high degree of retardation efficiency for metals and non-polar organic substances, but less for the polar compounds such as benzothiazoles and benzotriazoles.

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Part IV
Mitigation Measures – Technical and Socioeconomic Instruments

Chapter 25
Options for Mitigation: An Overview of Measures

Cajsa Wahlberg and Arne Jamtrot

Abstract Historically, the focus concerning emissions of xenobiotics has been on industrial effluents and point sources, but nowadays there is a recognition of the existence of diffuse emissions of hazardous substances from many different sources, including materials and consumer goods. In this chapter different mitigation strategies against such emissions are discussed. Mitigation is here defined as upstream source control. Removal of xenobiotics by sewage treatment methods is not covered. The main focus is on the options that national, regional and local authorities have to reduce emissions of hazardous substances at their sources but other actors, such as businesses and non-governmental organisations, are also discussed. The tools for mitigation include green procurement, use of current legislation, voluntary agreements, cooperation, financial initiatives, information campaigns, ecolabelling, etc. Examples of each tool are given and follow-up and costs are discussed.

25.1 Introduction

As a result of the introduction of environmental legislation and the establishment of environmental authorities in the late 1960s, emissions from point sources such as production facilities have decreased. Parallel to this, the emissions of a number of substances from construction materials and consumer goods such as textiles, electronics, household chemicals and personal care products have increased, and in

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C. Wahlberg (✉)
Waste Water Treatment Department,
Stockholm Water Co, SE-10636 Stockholm, Sweden
e-mail: cajsa.wahlberg@stockholmvatten.se

A. Jamtrot
City of Stockholm, Environment and Health Administration, PO Box 8136, SE-10420
Stockholm, Sweden
e-mail: arne.jamtrot@miljo.stockholm.se

D. Fatta-Kassinos et al. (eds.), *Xenobiotics in the Urban Water Cycle: Mass Flows, Environmental Processes, Mitigation and Treatment Strategies*, Environmental Pollution, Vol. 16,
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population centres, they are now the dominating emissions. This has been shown for heavy metals and organic substances in a number of studies at the local, regional and national levels (Bergbäck 1992; Sörme et al. 2001; Jonsson et al. 2008). This development has produced a need for more up-stream oriented mitigation measures, since end-of-pipe solutions are not always sufficient in dealing with such emissions.

Within this context, the term mitigation refers to upstream source control, that is direct and indirect non-structural approaches to managing fluxes of pollutants. Technical solutions such as sewage treatment methods are not covered within this chapter. Mitigation measures may be taken by different types of actors, such as national and local authorities, individuals, non-governmental organisations (NGOs) and industry, and include both voluntary initiatives and legislative measures.

What are the benefits of mitigation compared to structural end-of-pipe solutions? With mitigation, pollution is avoided before the pollutants are emitted, and there is no waste or by-product to be discarded of. The obvious purpose is the protection of the receiving waters. But the quality of the sludge produced in the wastewater treatment plants (WWTPs) is also improved, making it more attractive for use in soil amendment. The microbial processes at WWTPs, the working environment and the sewerage network are also protected by mitigation and there are savings in energy and infrastructure costs. Another benefit of mitigating chemicals at their sources is that the use of hazardous substances in consumer products will decrease, leading to less direct exposure of humans.

The City of Stockholm has recently presented the results of a four-year project entitled *New pollutants – new tools* (Bergbäck and Jonsson 2009). The report includes a list of the five groups of pollutants of highest priority for the city, and proposes ways in which the city and other actors can reduce the impact of these and other substances on the environment. The priority groups of pollutants identified in the project include alkylphenols and alkylphenol ethoxylates, antibacterial agents such as triclosan and silver, brominated flame retardants, phthalates and polyfluorinated compounds such as perfluorooctane sulfonate, pefluorooctanoic acid and fluorotelomer alcohols.

Because the question of diffuse emissions of xenobiotics is very complex, a whole spectrum of measures is needed. The suggestions from the project include end-of-pipe treatment options, as well as mitigation strategies that are included in the discussion in this chapter.

Similar approaches have been applied for example in the Danish project *Dogme 2000* (Dogme 2000 2009), and the Danish/Swedish project *the Source Partnership* (The Source Partnership 2008). *Dogme* 2000 was carried out jointly by environmental authorities in a number of Danish municipalities. Among the achievements of this project were the selection of priority xenobiotics and the compilation of a list of methods for upstream source control and the target groups these methods were addressing. In *the Source Partnership* municipalities and WWTPs in the Öresund region have worked together to identify the sources of environmentally hazardous substances in wastewater and to minimise emissions.

This chapter is built on the results of these projects as well as from our own experiences of upstream source control and mitigation at a local environment and health administration and a water company, respectively.

25.2 Actors and Their (Sense of) Responsibility

There are usually a number of different actors who could take measures depending on the issue in question. A specific measure often calls for cooperation between several actors who together take responsibility to act.

In a recently published study (Lindström 2007), individuals from different groups were asked to rank several actors according to who they perceived had the greatest responsibility for reducing the risks associated with hazardous substances in consumer goods. The responding groups represented consumers, retailers, local politicians and experts (researchers and authority officials). It was obvious from the results that all groups ranked their own group lower than the others did, indicating that everybody thinks that the responsibility lies not on themselves but on someone else. This is a concern, since it may make it difficult to make actors feel responsible for taking measures they actually have the possibility to take. It also shows that cooperation between actors is crucial, to make everybody contribute.

Individuals differ in their attitudes towards incorporating new environmental habits, such as avoiding products that contain hazardous substances. This can be illustrated by a model first presented to describe the diffusion of technical innovations (Rogers 2003), but which is also applicable to describe different attitudes towards other novelties, such as new measures against pollutants. This model talks about five different groups of people, based on their attitudes: *Innovators* come up with new solutions. They are keen on trying new ideas, well-educated and have international networks. *Early Adopters* easily pick up new ideas. They are well respected locally, and other people turn to them for advice. The *Early Majority* carefully consider new things, but still belong to the 50% of the population that most readily accept them. The *Late Majority* adopt an attitude of reserve towards innovations. The uncertainties that are connected with the new ideas have to be eliminated before they can be accepted. The *Laggards*, finally, are suspicious towards novelties, and actively resist innovations. They prefer to stick to traditional values. Of course, the same individuals may not act in the same way in relation to new information and measures concerning hazardous substances as in relation to technical innovations, but the categories are useful to illustrate the fact that new information will be received in different ways by different people, and that mitigation measures have to deal with this, through adjustments to the people in question.

It can also be noted that different actors will respond to different driving forces. Expressed very simply, the Late Majority will do what the surrounding world demands of them. Irrespective of whether the demands are represented by legislation or by market pressure, they act when they have to, not earlier. The Early Majority, Early Adopters and Innovators will increasingly act based on what they can achieve, that is they have an environmental agenda of their own. Laggards, finally, will be occupied with finding ways of doing even less than they are obliged to.

