CHIMIA **2003**, *57*, No. 1/2

Chimia 57 (2003) 22–34

ISSN 0009–4293

Focal Point: Environmental Analytical Chemistry

October 15, 2002

Emerging Contaminants and Water Analysis

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Sophisticated analytical techniques are necessary for the determination of trace contaminants in various environmental compartments. Qualitative identifications are followed by quality controlled quantitations and applications to a broad range of samples. The presented case studies cover several relatively biopersistent chemicals and corresponding metabolites. The term emerging contaminants refers to environmental pollutants that have been only discovered and intensively studied during the last five years. Environmental field studies provide results which allow significant conclusions with regard to input sources and environmental behavior. Improving the control of chemical water quality is a challenging task, for which the progress of analytical techniques is a significant base. Besides anthropogenically introduced contaminants, naturally derived water constituents must also be thoroughly investigated in different parts of the environment. A well-established exposure assessment is crucially important for the evaluation of environmental risks posed by various chemicals, which occur in wastewaters, and of which residual amounts can enter ambient waters and drinking water.

Keywords: Ambient waters · Environmental analytical chemistry · Flame retardants · Pharmaceuticals · Pollutants · Surfactants · Wastewater

Fluorinated Alkyl Surfactants in Groundwater and Wastewater

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Introduction

Perfluorinated alkyl sulfonates and carboxylates been found in remote, less densely populated regions of the world that have no local commercial, municipal, or industrial sources of fluorinated alkyl substances [1] as well as in human blood [2]. Perfluorooctane sulfonate (PFOS; Table 1) and perfluorooctanoate (PFOA) do not to biodegrade under aerobic nor anaerobic conditions such that they have the potential for persisting in the environment [3–5]. In addition, PFOS has both bioaccumulative [1] and toxic [3] characteristics.

Electrochemical fluorination and telomerization are the two principal synthetic routes to the synthesis of fluorinated alkyl chemicals [4]. Electrochemical fluorination is neither efficient nor selective and it produces complex mixtures containing numerous byproducts. The perfluoroalkyl chains themselves contain a homologous series of odd- and even-numbered carbons in isomeric linear (~75%) and branched (~25%) forms ranging from 4–12 carbons (Table 1). Telomerization, on the other hand, generates fluorinated alkyl chains that are linear and contain only even numbers of fluorinated carbons (Table 1). Fluorinated chemicals derived from telomerization are distinguished by the presence of the C_2H_4 group on the end of the perfluoroalkyl group, again yielding homologs by telomerization that have only an even number of carbons.

The analysis of fluorinated alkyl substances is problematic due to their nonvolatility and their lack of chromophores. To date, high-performance liquid chromatography combined with negative-ion electrospray tandem mass spectrometry (HPLC/MS/MS) is the current method of choice due to its sensitivity and selectivity. It has been applied for the analysis of perfluoroalkyl sulfonates and carboxylates in a wide range of sample matrices including human serum [5] marine mammals [6][7], fish-eating water birds [8], oysters [9], and surface waters [10][11].

The objective of this research was to adopt and adapt existing LC/MS/MS methodology from the literature for the quantitative analysis of perfluoroalkyl sulfonates and carboxylates in groundwater [12]. Due to the fortuitous detection of

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Chemical class	General formula	Specific Example
Perfluoroalkyl-sulfonates	$R_fSO_3^-$ where $R_f = F_3C(CF_2)_n$ and n = 3-11 and 25% terminally branched (electrofluorination)	Perfluorooctane sulfonates (PFOS) when n = 7
Perfluoroalkyl-carboxylates	R_fCOOH where $R_f = F_3C(CF_2)_n$ and n = 3-11 and 25% terminally branched (electrofluorination) OR $F(CF_2CF_2)_n$ n = 3-7 with no terminal branching (telomerization)	Perfluorooctanoic acid (PFOA) when n = 7 (electrofluorination) OR when n = 4 (telomerization)
Telomer sulfonates	$R_fCH_2CH_2SO_3^-$ where $R_f = F(CF_2CF_2)_n$ n = 3-7 with no terminal branching (telomerization)	6:2 Telomer sulfonate when n = 6

Table 1. Fluorinated alkyl chemical classes investigated for this study with specific examples and nomenclature

telomer sulfonates in groundwater, the analysis of telomer sulfonates became a second objective of this research.

Results and Discussion

Samples of groundwater contaminated by aqueous-film-forming (AFFF) foam were analyzed by the direct injection LC/MS/MS method (see Experimental). Chromatograms for groundwater sample indicate the various homologs of perfluoroalkyl sulfonates (Fig. 1) and perfluoroalkyl carboxylates (Fig. 2). For these analyses, the initial intention was to use the 6:2 telomer sulfonate as an internal standard as attempted by other groups. However, upon scanning groundwater samples with the intention of showing that the 6:2 telomer sulfonate was not present, it was determined that the groundwater actually contained the chemical as well as the 8:2 telomer sulfonate (Fig. 3). Consequently, hexafluoroglutaric acid was adopted as the internal standard.

In order to obtain low baselines for the analysis of telomer sulfonates, all the Teflon tubing was removed from the HPLC. The concentrations of the 6:2 telomer sulfonate ranged from the limit of quantitation (0.5 µg/l) to 173 µg/l and was present in 15 out of 18 samples collected from the site. No sample clean up or preconcentration was required to reach detection limits (signal-to-noise ratio >3) of 1 µg/l and a quantitation limit of 5 µg/l (signal-to-noise ratio >10).

To the best of our knowledge, this is the first report of the telomer-derived sulfonates in environmental samples. This finding establishes that the 6:2 telomer sulfonate should not be used as a surrogate or internal standard for environmental analysis. Ultimately, these quantitative methods will be modified as necessary for the determination of these classes of chemicals in municipal wastewater and sludges for the purpose of understanding the mass flows of fluorinated alkyl surfactants during municipal wastewater treatment.

Finally, several precautions are urged when attempting to analyze for fluorinated alkyl surfactants such as eliminating Teflon materials from analytical instruments as well as aluminum foil, paper food containers and wrappings, and from wearing new clothes since they may be treated with fluorinated alkyl substances. Any filters should be analyzed prior to use to test for potential contamination. Standards should be stored in a laboratory away from that portion of the laboratory where analyses are conducted.

