

Xenobiotics in the Urban Water Cycle

ENVIRONMENTAL POLLUTION

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Xenobiotics in the Urban Water Cycle

Mass Flows, Environmental Processes,
Mitigation and Treatment Strategies

Edited by

Despo Fatta-Kassinou

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



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Editors

Despo Fatta-Kassinou
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– μ g/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
Aalborg, Denmark
Freiburg, Germany

Despo Fatta-Kassinou
Kai Bester
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 anthropogenic 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 be 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

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 lipophilic, 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, ethylenebrassyolate 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

Compound	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
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	nr	5–20	0.5–2	2	0.1	This book chapter (3 WWPT in the Rhine-Ruhr area), Simonich et al. 2000 This book chapter
Musk xylene 4-amine (metabolite of MX)	na	na	nr	0	10–20	0	0.5–3	This book chapter (3 WWPT in the Rhine-Ruhr area), Simonich et al. 2000
Musk ketone	4.9	nr	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	<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	Lindström et al. 2002, Bester 2003, 2005b, Singer et al. 2002, Halden and Paul 2005
Triclosan-Methyl	5.0	na	nr	0	6–20	0	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	Bester 2007, unpublished data
TCEP	1.7	3.3*E-6	nr	110–250	130–250	30–710	Bester 2007, unpubl. Inchem (1998)
TDCP	3.8		nr	150–250	150–250	20–610	Bester 2007 unpubl.
Plasticizer							
TiBP	3.5	na	nr	60–200	120–1,000	21–1,300	This book chapter
TnBP	3.7	na	nr	80–200	50–60	21–1,000	This book chapter
TPP	4.7	na	nr	20–160	10–27	5–390	This book chapter
TBEP	3.7	na	nr	3,500–7,800	100–2,500	900	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; Mehy et al. 2003; SCOOP 2003
Nivalenol	-0.75 ^a	na	11.8 ± 0.7 ^a	na	na	0.2–2.0 ^c	na	SCOOP 2003, JECFA 2001
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	0.006-0.066	na	Gilbert et al. 2001, Castagnaro 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	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	15-1,570	0-39% of 15-1,570 mg/a	See literature in Text
Benzotriazoles						
Benzotriazole	1.23	na	1.6; 8.2	2,000	1,400	Voutsas 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)	na	Weiss and Reemtma 2006

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

^aData 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).

^bAt pH 3 and 7, respectively.

^cFrom dietary intake, assuming 100% excretion (Valenta 1998).

^dRothwell et al. 2005.

^eEstimated, using the method by Meylan and Howard 1991.

^fZielonka et al. 2003.

^gAnalogous to genistein.

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

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 off 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 lipophilic organobromine compounds such as the prioritised polybrominated biphenyl ethers (PBDE), brominated bisphenol A, hexabromocyc-

clododecane etc. and on the other hand the hydrophilic 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 where 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 ($\log K_{ow}$ 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).

These 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 lipophilic 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) its 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$) to up to 0.3 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ range in the samples of primary and secondary effluents from 24 municipal WWTPs in Switzerland (Voutsas 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 $\mu\text{g/L}$, 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 $\mu\text{g/L}$ (BT), 2.1 $\mu\text{g/L}$ (4-TT), and 1.3 $\mu\text{g/L}$ (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 metabolites 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: Meko 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 μ g/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 μ g/(capita*a), while JECFA 2001 published somewhat

higher number, that is, 135 $\mu\text{g}/(\text{capita}\cdot\text{a})$. This is also exhibiting a good match with excretion estimates (see above). For nivalenol SCOOP (2003) published 0.2–2.0 $\text{mg}/(\text{capita}\cdot\text{a})$. For HT-2 toxin SCOOP 2003 and JECFA 2001 found 0.2–2.7 $\text{mg}/(\text{capita}\cdot\text{a})$. The T-2 toxin was emitted with similar amounts (0.2–1.3 $\text{mg}/(\text{capita}\cdot\text{a})$), according to SCOOP 2003 and JECFA 2001). ZON was detected with 0.02–0.7 $\text{mg}/(\text{capita}\cdot\text{a})$ (SCOOP 2003; JECFA 2000; Zinedine et al. 2007), while fumonisin B1 (FB1) was described by SCOOP (2003) with <0.1–15 $\mu\text{g}/(\text{capita}\cdot\text{a})$, and by JECFA (2001) with 440–4,380 $\mu\text{g}/(\text{capita}\cdot\text{a})$.

The data is less clear for FB1. Mean urinary FB1 concentrations ranged from 13 to 54 $\mu\text{g}/(\text{capita}\cdot\text{a})$ 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 $\text{mg}/(\text{capita}\cdot\text{a})$, and from 15 to 1,570 $\text{mg}/(\text{capita}\cdot\text{a})$ 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.