In a similar way, the environmental work of manufacturing companies in Sweden was described by Arnfalk et al (2008) using five categories of increasing awareness. The categories they used were: Environmentally Passive, Requirement

Oriented, Requirement Optimized, Environmentally Conscious and Environmentally Adjusted. They found that bigger companies generally belonged to the more active categories, and that most companies – irrespective of size – have improved their environmental work approximately one category level since the first study in 1991.

National, regional and local authorities are important actors as well as the European Union and other international organisations. The most evident actions are the instituting of new laws and regulations and the enforcement of them. But in addition, authorities can initiate research activities, information campaigns and dialogue projects with different business domains, etc. Public authorities also have the opportunity to set good examples, for example by including environmental considerations in their own procurement.

Business organisations at the national and European level may also take their share of responsibility by removing environmentally hazardous substances from the market. Retailers can put pressure on their upstream suppliers to provide information about the chemical ingredients of their products and to replace hazardous substances with less harmful alternatives.

Individual business domains with common interests can take joint actions or launch common campaigns regarding the environmental properties of their products. One example is the Swedish construction sector which has agreed on a common scheme of self declaration of goods (BASTA 2009), under which the suppliers are responsible for putting environmental information about their products into a joint database. An auditing system for quality assurance complements the database.

The general public and individuals may reduce the use of hazardous substances by making the right purchase when this is possible, based on information on the chemicals included. It is however unrealistic to expect that the general public should have all the information and knowledge to be able to choose the most environmentally friendly products.

Other important actors are environmental and consumer NGOs which often generate new information about chemicals in use, and ecolabelling organisations which help the general public make good environmental choices, at the same time as they help the producers market new alternatives. Researchers also have a responsibility to make their results publicly available and take part in the general debate about chemicals.

The market pressure that is sometimes needed to motivate producers to substitute unwanted substances, can also be exerted through media giving attention to issues about hazardous substances in consumer goods.

25.3 Measure Options: Tools for Mitigation

A number of ‘tools’ are presented below as examples of mitigation measures. The main focus will be on measures that public actors, such as municipalities, have the possibility to enforce. Cooperation, collaboration and dialogue are however key words for most of these tools, meaning that the measure is often dependent on more than one actor.

The measures can be divided into direct and indirect measures. Direct measures deal with the actual use of unwanted substances. They lead to quantifiable results that at least in principle can be estimated in advance. Examples of direct measures are public procurement and the substitution of chemicals. Indirect measures on the other hand aim at making someone else reduce their use of unwanted substances. The results of indirect measures are dependent on other factors and their effects are thus more diffucult to quantify. Examples of indirect measures are ecolabelling, new laws or regulations and information campaigns.

25.3.1 Green Procurement

Green procurement means that purchasers take environmental considerations into account when buying chemical products, goods or services. The concept includes avoiding unnecessary purchases and considering different environmental aspects, such as contents of xenobiotics, energy consumption, possible reuse or recycling, life span and disposal of the products.

In London, The Mayor of London's Green Procurement Code is an initiative supported by the London Development Agency. The code provides practical advice to both the private and the public sector in integrating environmental considerations into all aspects of their business. Businesses are asked to sign up to the code, thereby committing to making progressive reductions in their environmental impact. Practical guidance on how to find green products and suppliers as well as a forum for discussions are accessed on a specific website, www.greenprocurementcode.co.uk, for those who have signed-up (Wickman et al. 2009).

When public authorities use green procurement they serve as good examples for the private sector. The public sector is also in itself an important economic actor and can put great pressure on the market by requiring that purchased goods do not contain hazardous substances. A demand for such alternatives can be created, thereby facilitating an adjustment of the market so that products free from hazardous chemicals will be available also to the general consumer. It should be pointed out that the same criteria used by the public authority when products are purchased should also be applied to the procurement of contracting services such as healthcare, transportation, building and construction and in turn their use of chemicals and products.

It is important how the call for tender is formulated in a public procurement and the legislation places restrictions on the type of requirements that can be included in the technical specifications. For example, when purchasing chemicals, it is not possible to demand that the products are environmentally labelled, but it is allowed to require that the products must *pass the criteria* for environmental labelling. It is also legitimate to ask that specific chemicals are not included in the product, that is to include a so-called blacklist in the specification. EU provides a handbook for public green procurement in several languages (Buying Green! – Handbook on green public procurement 2008).

The city of Stockholm makes annual purchases of goods and services worth €1,000,000,000 per year in the field of health care, computer and office machines, transportation etc. These large purchases indicate that the city has a good chance to influence the market and contribute to the development of new, greener products. A guideline with a blacklist and suggested tendering criteria has been produced for the purchasers in the different parts of the city's administration (Guide to non-toxic products 2006).

In order to establish good and well-working criteria in the procurement process there is a need for knowledge of chemicals and of procurement regulations. The purchaser must also be positive to new innovations and solutions and sometimes also to larger initial costs.

25.3.2 Legislation and Regulations

Legislation places minimum requirements on industry, importers and retailers. It is the means by which supervision by authorities is possible. But environmental legislation is still mainly focused on point sources such as discharges from industrial sites. The regulations concerning diffuse pollution from the use of hazardous substances in consumer goods, articles or construction materials are far from sufficient. Emissions from individual users are considered as a negligible contribution to the total load and according to the legislation it is therefore not possible to take legal measures against such emissions.

There are a number of substances with special restrictions in the present common EU legislation. One example is the RoHS Directive (Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment) which places restrictions on the content of lead, mercury, cadmium, hexavalent chromium and the two brominated flame retardants polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) in electronic and electric devices. Another directive (2005/84/EC) limits the concentrations of certain phthalates in toys and childcare articles.

REACH, the new European regulation on chemicals (REACH 2006) came into force in June 2007. It requires that all manufacturers, importers, and downstream users register the chemicals they use or produce in volumes of one tonne or more per year, and provide information regarding their uses and environmental and health properties. If a substance is included in the EU List of Substances of Very High Concern (SVHC) the company must obtain an authorisation from the EU. REACH will not replace sector-specific legislation, for example on chemicals in cosmetics, food or medicine. These are covered by other EU laws.

Concerning articles, the information requirement in REACH only applies if certain criteria are met, i.e. if the chemical is intended to be released from the product and is manufactured or imported at more than one tonne per year or if the article contains chemicals from the SVHC-list.

REACH will lead to more publicly available information on environmental properties of chemical substances and hopefully the new legislation also means that the release into the environment of hazardous substances will be reduced.

But this will probably take time since the implementation of the last parts of REACH is scheduled for 2018. Until then, there is a need for more detailed product-specific legislation on the use of certain chemicals in certain goods, analogous to the approach used in the RoHS-directive. For example, such regulations would be very useful in the case of chemicals in textiles.

The Water Framework Directive (WFD 2000/60/EC) requires that environmental quality standards (EQS) are defined in each EU member country for the list of substances in annex X of the directive (2008/105/EC). This list currently consists of 33 substances or substance groups and will according to WFD be amended every fourth year. Manufacturing industries and WWTPs discharging effluents into receiving waters may run into problems to meet the EQS for water bodies which may be taken as a motive for mitigation measures.