Experimental

Reverse-phase high-performance liquid chromatography (HPLC) was coupled with electrospray ionization (ESI) mass spectrometry/mass spectrometry (MS/MS). A

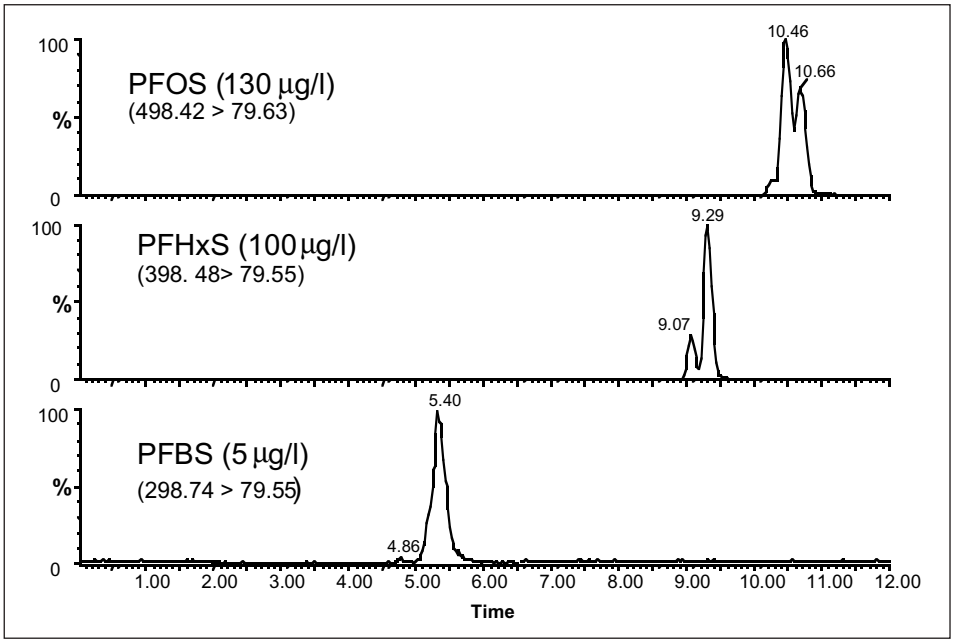

Fig. 1. Perfluoroalkyl sulfonates in groundwater from Wurtsmith Air Force Base, MI. Mass transitions used for identification and quantification are given in parentheses. PFOS = perfluorooctane sulfonate; PFHxS = perfluorohexane sulfonate; PFBS = perfluorobutane sulfonate.

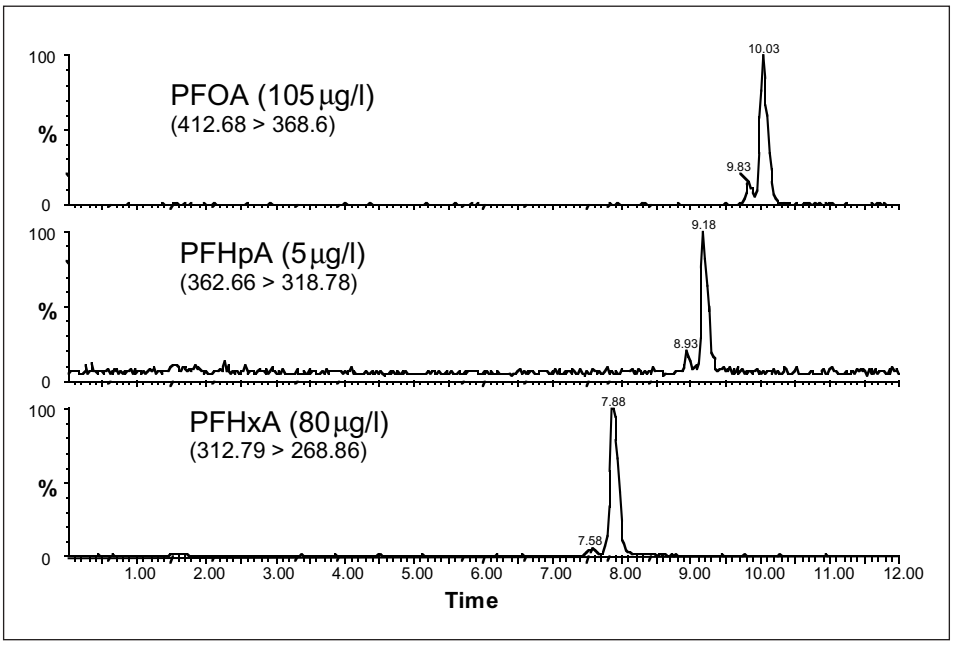

Fig. 2. Perfluoroalkyl carboxylates in groundwater from Wurtsmith Air Force Base, MI. Mass transitions used for identification and quantification are given in parentheses. PFOA = perfluorooctanoate; PFHpA = perfluoroheptanoate; PFHxS = perfluorohexanoate.

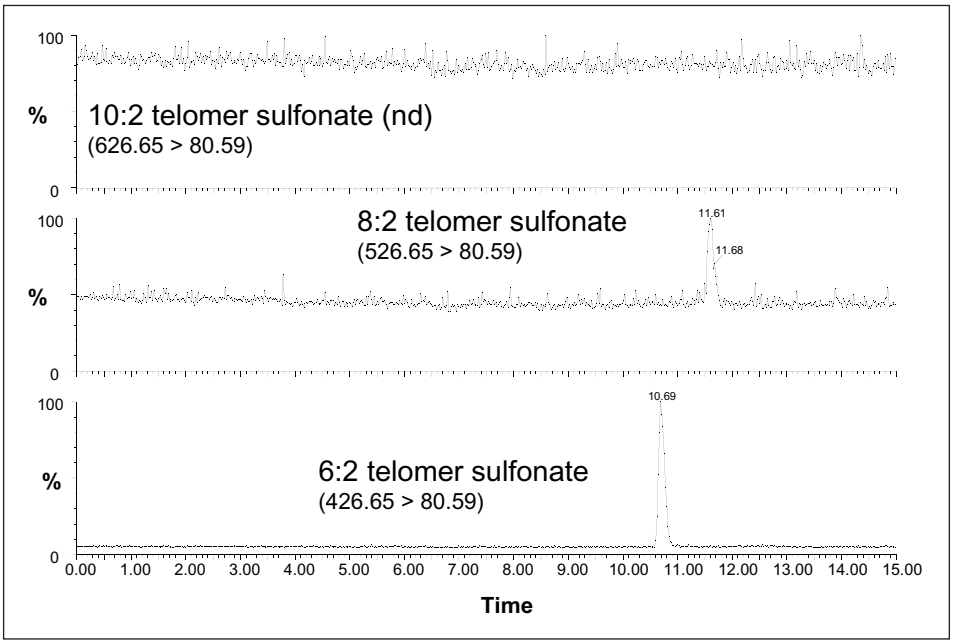

Fig. 3. Telomer sulfonates (6:2 and 8:2) in groundwater from Wurtsmith Air Force Base, MI. Mass transitions used for identification and quantification are given in parentheses.

reverse-phase 150 mm × 2 mm Betasil C18 (Thermo Hypersil-Keystone, Bellefonte, PA) column, heated to 35 °C, was used for all separations. The HPLC solvents included Milli-Q (Bedford, MA) water and Optima grade methanol (Fisher Scientific, Pittsburgh, PA) that had been prefiltered through C18 and strong anion exchange cartridges (Thermo Hypersil-Keystone, Bellefonte, PA). The aqueous phase contained 2 mM NH_4Ac. The solvent gradient was 30–90% methanol over 5 min and a 5 min hold at 90% methanol. In order to eliminate background concentrations of the telomer sulfonates, all Teflon was removed from the HPLC and replaced with PEEK tubing.