In Stockholm, the Local Environment and Health Administration together with Stockholm Water Company in 1989 used the Swedish Water and Sewerage Act to require the replacement of car washing detergents containing nonylphenol ethoxylates. This was possible because the act states that WWTPs do not need to accept wastewater which differs in composition from ordinary domestic wastewater. This resulted in a decrease of nonylphenol (a degradation product from nonylphenol ethoxylates) in the sewage sludge of approximately 90% over a few years from 1990 and onwards, see Fig. 25.1. In 1992 there was a PARCOM recommendation to phase out nonylphenol in domestic detergents by 1995 and in all detergent applications by 2000 (OSPAR Commission 2001) that further facilitated the decrease in sludge.

Relying on new regulations coming into force requires a lot of patience. It generally takes a long time from the first initiative to the execution of a new law. But once the regulations are in place they are very effective and easy for a public authority to use in supervision work.

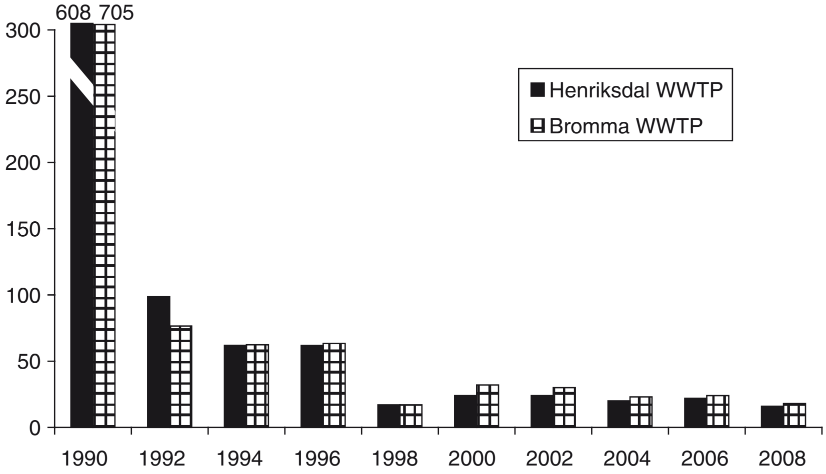

Fig. 25.1 Nonylphenol in digested sludge in WWTPs in Stockholm (mg/kg dry matter)

25.3.3 Cooperation and Voluntary Agreements

Dialogue and cooperation between stakeholders is crucial for making things happen when it comes to mitigating chemicals at their sources. The clue here is to make use of the willingness of those within a certain business domain or group of stakeholders who want to be pioneers; the Innovators and Early Adopters. The challenge is to subsequently implement the developed tool or agreement to a standard comprising most actors within the domain or group. A few examples are discussed here.

The Future Trade Dialogue was an alliance formed between Swedish companies, local authorities, regions and the government. It was designed to achieve the sustainable development of trade in convenience goods. One of the achievements of this alliance was a written guide intended for the retailers, Environmental Requirements for Chemicals in Products – a Guide for Purchasers. It includes a five-step model for how to prioritise on which products and on which substances to focus environmental requirements when making purchases (Future Trade Dialogue 2006).

Another good example of an agreement between stakeholders is the environmental information on pharmaceuticals that have been made publicly available in Sweden at www.fass.se, a website produced by the industry to be used as guidance for both subscribers and the general public. The environmental data is supplied by the industry under the supervision of an independent body. Subscribing doctors are presented with pharmaceuticals with similar efficacy, from which they can choose the one with the best properties from an environmental point of view. The model has been developed by the pharmaceutical industry, the Swedish Medical Products Agency, Apoteket AB (the Swedish Pharmacies), the Association of Local Authorities and Regions, and Stockholm County Council (FASS.se 2007). The objective is that all pharmaceuticals will be environmentally classified by the year 2011.

25.3.4 Financial Incentives

Economic policy instruments, in the form of financial subsidies, taxes or fees, can bring about changes in behaviour. Sweden currently has taxes on pesticides, nitrogen fertilisers and cadmium in phosphorus fertilisers. A report from the Swedish Chemicals Agency (Hammar and Drake 2007) indicates that ‘there is reason to believe that increased and supplementary control through financial incentives, subject to certain conditions, may increase cost-effectiveness in chemicals policy’.

The Swedish Chemicals Agency (2008) has thus recently proposed taxes on lead shot for hunting. The revenue will subsequently be used for governmental subsidies for environmental bullet retrieval arrangements for shooting with leaded bullets at shooting ranges. The motives for the proposal are that lead contaminates the ground, especially in shooting areas, and that birds are easily poisoned.

An example of financial subsidies is the Stockholm campaign to remove mercury (Hg) from sewer pipes. With the help of a governmental contribution of €1.2 million, Stockholm Water Company could offer landlords, enterprises and institutions a

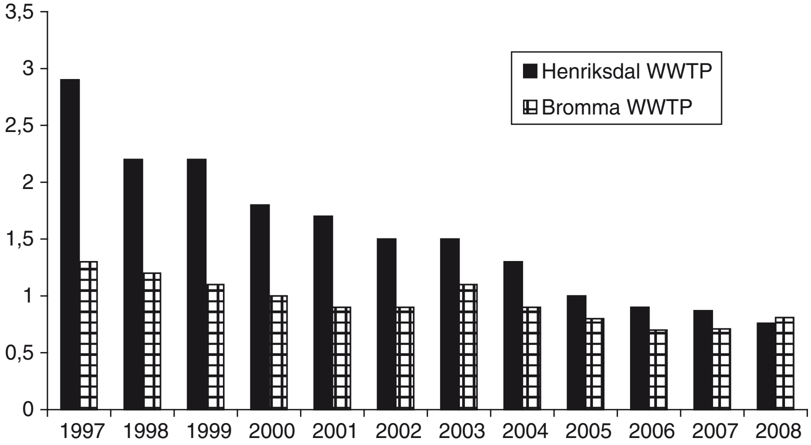

Fig. 25.2 Mercury in digested sludge in WWTPs in Stockholm (mg/kg dry matter)

60% subsidy towards the costs of the removal of sewer pipe sediments containing Hg. The sewer systems in buildings used as dental clinics, hospitals and industries where Hg had been handled were cleaned by high pressure water jetting and the sediment flushed out was subsequently taken care of as hazardous waste. In six years, between 1998 and 2004, almost 280 kg of Hg was removed by these measures, to be compared with the total influx of 20 kg Hg to Stockholm's largest WWTP in the year 2003, Fig. 25.2. The Hg level in the sewage sludge was reduced by 55% during these years and roughly half of this reduction is attributed to the removal of sediment in sewer pipes (Wistrand 2007).

25.3.5 Information Campaigns and Public Awareness Programmes

Information campaigns and public awareness programmes are different tools to help the public to act green and to make environmentally good choices. They can either be addressing the whole general public or specific groups, such as the farmers or the artists in the examples below. The campaigns are usually successful if they are carried out professionally and allowed to run long enough or repeated many times.

Again the task becomes more difficult when it comes to information on hazardous substances in materials and articles. The issue about hazardous substances in goods involves a multitude of substances and information which is neither unambiguous nor easily accessible. This is especially the case for articles such as clothing, electronic equipment etc where there is no legitimate demand to list all chemicals included. The general public can therefore not be expected to have the knowledge needed to make good environmental choices. Provided the campaign deals with a well defined group of articles containing a limited number of specific chemicals, which are recognizable for the consumer, it is still possible to achieve a good result.

Two good Scottish examples of public awareness programmes are described by Wickman et al. (2009). One was aimed at educating consumers about the safe disposal of oil residues and wastes (Yellow fish Campaign 2004), and the other (WaterSense Initiative 2009) has the purpose to raise public awareness of toxic chemicals used in everyday household products. The latter project has a user-friendly website which describes how the chemicals we put down the drain can end up in the water environment.

An example from overseas is the 'No Drugs Down the Drain!' campaign in California. A coalition of local, regional, state and federal agencies conducted a state-wide campaign during October 2008 to educate the public that disposing of leftover pharmaceuticals down the toilet has environmental costs and is no longer acceptable. The public was provided with information on alternative disposal options throughout the state. The campaign was a positive experience in terms of execution as well as the reception by their residents and local media, according to the final report (No drugs down the drain! 2008).

In Sweden many information campaigns have been launched against triclosan in toothpaste during the last 8–10 years. Attention in media and support from the Swedish Dental Association (Edwardsson et al. 2005) laid great pressure on the retail trade to remove triclosan-containing toothpaste and other products from the shop shelves, an effort that recently bore fruit. Today it is hard to find toothpaste containing triclosan, at least in the larger supermarket chains.

A number of campaigns aimed at reducing the environmental impact of pesticides have been addressed at farmers. The European Crop Protection Association (RECAP) has taken a number of initiatives to promote the best management practice in the use of plant protection products. Education and the development of physical and technical solutions helped the farmers to better protect themselves and to reduce emissions in ground and surface water.

A follow-up to this was the five year program of voluntary measures, The Voluntary Initiative (VI), launched in 2001 by the UK Crop Protection Association together with a range of stakeholder organisations. Over 30 different voluntary actions have been included, such as a program to ensure the correct maintenance of the spraying equipment, providing training and information to sprayers and the development of a self-assessment form to support farmers in assessing the risks associated with crop protection on their farms. Monitoring data after the campaign indicates that the use of these farmer-led initiatives can lead to an improvement in water quality of over 90%, although it takes approximately 15 months for positive results to be seen (Wickman et al. 2009).

The levels of cadmium (Cd) in sludge intended for soil amendment has given rise to a lot of debate in Sweden during the past years. There are hardly any point sources left and the major sources of Cd to the Stockholm WWTPs are car washing facilities, domestic wastewater and storm water. Food and artists' paints are some of the sources of the Cd content in domestic wastewater (Sörme and Lagerkvist 2002). To make artists aware of the negative environmental properties of their paints, Stockholm Water Company has been running an information campaign since 1998 encouraging artists to either substitute their paints for alternatives without Cd or to treat any water containing Cd with precipitation chemicals (works well in a coffee filter) before it is discharged into the sewer. The campaign had until 2007 resulted in a removal of 37 kg of Cd which otherwise would have reached the sewers and ended up in the WWTP sludge. This amount was estimated by Soutukorva et al. (2008) by comparing the declining concentrations of Cd in sludge from the two WWTPs in Stockholm, of which the one serving the central part of the city, where a majority of the art schools and artists cooperatives are situated, showed the largest decrease (Cd levels are also declining due to earlier restrictions on Cd, for example in pigments, stabilisers and platings).

25.3.6 Ecolabelling

Whereas it may be difficult for consumers to have the information and knowledge needed to avoid hazardous substances in purchased goods, a good help is to look for ecolabelled products.

The first ecolabel was the German ‘Der Blaue Engel’ which was established in 1978. Within Europe ‘the EU-flower’ can nowadays be found on washing detergents, office equipment, textiles, lubricants, papers, to name but a few groups of products. Different countries also have their own ecolabelling schemes. In the Nordic countries there is the official ecolabel, ‘the Swan’, and in Sweden the label issued by the Swedish Society for Nature Conservation, ‘Good Environmental Choice’, with the Falcon symbol is common. The Swan and the Falcon are both recognised by a large portion of the general public in Sweden (96% and 80% respectively) (Lindström 2007).

To be awarded an ecolabel the products have to comply with certain criteria concerning for example contents of hazardous chemicals and energy consumption, decided by the labelling authority. In addition, services such as tourist accommodation, car washing facilities and grocery stores can obtain the ecolabel.

The ecolabelling of products is a big help to consumers when they want to buy green and an expansion of ecolabelling to new groups of products and services would further promote greener shopping. A drawback is that too many different green labels and claims can make it difficult for consumers to keep track of the environmental benefits of the different labels, as seems to be the situation today in the UK (Wickman et al. 2009).

25.3.7 Substitution

Substitution is a term applied to a varying range of measures. In the above mentioned information campaigns the objective is sometimes to replace a hazardous chemical with one that has better environmental performance or to have it completely removed from the product. A hazardous chemical can also be phased-out by choosing a different product or material or using another technique or behaviour. Wool is an example of a material that has a built-in surface protection and is naturally flame retarded (Gustafsson 2004). Wool is thus a good environmental choice compared to other fabrics that may need both flame retardants and surface protection chemicals. An example of a simple new technique is the use of micro fibre cloths in every-day household cleaning instead of household cleaners. By airing clothes after use it is possible to reduce the frequency of washing or dry cleaning. But there are also more direct substitution measures addressing the manufacturing industries.

The environmental legislation makes it possible for the enforcing authorities to request from industries that they report all chemicals they use, including the particular ingredients, and the environmental and health classification of these. This has been enforced in a number of cities in Sweden, with the main objective of urging the companies to substitute hazardous substances with less hazardous ones. The industries have been provided with a template to fill out, accounting for CAS-numbers identifying the chemicals, environmental information and the quantities used per year. This way, 53 phase-out chemicals and 70 risk-reduction chemicals have been identified in Stockholm and the industries have been made aware of the environmental properties of the chemicals they use.

In 2008 the NGO ChemSec (International Chemical Secretariat) together with a group of businesses introduced the database REACH SIN-list (Substitute It Now) with the aim 'to ensure that REACH Authorisation procedure will be an effective tool to fast-track the most urgent Substances of Very High Concern for substitution, and to facilitate toxic use reduction by businesses' (ChemSec 2008). The database consists of 267 chemicals identified as SVHC based on the criteria established by REACH. The supporting group of stakeholders included companies such as Sony Ericsson, Sara Lee, NCC, Fred Butler and H&M, as well as EUREAU, the European Union of National Associations of Water Suppliers and Waste Water Services and BEUC, the European Consumers´ Organisation (Rosander and Nimpuno 2008).

25.3.8 Green Chemistry

The term green chemistry covers both green production and green products. Chemicals are manufactured in a sustainable way, using alternative or fewer chemicals and with reduced energy consumption. The green products are designed to have better inherent environmental properties. They are for example less toxic and more readily degradable. This is a good example of preventing pollution at its source. More about green chemistry can be found in Chapter 20 in this book.