The HPLC was directly interfaced to the electrospray ionization source of a Micromass Quattro Micro triple quadrupole mass spectrometer (Beverly, MA). The triple quadrupole was operated in negative ESI mode and multiple reaction monitoring was used for quantitation. The surrogate internal standard used for quantitation is hexafluoroglutaric acid.

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Organic Flame Retardants in Wastewater Treatment Plants

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Introduction

Flame retardants [1][2] are a chemically diverse group of inorganic and organic compounds widely used in plastics, textiles, rubber, paint and other materials to prevent fires. The majority of the produced flame retardants (>80%) is used to lend ignition resistance and reduce flammability to plastics. Flame retardants can be either added or mixed into the materials, whereas reactive flame retardants are covalently bound. Additive flame retardants are expected to leak out from the product to a certain extent [3].

Inorganic flame retardants constitute about 50% of flame retardant production worldwide and include *e.g.* aluminum trihydroxide, antimony oxides and zinc borates. The group of organic flame retardants can be divided mainly into three subgroups: organohalogens (*ca.* 25% of global produc-

tion), organophosphates (*ca.* 20% of global production) either non-halogenated, such as triphenyl phosphate, or halogenated, such as tris-(2-chloroethyl)phosphate (TCEP), and N-based flame retardants and others (*ca.* 5% of global production). The global flame retardant market has continuously increased over the passed years and is estimated to be *ca.* 1.2 billion US dollars in 2002.

At present polybrominated flame retardants are the dominating group with a total worldwide consumption of over 300000 metric tons per year (32% of total US flame retardant market in 1995). This group consists mainly of four compound classes: polybrominated diphenyl ethers (PBDE), tetrabromobisphenol A (TBBPA; consumption >150000 tons per year), hexabromocyclododecane (HBCD) and polybrominated biphenyls (PBB). Areas of use are electronic equipment, textiles and building materials. Due to their persistence and tendency for bioaccumulation they can be found in the environment and were detected in wildlife and humans (*e.g.* in mothers' milk).

The extensive use of flame retardants has led to increasing levels in the environment. Previously we have studied the presence of organophosphates in wastewater, surface water, ground water and sediment [4]. In the present study we have investigated 32 sewage sludges from municipal waste water treatment plants in the state of Baden-Württemberg, Germany, and searched for the presence of polybrominated diphenyl ethers (PBDE), and tetrabromobisphenol A (TBBPA) (structural formulae see Fig. 4).

Polybrominated Diphenyl Ethers (PBDE)

The theoretical number of congeners of PBDEs is 209. PBDEs have a structural similarity to polychlorinated biphenyls (PCB) and perchlorinated dibenzodioxins and -furans (PCDD/F). There are mainly three technical products commercially available: penta- (PeBDE), octa- (OcBDE) and decabrominated diphenyl ether (DeBDE). Each of these mixtures contain one dominating congener and additionally varying contents of further congeners (technical PeBDE, for example, contains 50–60% pentaBDE, 24–38% tetraBDE and 4–8% hexaBDE). The worldwide annual production is 4000 tons for PeBDE, 6000 tons for OcBDE and 30000 tons for DeBDE. PBDEs have low vapor pressures and are very lipophilic with $\log K_{ow}$ values from 5.9–6.2 for tetraBDE up to 10 for decaBDEs, which results in low water solubility, high binding affinity to particles and accumulation in sediments. There are

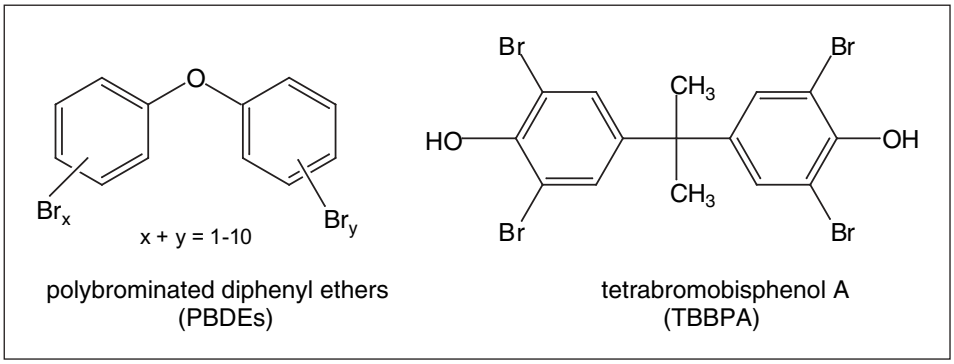

Fig. 4. Structural formulae of PBDE and TBBPA

indications that higher BDEs are photodegraded to lower BDEs in the environment. PBDEs were shown to have weak dioxin-like effects. They have been found in human mothers' milk and human fat tissue.

Tetrabromobisphenol A (TBBPA)

This reactive flame retardant is the most common one used today with a worldwide consumption of 150000 tons. It has a $\log K_{ow}$ of 4.5. It was shown that O,O'-dimethylation occurs in sediment leading to dimethylated TBBPA with a $\log K_{ow}$ of 6.4. TBBPA has a high toxicity for aquatic organisms (*e.g.* daphnae). Due to the structural similarity with the thyroid gland hormone thyroxin hormonal-like effects are assumed for both PBDEs and TBBPA.