25.4 Follow-up and Cost Associated with Mitigation Measures

To verify if the chosen mitigation measures really had any effect it is recommended that the results are assessed in one way or another. Depending on the selected tool, it is possible to measure the reduction in concentration of a particular substance in influents, effluents or digested sludge from WWTPs, look at the sales volumes, carry out interview surveys of the general public or of specific groups of retailers or producers, etc.

Any ordinary environmental monitoring carried out by national, regional or local authorities may also indicate if the measure taken was successful, but generally changes in levels in water bodies, biota or sediments are too slow to show any direct results from mitigation activities.

It is also advisable to look at the costs of the measures in order to estimate the cost-benefit of the different activities in economical and environmental terms. In the above mentioned campaign, informing artists about the Cd content of their paints, the costs until 2007 were calculated to €4,750 per kilogram of Cd retained (Soutokorva et al. 2008). The costs per kg will be lower if the campaign continues to have effect and the Cd content in sludge keeps on declining. The total costs for the removal of Hg contaminated sediments in sewer pipes amounted to approximately €7,700 per kilogram Hg removed.

There are also costs for disposal of digested sludge, paid by the Stockholm WWTPs. Today the sludge is used to reclaim mined areas in the very north of Sweden. It is taken care of by Boliden, a Swedish metals company, transported by railway and spread out to provide quick new growth on the mined ground. For this Stockholm Water Co pays approximately €26 per ton digested and dewatered sludge. These costs will be reduced if the contents of pollutants are brought down, thereby promoting better acceptance for alternative uses for the sludge, for example for agricultural soil amendment or soil production.

There are also other costs connected to pollutants, such as expenses for hospitalisation or reduced ability to make an income due to bad health from chemicals. Soutukorva et al. (2008) suggest that €10–40 million per year might be interpreted as a lower boundary for the damage costs due to toxic pollutants in Stockholm.

25.5 Conclusions and Future Perspectives

Whereas legislative measures may be efficient in influencing some actors, primarily the Late Majority, the development of new solutions, leading to lower emissions of xenobiotics into the environment, requires measures that encourage more progressive actors, Innovators and Early Adopters, to come up with and put these solutions on the market.

In order to reduce emissions from diffuse sources such as consumer goods, personal care products and building materials, a lot of voluntary measures have to be taken by consumers, industry, trade organisations and public organisations.

This requires new methods of cooperation between these actors. A few such examples have been mentioned in this chapter. The City of Stockholm is also developing new arenas to act together with local industry and business actors.

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Part V
Outlook

Chapter 26
Outlook

Kai Bester, Despo Fatta-Kassinos, and Klaus Kümmerer

The idea to compile this book arose from the COST Action 636 'Xenobiotics in Urban Water Cycle' and this reflects on the knowledge and discussions assembled in the last three years in this Action. In parallel to working on this book and COST Action, several issues were discussed. Although some of these issues have been widely established on a research level, others still remain open and speculative. This book aims at providing the reader with a review of current issues on xenobiotics in urban waters.

26.1 Lessons Learned

Several issues on managing xenobiotics are described below.

1. It can generally be assumed that mass flows and sources for water and wastewater contamination in dry weather situations are relatively well known. However, in most European urban water systems, the so-called prioritised compounds of Annex X of the Water Framework Directive are not necessarily the most relevant with respect to concentration or effect levels. Other compounds exist that have a higher priority.
2. Most of the contributions in this book focus on managing xenobiotic compounds in water, as a result of most research initiatives triggered by the Water Framework

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D. Fatta-Kassinos
Department of Civil and Environmental Engineering, University of Cyprus,
School of Engineering, Nicosia, Cyprus
e-mail: dfatta@ ucy.ac.cy

K. Bester (✉)
Department of Biotechnology, Chemistry and Environmental Engineering,
Aalborg University, Aalborg, Denmark
e-mail: kb@ bio.aau.dk

K. Kümmerer
University Medical Center, Freiburg, Germany
e-mail: klaus.kuemmerer@uniklinik-freiburg.de

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Directive and other relevant laws. An overview on technical solutions further to conventional activated sludge treatment, such as membrane bioreactors (microfiltration/MBR), nanofiltration and advanced oxidation (AO) are demonstrated, in addition to sorption and soil filtration. The current consensus in the research community is also reflected in this book; there is no one technology that solves all issues under all conditions. What might give the desired gains in one situation, may not give the desired results in another. For example, the fact that microfiltration/MBR has higher sludge retention times and higher sludge density than conventional activated sludge treatment suggested that it might be successful in increasing the elimination rates of compounds that are degraded in conventional activated sludge treatment. Although this was effectively demonstrated, for compounds that are difficult to degrade, MBRs are usually not successful as shown by several contributions. Nanofiltration can be quite successful in removing some xenobiotic compounds. However, the rejected water it produces contains high amounts of other xenobiotic compounds that need other means of treatment. Much research remains to be accomplished before nanofiltration becomes an established technology for drinking water production (reuse of water). Advanced oxidation tends to work very well in removing highly active molecules such as steroid hormones. On the other hand, advanced oxidation may produce oxidation products of higher environmental potency than the initial compounds if not well evaluated and properly applied. This suggests that oxidation processes need a careful assessment before their application. Use of sorption for elimination is limited to compounds that can sorb. There will probably always be some compounds that are hard to remove by this method, in particular, pharmaceuticals. Consequently, a combination of treatment technologies may prove essential to handle today's mixtures of compounds in wastewater.

3. Several contributions focus on mitigation strategies. These have been successfully demonstrated, particularly in Scandinavian countries (e.g. for pharmaceuticals, tensides etc.) and the Anglo-Saxon world (e.g., yellow fish oil campaign). This option is usually very cost-effective, but the prerequisite is that the issue can be communicated to the consumer. Therefore, countries with attentive consumers and openess to discussions will find it easier to apply this option rather than countries that work more on an expert meeting basis and often work less open and more on confidential basis.

26.2 Knowledge Gaps and Issues That Need to be Resolved

1. There is no overlying "one" way to control xenobiotics in urban waters. Each catchment has its own specific situation in water contamination and water management. To solve this, in depth knowledge of the respective catchment and the relevant processes need to be considered.
2. Though mass flows of xenobiotics in dry weather is well known, relatively little is known about how to quantitatively assess, understand and predict

stormwater contamination. In stormwater, different sources may become relevant, such as road wash-off (run-off), mobilisation from facades and rooftops. As a result, fuel components, plasticisers, polycyclic aromatic hydrocarbons (PAHs), biocides, UV-filters and flame-retardants among others, are emitted during these events. Additionally, combined sewer overflow lead to discharge of waste water with no or only minimal treatment and thus no elimination. This might also be an important pathway of xenobiotics into surface waters. However, there is a lack of experimental data in addition to theoretical understanding.

3. Soil filtration, retention soil filters or biofilters may be an interesting approach/technique to manage stormwater and improve wastewater treatment plants discharge quality. However, currently only a basic understanding exists.
4. Although the research community is aware that transformation products are relevant in most processes, the majority of studies focus only on parent compounds. Limited resources make it difficult to include these transformation products that are often hard to analyse. Additionally, the transformation products in environmental processes are frequently not known, thus, structural elucidation is needed for each process. Perhaps more will be learnt from the registration documents that include transformation processes in vertebrates in the future.

Answers to these issues are urgently needed, especially in view of the increasing water reuse worldwide. Water reuse is currently the most important source of potable water in cities such as Berlin, the Ruhr megalopolis, large parts of the Rhine delta (Netherlands and Western Germany), the cities in the Severn catchment in Great Britain, Los Angeles and Singapore. Wastewater reuse is a practice that is of great importance for countries facing water scarcity all over the world.

We hope that this book conveys the importance of this research field as it deals with public health impacts and aquatic environments. Furthermore, we hope that the reader will find this book as exciting and stimulating as we, the editors have.

Despo Fatta-Kassinos Kai Bester Klaus Kümmerer

ERRATUM TO:

Chapter 12

Transport and Fate of Xenobiotics in the Urban Water Cycle: Studies in Halle/Saale and Leipzig (Germany)

Mario Schirmer, Frido Reinstorf, Sebastian Leschik, Andreas Musolff, Ronald Krieg, Karsten Osenbrück, Marion Martien, Kristin Schirmer, and Gerhard Strauch

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In this chapter the name of co-author “Marion Martienssen” is only given as “Marion Martien”

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Abbreviations

A

A	Acceptor
3-ABS	3-Aminobenzenesulphonate
2-ABT	2-Aminobenzothiazole
AC	Activated carbon
AC	Alternate cycles
ADBI	Celestolide (i.e. 1-[6-(1,1-dimethylethyl)-2,3-dihydro-1,1-methyl-1H-inden-4-yl]-ethanone)
ADTV	Average daily traffic volume
ADWG	Australian Drinking Water Guidelines
AEOs	Alcohol ethoxylates
AES	Alkyl ethoxysulfates
Ag	Argentum, silver
AHDI	Phantolide (i.e. 1-[2,3-dihydro-1,1,2,3,3,6-hexamethyl-1H-inden-5-yl]-ethanone)
6-A-4-H-2-NS	6-Amino-4-hydroxy-2-naphthalenesulfonic acid
AHTN	Tonalide (i.e. 1-[5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl]-ethanone)
ALCH	Aliphatic chlorinated hydrocarbons
6-AM	6-Acetylmorphine
AMDOPH	1-Acetyl-1-methyl-2-dimethyloxamoyl-2-phenylhydrazide
AMO	Ammonia monooxygenase
AMP	1-Phenylpropan-2-amine or amphetamine
AMPA	Aminomethyll phosphon acid
AMS	Area and Mobile Source (USA)
AOP	Advanced oxidation process
AP	Alkylphenol
APEC	Alkylphenoxy carboxylate
APEO	Alkylphenol ethoxylate
Approx	Approximated
ARCH	Aromatic chlorinated hydrocarbons

ARQ	Annual report questionnaire
AS	Activated sludges
ASP	Activated sludges process
ATII	Traseolide (i.e. 1-[2,3-dihydro-1,1,2,6-tetramethyl-3-(1-ethyl-ethyl)-1H-inden-5-yl]-ethanone)
ATS	Amphetamine type stimulants

B

BAC	Biological activated carbon
BAS	Biofilm airlift suspension
BAT	Best available techniques
BBP	Butylbenzyl phthalate
BCF	Bioconcentration factor
BDD	Boron doped diamond
BDE209	Decabromodiphenyl ether
BE	Benzoylecgonine
BET	Analysis technique for the measurement of the specific surface area of a material (S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc., 1938, 60, 309).“BET” consists of the first initials of their family names.
BEUC	Bureau Européens des Union de Consommeaturs (the European Consumers´ Organisation)
BFR	Brominated flame retardant
BFRs	Polybrominated flame retardants
BMAA	Beta-methyl amino alanine
BOD	Biological oxygen demand
2,3-BON	3-Hydroxy-2-naphthoic acid
BP	British petroleum
BP	n-Butylparaben
BP	4-tert. Butylphenol
BPA	Bisphenol A
BPA	Bisphenol A=2,2′-Bis(4-hydroxyphenyl)propane
BPC	Blood plasma levels
BPC_{ss}	Human blood plasma concentration at steady state
BSL	Buffalo Springs Lake
BTC	Benzothiazol-6-carbonic acid
BTEX	Benzene, toluene, ethylbenzene, xylene
BTSA	Benzothiazole-2-sulfonate
BTtri	Benzotriazole
BTX	Benzene toluene xylene
BzP	Benzylparaben
BZPN	Benzophenone

C

CA	Monochloroethane
CAFOs	Concentrated animal feeding operations
CAPEC	Carboxylated alkylphenoxy carboxylate
CAS	Conventional activated sludge
CASP	Conventional activated sludge process
CBA	Chlorobenzoate
CBZ	Carbamazepine
CBZ10	Chloro-10-hydroxy-CBZ
CBZ11	Chloro-dihydroxy-CBZ
Cd	Cadmium
Ce	Cerium
CESIO	Comité Européen des Agents de Surface et de leurs Intermediaries Organiques
CF	Chloroform
CF	Concentration factor
ChemSec	International Chemical Secretariat
CM	Monochloromethane
COC	Cocaine
COD	Chemical oxygen demand
CP	Chlorophenol
CP	Control plane
CPC	Compound parabolic concentrator
CPSC	Consumer product safety commission
CSTR	Completely stirred tank reactor
CT	Carbon tetrachloride
Cu	Copper
CWAO	Catalytic wet air oxidation
Cyano-HABs	Cyanobacterial harmful algal blooms

D

D	Donor
DAP	Diamyl phthalate
DAT	Debromoaplysiatoxin
DBCP	1,2-Dibromo-3-chloropropane
DBoEP	Bis(2-*n*-butoxyethyl phthalate
DBP	Dibutyl phthalate
DBPs	Disinfection by-products
DCA	Dichloroethane
DCB	Dichlorobenzene
DCBA	Dichlorobenzoate
DCE	Dichloroethene
DCF	Diclofenac

DCHP	Dicyclohexyl phthalate
DCM	Dichloromethane
DCP	2-4-Dichlorophenol
DCP	Dichlorophenol
DDD	pp′-Dichlorophenyldichlorodiene
DDE	1,1-Dichloro-2,2-bis(p-chlorophenyl) ethylene
DDT	Dichlordifenyltrichlormethylmethan
DEET	N,N-Diethyl-m-toluamid
DEHP	Bis(2-ethylhexyl) phthalate
DEHP	Di-(2-ethylhexyl) phthalate
DEoEP	Bis(ethoxyethyl) phthalate
DEP	Di-ethyl phthalate
DHP	Dihexyl phthalate
DIBP	Diisobutyl phthalate
DL	Detection Limit
d.m.	Dry matter
56DMBTr	5,6-Dimethyl-1H-benzotriazole
DMoEP	Bis(methoxyethyl) phthalate
DMP	Dimethyl phthalate
DMPP	Bis(methylpentyl) phthalate
DMSO	Dimethylsulfoxide
DnOP	Di-*n*-octyl phthalate
DNP	Dinonyl phthalate
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DP	Detention pond
D. polymorpha	Dreissena polymorpha
DVRH	Deutscher Verband der Riechstoffhersteller
DW	Drinking water
DWF	Dry weather flowrate
DWTP	Drinking water treatment plant