Results

Analysis

In this study we collected 32 sludge samples from different WWTPs in Baden-Württemberg, Southwestern Germany. Sludge samples with a dry weight (d.w.) between 25 and 38% were directly freeze-dried and Soxhlet-extracted with n-heptane/acetone 3:1 (v:v), sludge samples with 3 to 6% d.w. were centrifuged prior to freeze-drying. As internal standard ^{13}C-decachlorobiphenyl and ^{13}C-TBBPA were added. The organic phases were extracted with 2N potassium hydroxide. The organic phase containing the PBDEs was treated with sulfuric acid to remove lipids and then chromatographed on an aluminum oxide column using n-heptane and then n-heptane/dichloromethane 1:1 (v:v). Tetra- to heptabrominated diphenyl ethers were analyzed with GC-MS. The aqueous phase containing TBBPA was derivatized with dimethylsulphate. Then a liquid–liquid extraction with toluene and a clean-up step followed using chromatography on silica using n-heptane and then n-heptane/dichloromethane 1:1 (v:v). Analysis was done by GC-MS. The response factors relative to the internal standard ^{13}C-PCB-209 were determined by five point calibration with standard solutions (BDE-47, BDE-99, BDE-100, BDE-153, BDE-180, BDE-209, PCB-209 and TBBPA$(OMe)_2$).

A typical GC-MS chromatogram of a sewage sludge sample containing the signals of the tetra-, penta- and hexabrominated diphenyl ethers is shown in Fig. 5. The

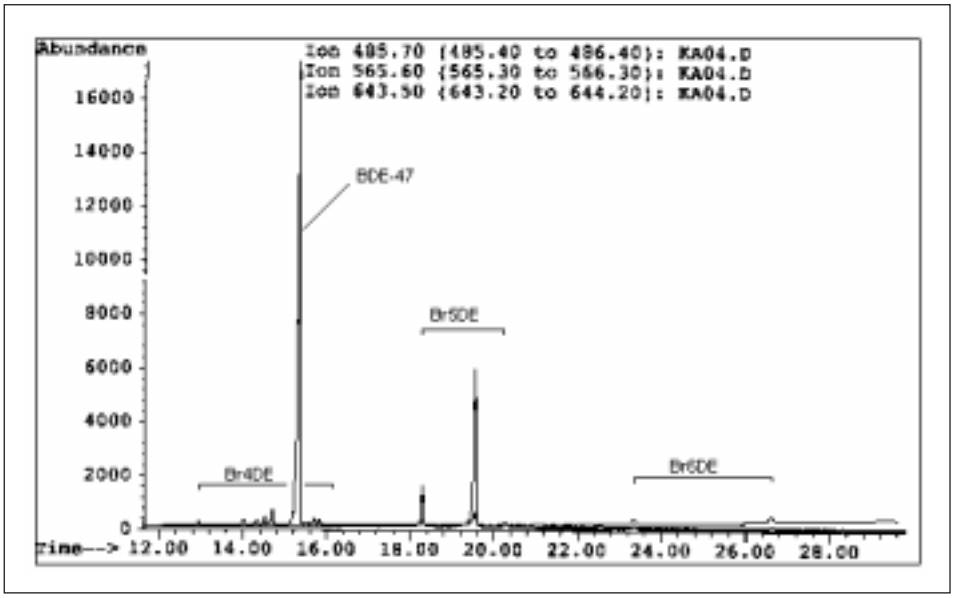

Fig. 5. GC-MS of tetra-, penta- and hexabrominated diphenyl ethers

intensity distribution observed is similar to that found for the technical flame retardant mixtures.

The method applied cannot be used for the determination of DecaBDE. For this compound we are presently developing a method based on GC-ECD.

PBDE and TBBPA in Sewage Sludge

Due to the high $\log K_{ow}$ values we expected brominated flame retardants to be present in sewage sludge. We therefore took sewage sludge samples from 32 municipal wastewater treatment plants in the state of Baden-Württemberg, Germany. We quantified the tetra-, penta-, hexa- and heptabrominated diphenyl ethers ((4–7)BDEs) and found a total concentration of 50–460 µg/kg d.w. TBBPA was found in concentrations of 0.6–62 µg/kg d.w. (Fig. 6). There was no obvious dependence between size (capacity) and the kind of technical equipment of the sewage treatment plant on the concentration of flame retardant found in the sludge. It seems that the brominated flame retardants investigated pass the wastewater treatment plant essentially unchanged.

The brominated flame retardants were also found in lesser concentrations in the aqueous phase (TBBPA>PBDE).

Summary

Brominated flame retardants are ubiquitous environmental contaminants. Due to their lipophilic character PBDEs and TBBPA bind to sewage sludge. The mean concentration in sewage sludge observed was *ca*. 100 µg/kg d.w. for the sum of tetra- to heptabrominated diphenylethers and 16 µg/kg for TBBPA. Possible pathways allowing these flame retardants to enter wastewater are most likely *via* textiles and in some cases process waters from the production of flame retardants itself. Since we have found significant amounts of TBBPA (up to 25 µg/kg d.w.) and PBDEs (up to 180 µg/kg d.w.) in toilet paper [5], this may also be a pathway, which has to be investigated in further studies. Interestingly, recycled toilet paper contained significantly higher concentrations than non-recycled paper. Possibly the contamination comes from the ink used for printing or special flame-protected papers used for recycling; obviously the de-inking process is not able to remove these compounds from the paper.

Acknowledgement

This work was supported by the Ministry for Environment and Traffic, Baden-Württemberg, Germany.

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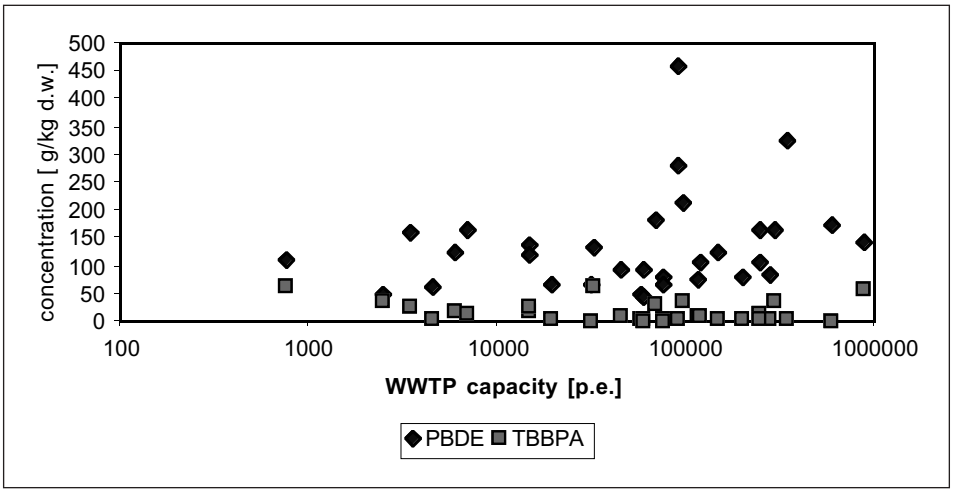