E

E1	Estrone
E2	17β-Estradiol
E3	Estriol
Eawag	EAWAG, Swiss Federal Institute of Aquatic Science and Technology
EBITDA	Earnings before interest, taxes, depreciation and amortization
EC	Effective concentration
EC	Electrocoagulation-flotation
EC	European Commission

EC_{50}	Concentration at which 50% of the effect is observed
ED	Electrodialysis
EDA	Effect directed analysis
EDC	Endocrine disrupting chemicals
EDDP	2-Ethyldione-1,5-dimethyl-3,3-diphenylpirrolidine
EDTA	Ethylen diamine tetra acetic acid
EE2	17α-EthinylEstradiol
EEA	European Environment Agency
EEQ	Estrogenic equivalent
EI	Electron impact
EIC	Environmental introduction concentrations
ELISA	Enzyme-linked Immunosorbent Assay
EMEA	European Medicines Agency
EMS	Enhanced mass scan
EP	Ethylparaben
EPA	Environmental Protection Agency
EPER	European Pollutant Emissions Register
EPI	Enhanced production
E-PRTR	European Pollutant Release and Transfer Register
EPS	Extracellular polimeric substances
EQS	Environmental quality standards
Eqv	Estradiol equivalent
ERA	Environmental risk assessment
ER-CALUX	Estrogen receptor mediated chemical activated luciferase gene expression assay
ERY	Erythromycin
ESI	Electrospray ionization
EU	European Union
EUREAU	The European Union of National Associations of Water Suppliers and Waste Water Services

F

FDA	Food and Drugs Administration
FDA	United States Food and Drug Administration
Fe	Ferrum, iron
FER	Functional equivalence ratio
FLX	Fluoxetine

G

GAC	Granular activated carbon
GC-MS	Gas chromatography – mass spectrometry
GOT	Glutamic oxaloacetic transaminase

H

H	Henry’s constant
H	Hydrogen
HA	Humic acid
HAAs	Haloacetic acids
H-acid	1-Amino-8-naphthol-3,6-disulphonic acid
HBCD	Hexabromocyclododecane
1HBTr	1-H-benzotriazole
HCA	Hexachloroethane
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane(lindane)
HEHP	Hexyl-2-ethylhexyl phthalate
Hg	Mercury
HHCB	Galaxolide
HHCB	Galaxolide (i.e. 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyran)
HHCB-lactone	1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyran-1-one
HMN	2,2,4,4,6,8,8-Heptamethylnonane
HO•	Hydroxyl radical
HPD	Household Products Database (USA)
HPLC	High performance liquid chromatography
HPVC	High production volume chemical
HR-MS	High-resolution mass spectra
HR-MSMS	High-resolution product ion spectra
HR-MS-TIC	High-resolution mass spectrometry total ion chromatogram
HRT	Hydraulic retention time
HSDB	Hazardous Substances Data Bank (USA)
HSP70	70 kilodalton heat shock proteins

I

IBF	Ibuprofen
IBP	Ibuprofen
IDA	Information-dependent acquisition
i.e.	id est
IFRA	International Fragrance Association
Inh	Inhabitants
IPCC	Integrated Pollution Prevention and Control Directive (EU)
IPM	Iopromide
IPT	Integral pumping test
Ir	Iridium
IT	Ion trap
ITD	Ion trap detector
IWW	Rheinisch-Westfälisches Institut für Wasserforschung ggmbH

J

J-acid	2-Amino-5-naphthol-7-sulphonic acid

K

K-acid	1-Amino-8-naphthol-4,6-disulphonic acid
K_{biol}	Biodegradability kinetic constant
K_d	Solid-water distribution coefficient
KETO	Ketoprofen
KETO1	3-(Ethylphenyl)(phenyl)methanone
KETO2	3-(1-Hydroxyethyl)(phenyl)(phenyl) methanone
K_{ow}	Octanol-water partition coefficient

L

LA	Leucine alanine
LAS	Linear alkylbenzene sulfonate
LC	Liquid Chromatography
LC_{50}	Concentration at which 50% of the individuals exposed to a compound are dead
LCD glass	Liquid crystal display glass
LC-ESI-MS	Liquid chromatography-electrospray ionization-mass spectrometry
LC-MS	Liquid chromatography-mass spectrometry
LC/MS/MS	Liquid chromatrography/mass spectrometry/mass spectrometry
LIT	Linear ion trap
LOD	Limit of detection
LOEC	Lowest observed effect concentration
LOQ	Limit of quantification
LPVC	Low production volume chemical
LR	Leugine arginine
LRC	Lake Ransom Canyon
LRWRP	Luggage Point Water Reclamation Plant
LSD	Lysergic acid diethylamide
LSD-OH	2-Oxo-3-hydroxy-lysergic acid diethylamide
LTQ	Linear ion trap quadrupole
Lu	Lutetium
LY	Leucine tyrosine

M

4-MBC	3-(4-Methylbenzylidene) camphor
MBR	Membrane BioReactor
MBT	2-Mercaptobenzothiazole
MC	Mycrocystin
MCB	Monochlorobenzene

M_{CP}	Mass flow rate control plane
MCPP	Mecoprop
MD	Membrane distillation
MDA	3,4-Methylenedioxyamphetamine
MDEA	3,4-Methylenedioxyethamphetamine
MDMA	3,4-Methylenedioxymethamphetamine or ecstasy
MEPC	Marine Environmental Protection Committee
MES	Mestranol
METH	n-Methyl-1-phenylpropan-2-amine or methamphetamine
MF	Microfiltration
MFAC	Mefenamic acid
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
MMHg	Monomethyl mercury
MoA	Mode of action
MP	Methylparaben
MS	Mass spectrometry
M_{sewer}	Mass flow rate leaky sewer
MSPME	Micellar solid-phase microextraction
MSV	Mineral, salt vitamin
MTBE	Methyl tert-butyl ether
MTBT	2-(Methylthio)benzothiazole
MTPB	Methylparaben
mu	Muschelkalk (limestone)
MW	Molecular weight
MWCO	Molecular weight cut-off
m/z	Mass-to-charge ratio

N

NACE	Standard Nomenclature for Economic Activities (EU)
NAD(P)H	Nicotinamide adenine dinucleotide phosphate (reduced NADP$^+$)
NAEI	National Atmospheric Emissions Inventory (UK)
3-NBS	3-Nitrobenzenesulphonate; 3-nitrobenzene sulphonic acid
4-NBS	4-Nitrobenzenesulphonate
NC	Not calculated
NDMA	*N*-Nitrosodimethylamine
1,5-NDS	1,5-Naphthalene sulphonic acid
2,6-NDS	2,6-Naphthalenedisulfonic acid disodium salt
NDSA	Naphthalene disulfonates
1,3-NDSA	1,3 Naphthalene disulfonate
1,5-NDSA	1,5-Naphthalene disulfonate
NF	Nanofiltration
NGOs	Non-governmental organisations

2-NH_2-5,7-NDS	2-Aminonaphthalene-5,7-disulfonic acid
NMR	Clear magnetic resonance
NOEC	Non observed effect concentration
NOM	Natural organic matter
Nor-LSD	Nor-iso-lysergic acid diethylamide
NOSE	Nomenclature for Sources of Emissions (EU)
NP	4-iso Nonylphenol
NP	Nonylphenol
4NP	4-Nitrophenol
NP1EO	Nonylphenol monoethoxylate
NP2EO	Nonylphenol diethoxylate
NPR	Naproxen
NPR1	1-Ethyl-6-methoxynaphthalene
NPR2	1-(6-Methoxy- 2-napthyl) ethanol
NPR3	2-Acetyl-6-methoxynaphthalene
1-NS	1-Napthalene sulphonic acid
2-NS	Naphthalene-2-sulphonic acid; 2-naphthalenesulphonate
NSA	Naphthalene monosulfonates
NSAIDs	Nonsteroidal anti-inflammatory drugs
NTS	1,3,6-Naphthalenetrisulphonic acid

O

OC	Octocrylene
OCPs	Organochlorine pesticides
OHBT	2-Hydroxybenzothiazole
2-OH-3,6,8-NTS	2-Hydroxynaphthalene-3,6,8-trisulfonic acid
OMC	Octyl-methoxycinnamate
•OOR	Peroxy radicals
OP	Octylphenol
OP	4-tert. Octylphenol
OP1EC	Octylphenol monoethoxycarboxylate
Os	Osmium
OT	Octyl-triazone

P

PAC	Powdered activated carbon
PAH	Polynuclear aromatic hydrocarbon
PAOPs	Photochemical advanced oxidation processes
Pb	Plumbum, lead
PBB	Polybrominated biphenyls
PBDE	Polybrominated diphenyl ethers
PBT chemical program	Persistent bioaccumulative and toxic chemical program

PC	Phencyclidine
PCA	Pentachloroethane
PCB	Hexachlorobenzene
PCBs	Polychlorinated biphenyls
PCDDs	Dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzofurans
PCDD/Fs	Dibenzo-pdioxins and dibenzofurans
PCE	Tetrachloroethene
PCM	Paracetamol
PCMs	Polycyclic musks
PCP	Pentachlorophenol
PCP	Personal Care Product
Pd	Palladium
PEC	Predicted environmental concentration
PFA	Perfluorinated alkylated substances
PFA	Polyfluorinated alkylated substances
PFC	Polyfluorinated chemicals
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PGE	Platinum group elements
Pharm	Pharmaceuticals
Photo-TPs	Phototransformation products
PLE	Pressurized liquid extraction
PNEC	Predicted no-effect concentration
POP	Persistent organic pollutants
PP	n-Propylparaben
PPCP	Pharmaceuticals and personal care products
pp′-DDT	1,1,1-Trichloro-2,2,bis (4-chlorophenyl)ethane
ppm	Parts per million
Pt	Platinum
PTC	Parabolic-trough concentrator
pu	Pre-quaternary (Permian porphyrs)
PV	Pervaporation
PVC	Polyvinyl chloride

Q

QSAR	Quantitative structure activity relationships
QTOF	Quadrupole time-of-flight
QTRAP	Quadrupole linear ion trap
qu	Quaternary

R

REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (EU)
RECAP	The European Crop Protection Association

RF	Radio frequency
Rh	Rhodium
RIFM	Research Institute for Fragrance Materials
ro	Pre-quaternary (fractured sandstones and shists)
RO	Reverse osmosis
RoHS Directive	Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment
RP	Reversed phase
RQ	Risk quotient
RR	Arginine arginine
rRNA	Ribosomal ribonucleic acid
Ru	Ruthenium

S

S	Solubility
Sb	Stibnium, antimony
SBR	Sequencing batch reactor
SCC	Source Classification Codes (USA)
SCCNFP	Scientific Committee on Cosmetic and Non Food Products
SCCP	Scientific Committee on Consumer Products
SCWO	Supercritical water oxidation
Se	Selenium
SFE	Supercritical fluid extraction
SMP	Soluble microbial products
sm/so	Buntsandstein (sandstone)
SMX	Sulfamethoxazole
SPC C11	Sulfophenylundecanoic acid
SPE	Solid phase extraction
SPM	Suspended particulate matter
SRM	Selected reaction monitoring
SPME	Solid phase microextraction
SRT	Sludge retention time
SS	Suspended solids
STP	Indicates the location of the wastewater treatment plant
STP	Sewage treatment plant
STX	Saxitoxins
SVHC	Substances of very high concern (in REACH)
SW	South western
SWF	Storm weather flowrate

T

TBBPA	Tetrabromobisphenol A
TBT	Tributyltin

TCA	Trichloroethane
TCB	Trichlorobenzene
TCE	Trichloroethylene
TCEP	Tris-2-chloroethyl phosphate
TCN	Tetracycline
TCP	Trichlorophenol
TCPP	Tris(1-chloro-2-propyl) phosphate
te	Tertiary
TeCA	Tetrachloroethane
TFC	Thin film composite membranes
TFFBR	Thin Film Fixed Bed Reactor
TGD	Technical Guidance Document on Risk Assessment (EU)
THC	Δ9-Tetrahydrocannabinol or cannabis
THC-COOH	11-Carboxy-Δ9-tetrahydrocannabinol
THC-OH	11-Hydroxy-Δ9-tetrahydrocannabinol
THMFP	Trihalomethanes formation potential
THMs	Trihalomethanes
TIE	Toxicity identity evaluation
TN	Total nitrogen
t-nonylphenol	Technical 4-nonylphenol
TNT	2,4,6 - Trinitrotoluene
TOC	Total organic carbon
TOF	Time-of-flight
TP	Total phosphorus
TPPB	Two phase partitioning bioreactor
TPs	Transformation products
TPT	Triphenyltin
TR	Toxic ratio = $EC_{50\ \text{baseline toxicity}}/EC_{50\ \text{specific effect level}}$
TRI	Triclosan
TSS	Total suspended solids
TTr	Tolyltriazole
Ttri	Tolyltriazole
TUBITAK	Turkish Technological and Scientific Research Council

U

UF	Ultrafiltration
UFZ	Helmholtz Centre for Environmental Research – UF
UK	United Kingdom
UNESCO	United Nations Educational, Scientific and Cultural Organization
UNODC	United Nations office of drug and crime
UPLC	Ultra performance liquid chromatography
US	Ultrasound
U.S.	United States

USA	United States of America
US EPA	United States Environmental Protection Agency
UV	Ultra violet
UV_{254}	UV absorbance at 254 nm wavelength
UV-VIS	Ultraviolet-visible spectroscopy
V	
VOC	Volatile organic carbon
VSS	Volatile suspended solids
W	
WAS	Waste activated sludge
WAO	Wet air oxidation
WF21	Water Factory 21
WFD	Water Framework Directive
WHO	World Health Organization
WOE	Weight of evidence
WW	Wastewater
WWTP	Municipal wastewater treatment plant
Y	
YES	Yeast Estrogen Screen
YR	Tyrosine arginine
Z	
Zn	Zinc

Index