Fig. 6. Concentration of (4-7)BDE and TBBPA found in sewage sludge samples from 32 municipal wastewater treatment plants in Baden-Württemberg

Occurrence and Environmental Behavior of the Bactericide Triclosan and its Methyl Derivative in Surface Waters and in Wastewater

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Introduction

Anthropogenic compounds may undergo various transformation reactions in organisms and in the environment leading to more hydrophilic derivatives with higher mobility in the aquatic environment and less potential for bioaccumulation. Sometimes, however, transformation reactions may render a compound more lipophilic and thus more bioaccumulative than the parent compound itself. One such reaction is biological methylation such as the transformation of phenolic compounds into methyl ether derivatives [1–4]. Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol; structure, see Fig. 7) is an important bactericide used in various personal care (shampoo, toilet soap, deodorants, tooth paste) and consumer (foot wear, plastic wear) products [5–8]. Triclosan is a relatively stable, lipophilic compound. It has been found in human milk, but little is known about the effects on exposed infants [9]. Of further concern is the transformation of triclosan into chlorodioxins upon incineration and under the influence of sunlight [10]. Triclosan has previously been detected in wastewater, surface water, and sediments [11–15]. In fish, the presence of the methyl ether of triclosan, methyl-triclosan (5-chloro-2-(2,4-dichlorophenoxy)anisole; Fig. 7), was also reported [16]. However, it remained unclear whether methylation had taken place prior to or following uptake by the fish, and whether or not triclosan itself was also accumulated.

During an investigation on the occurrence of lipophilic contaminants in surface water using semipermeable membrane devices (SPMDs), the presence of methyl-triclosan was observed, but not the parent compound itself. This observation prompted a more thorough study on the environmental occurrence of triclosan and its methyl ether derivative. In this study, we report on these data and on the elimination

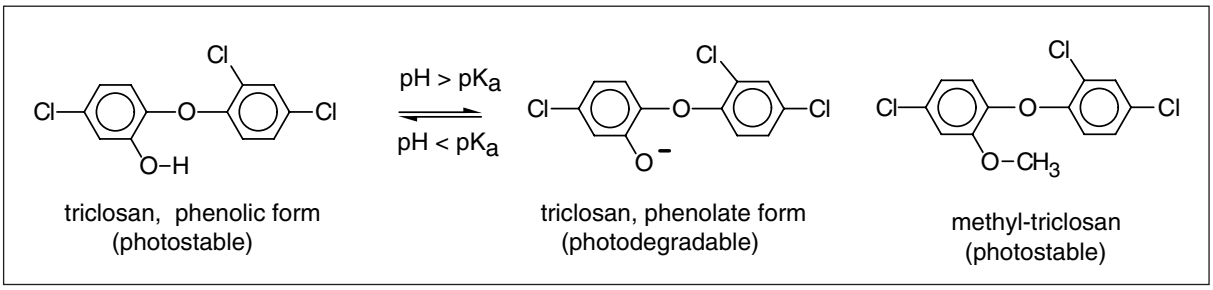

Fig. 7. Structures of triclosan and methyl-triclosan. In natural waters triclosan may be partially dissociated (pK_a = 8.1).

behavior of triclosan in the aquatic environment. We document the transformation of triclosan into methyl-triclosan and we assess the occurrence of the two compounds in the aquatic environment.

Materials and Methods

Waters from several lakes and rivers in Switzerland were analyzed. Of particular importance for this study were the lakes Greifensee and Zürichsee. Semipermeable membrane devices were exposed in Greifensee, Zürichsee, and in a mountain lake (Jörisee, 2450 m above sea level) remote from human activities, which receives inputs mainly from rain, snow, and dry deposition. The membranes were extracted and cleaned up according to established methods [17][18]. Surface water (1 l) was acidified for complete recovery of triclosan by solid-phase extraction [19][20] and the samples were then ethylated using diazoethane, cleaned-up, and analyzed for ethyl-triclosan and methyl-triclosan, the former compound representing parent triclosan. Wastewater samples (300 ml) were centrifuged and then treated in the same way.

GC-MS analysis was performed on a VG Tribrid mass spectrometer (MassLab Group, Manchester, UK) under EI and full-scan or SIM conditions using a 25 m 0.32 mm i.d. DB-5 fused silica column and split/splitless injection (250 °C). In the SIM mode, the following ions were monitored: m/z 288 for triclosan ($M^{+\cdot}$) and ethyl-triclosan ($M^{+\cdot}$–28), m/z 302 for methyl-triclosan ($M^{+\cdot}$) and $^{13}C_{12}$-PCB#80 ($M^{+\cdot}$), and Cl-isotope satellite and fragment ions for confirmatory purposes. The SPMD samples were analyzed under full-scan and SIM conditions, using $^{13}C_{12}$-PCB#80 as internal standard.

Results and Discussion

Triclosan was detected in several lakes and rivers. The Greifensee showed concentrations of up to 14 ng/l with some seasonal pattern (lower in summer); the concentrations in the Zürichsee were lower (up to 3 ng/l). Methyl-triclosan, if detected at all, was present at much lower levels in these lakes (up to 0.8 ng/l). The most clear indication for the presence of this compound came from the analysis of samples from a river (Glatt), where methyl-triclosan concentrations were up to 2 ng/l; the corresponding triclosan concentrations were up to 74 ng/l. Both compounds remained undetected (<0.4 ng/l) in water from a mountain lake (Jörisee).

In contrast to the results obtained from direct analysis of surface water samples, analysis of the SPMDs showed the presence of methyl-triclosan in the samples from the Greifensee and the Zürichsee (see Fig. 8), but not of triclosan itself. The concentration of methyl-triclosan in the SPMD from the Greifensee (33 ng/g) was higher than in that from the Zürichsee (16 ng/g); none (<1 ng/l) was detected in the SPMD from the mountain lake.

Triclosan was consistently detected in the influents to the biological stage of WWTP installations at concentrations of 0.6–1.3 µg/l; methyl-triclosan, if present at all, was detected at much lower concentrations (≤4 ng/l). The concentrations of triclosan in the corresponding effluents from these installations were between 110–650 ng/l. Methyl-triclosan was detected at low concentrations (up to 11 ng/l) in some of the WWTP samples. The concentrations were equal or higher, if methyl-triclosan was detected at all, in the effluent than in the corresponding influent, an indication of its formation in these installations.

There is evidence that methyl-triclosan observed in surface water and wastewater is formed from triclosan, possibly *via* biological methylation. This is based on i) the absence or near absence of methyl-triclosan in the influents to WWTPs (concentrations, <1% relative to triclosan), ii) the increased concentrations of methyl-triclosan relative to triclosan in the effluents of some installations despite the fact that methyl-triclosan is more lipophilic and therefore should partition to a larger extent into the sludge than triclosan. This is also supported by the concentration increase of methyl-triclosan from the source (0.6 ng/l) to the outflow of the river Glatt (2 ng/l), on the banks of which several WWTPs are located.

Indication for the occurrence of methylation reactions is also obtained from the presence of pentachloroanisole in SPMDs. This compound is not a commercial product, but rather the biomethylation product of pentachlorophenol [2][4]. In fact, pentachlorophenol was detected in in- and effluents of WWTPs. Although pentachloroanisole itself remained undetected in the effluents (concentrations, <4 ng/l), it was detected in the SPMDs from the Zürichsee and the Greifensee. Methylation of other chlorophenoxy phenols, byproducts of technical pentachlorophenol, was previously observed in aquatic environments [21]. Some fish contained methyl ethers of chlorophenoxy phenols while the parent compounds were not observed. Methoxy-polybromo diphenyl ethers were detected in biota as metabolites of polybromo diphenyl ether [22], compounds widely used as flame retardants for plastics, paints, electrical components, and synthetic textiles. Furthermore, tetrabromobisphenol A is known to be transformed to its dimethyl derivative in surface sediments [23]. Methylation of organic pollutants in the aquatic environment is thus a feasible pathway for phenolic compounds.

A regional mass balance for the Greifensee indicated significant removal of triclosan by processes other than flushing. Averaged loads of triclosan in WWTP effluents were ≈20 g/d (population, 107000 persons), leading to predicted concentrations (assuming flushing as the only elimination process) of ≈50 ng/l. Actual concentrations were in the range of 1.4–14 ng/l. The lowest triclosan concentrations were observed in the surface layer in summer. Higher concentrations were found in deeper regions of the lake in summer and throughout the water column in winter. The observed changes concentrations are consistent with a removal process such as photodegradation.

Laboratory experiments showed that triclosan in the dissociated form was rapid-

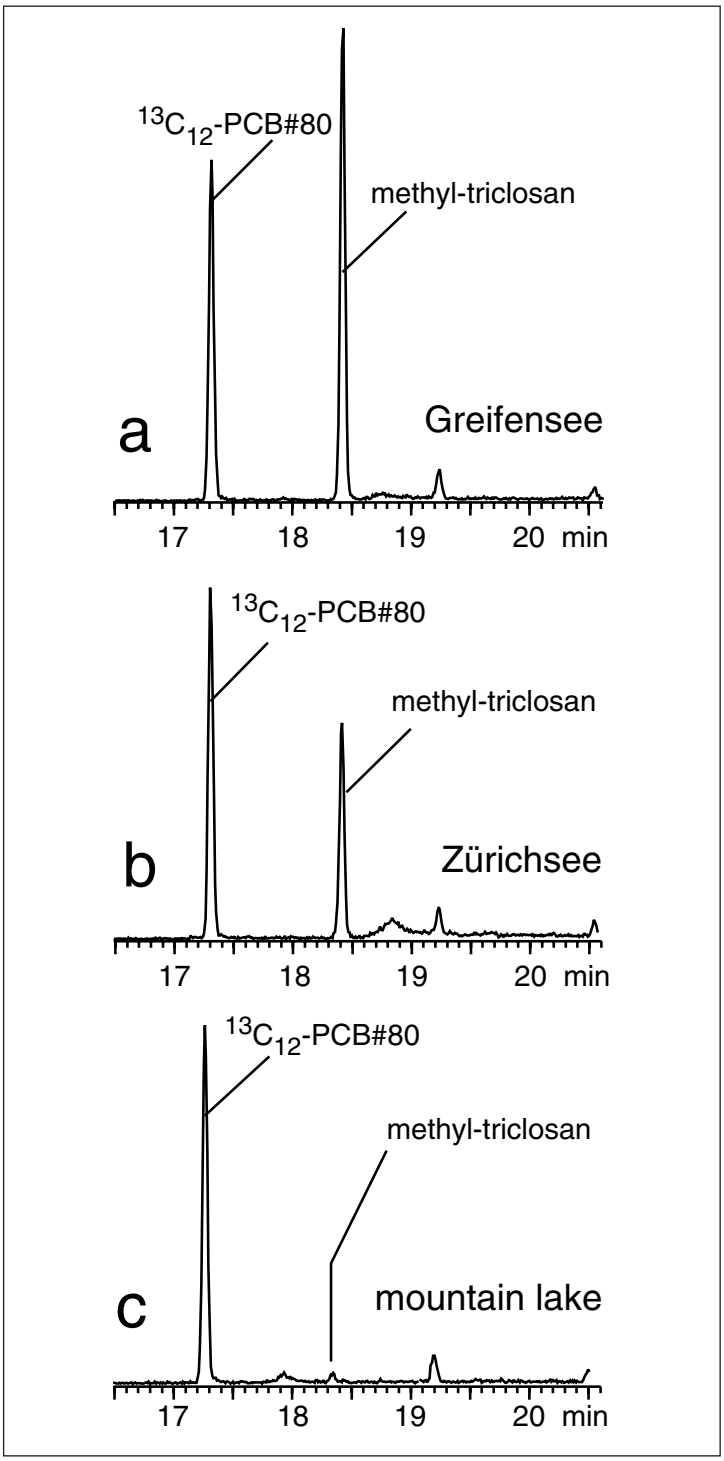

Fig. 8. EI SIM chromatograms (m/z 302) showing elution of $^{13}C_{12}$-PCB#80 and methyl-triclosan in SPMDs exposed in (a) Greifensee, (b) Zürichsee, and (c) Jörisee (mountain lake).

ly decomposed in lake water when exposed to sunlight. Methyl-triclosan and non-dissociated triclosan, however, were relatively stable toward photodegradation. It can be expected that triclosan is photolyzed orders of magnitude faster in the dissociated than in the non-dissociated form. The pH dependence of triclosan photolysis under natural sunlight can thus be described using the following rate equation:

$$dC/dt = - k_{phenolate} \cdot f_{phenolate} \cdot C$$

$$f_{phenolate} = K_a/(K_a + 10^{-pH}), \qquad pK_a = 8.1$$

where C is the (total) triclosan concentration, $k_{phenolate}$ is the photolysis rate constant for dissociated triclosan, $f_{phenolate}$ is the fraction of triclosan in the dissociated form as a function of pH, and K_a is the dissociation constant of triclosan. The observed photolysis rate coefficient (k_{obs}= $k_{phenolate} \cdot f_{phenolate}$) is thus pH-dependent. In contrast, methyl-triclosan, which does not dissociate, behaves similarly as non-dissociated triclosan and is not or only very slowly photolyzed at high and low pH.

Modeling these experimental data for the situation of the Greifensee indicated that photodegradation can account for the elimination of triclosan from the lake and suggested a seasonal dependence of the concentrations (lower in summer, higher in winter), consistent with observed concentrations. Methyl-triclosan, due to its much slower degradation, according to the model, reaches concentrations of 30% relative to those of triclosan in the epilimnion of the lake in summer, even though emitted from WWTPs at only ≈2% relative to triclosan.

Methyl-triclosan, likely formed from triclosan in WWTPs *via* biomethylation, thus appears to be more persistent and more bioaccumulative than tricosan under the conditions in lakes and, consequently, is preferentially accumulated in SPMDs, leading to concentrations comparable to those of persistent chlorinated organic pollutants.

Acknowledgments

This study was part of a project on anthropogenic markers in surface water, sponsored by the Office for Waste Management, Water, Energy, and Air of the Canton of Zürich (AWEL), Zürich.

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Pharmaceuticals in Ground and Surface Waters

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Today, the occurrence of pharmaceutical residues in domestic and industrial wastewaters is a well-recognized issue. Due to incomplete elimination in wastewater treatment plants, residues of pharmaceutical products can enter the aquatic environment (see Fig. 9) [1–4].

Initiated and financially supported by the Ministry for Environment and Transport in Baden-Wuerttemberg a research project was performed in the years 2000 to 2002 aimed at the systematic investigation of the occurrence of pharmaceuticals and endocrine disrupting chemicals in ground and surface waters of Baden-Wuerttemberg, Germany.

First, a list of 74 target compounds was set up, followed by the development and optimization of analytical methods in order to create a reliable data base with a limited set of different analytical techniques. The list of target pharmaceuticals included analgesics and antirheumatics as well as beta-blockers, broncholytics, antiepileptics, lipid-regulating agents, cytostatics, X-ray contrast media and antibiotics from different types (macrolides, sulfonamides, penicillins and others). Analysis of the pharmaceuticals in aqueous samples became possible with six different analytical methods, all based on solid-phase extraction (using different SPE materials) and determination of the compounds by GC/MS (after derivatization) or HPLC-ESI-MS-MS [5]. Using these methods, limits of detection for all of the pharmaceuticals in ground and surface waters were in the low ng/l range. Special attention was given to the internal and external validation of all methods. The results of this validation procedure proved the excellent performance of the methods and their suitability for the monitoring program.

With this set of analytical methods more than 150 groundwater samples and nearly 100 surface water samples were taken in the years 2000 to 2002 and analyzed in order to create a reliable data base on the occurrence of pharmaceutical residues in ground and surface waters in Baden-Wuerttemberg.

In about one third of all groundwater wells under investigation pharmaceuticals were detected including analgesics, antiphlogistics, lipid regulating agents, beta-blockers but also iodinated X-ray contrast media and antibiotics (Fig. 10). On the other hand a lot of groundwater wells were found to be uncontaminated by pharmaceutical residues, demonstrating the good protection of the respective groundwater resources.

For most of the groundwater samples a good correlation could be found between the concentration levels of pharmaceuticals and the concentration of boron which is a good marker for the impact of municipal waste water. A more detailed evaluation of the available information showed that most of the groundwater wells which turned out to be contaminated by pharmaceuticals are directly influenced by wastewaters (*e.g.* by leaching wastewater pipes) and, hence, the major sources of the pharmaceuticals in the groundwaters became evident. No release of pharmaceuticals into the groundwaters due to agricultural or farming activities could be found.

The occurrence of pharmaceuticals in surface waters in Baden-Wuerttemberg was systematically investigated *e.g.* in the rivers Rhine, Neckar and Danube, whereby seasonal changes of concentration levels were studied as well as spatial distributions in order to identify major sources. The results of this monitoring program clearly proved that pharmaceuticals could be found in all of the rivers under investigation and that their concentration levels strongly depend on the wastewater fraction of the receiving waters. In the river Neckar, for example, which is strongly influenced by municipal wastewaters, the concentration levels of

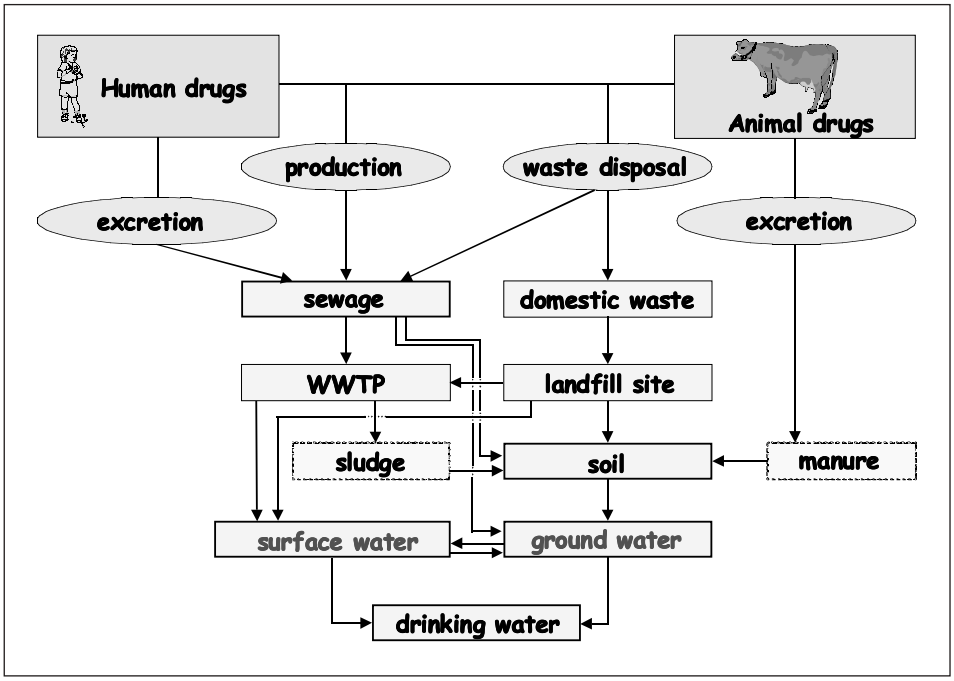

Fig. 9. Main sources and pathways of pharmaceuticals in the aquatic environment

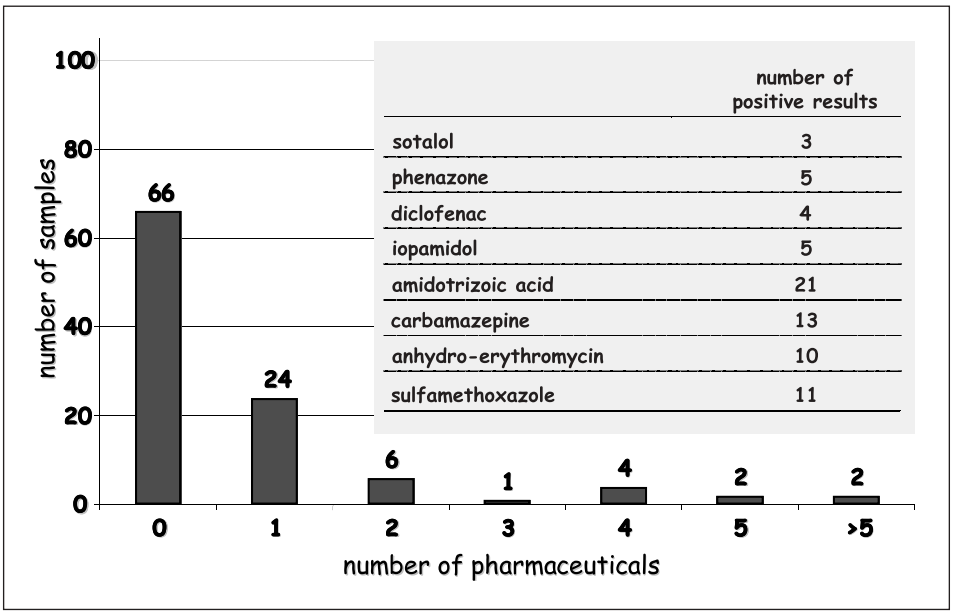

Fig. 10. Pharmaceuticals in 105 groundwater wells in Baden-Wuerttemberg (number of positive samples and pharmaceuticals most often detected)

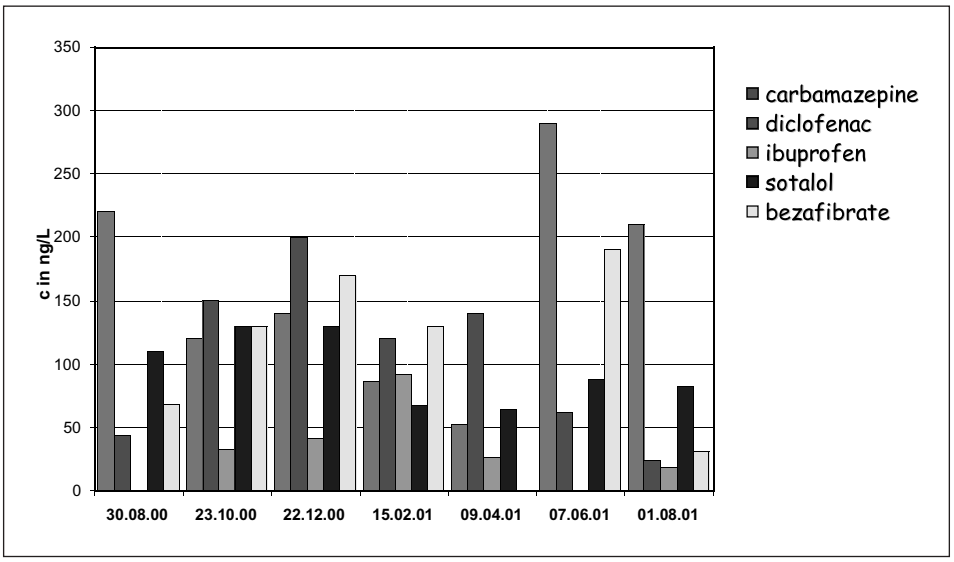

Fig. 11. Pharmaceuticals in the river Neckar at Mannheim

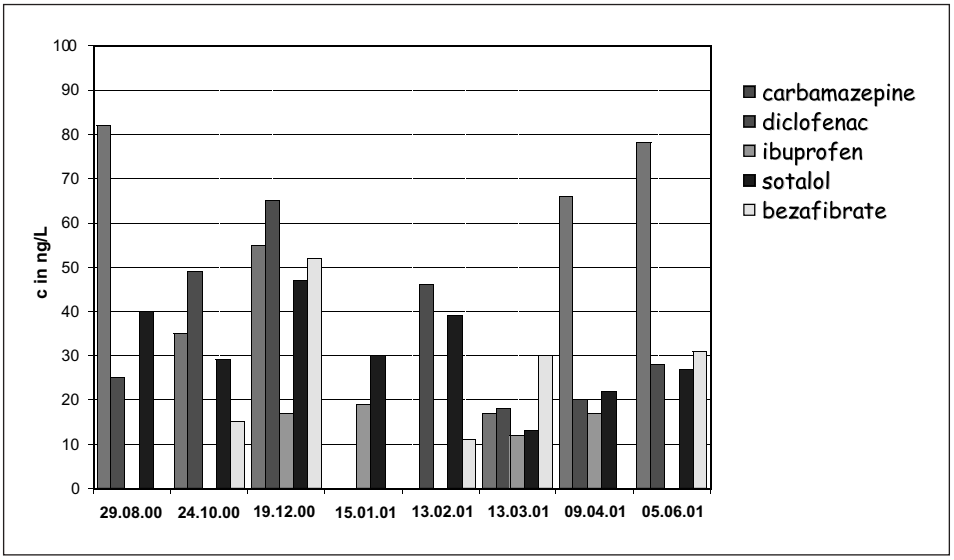

Fig. 12. Pharmaceuticals in the river Danube at Wiblingen

pharmaceuticals like the antiepileptic carbamazepine (which is also used as antidepressant), the antirheumatics and antiphlogistics diclofenac and ibuprofen, the beta-blocker sotalol and the lipid-lowering agent bezafibrate are significantly higher than in the river Danube, where the wastewater fraction is much lower than in the river Neckar (see Fig. 11 and Fig. 12).

The cocktail of pharmaceuticals found in the different rivers was quite similar. Among the compounds most often found are the antirheumatics and antiphlogistics diclofenac and ibuprofen, the antiepileptic carbamazepine, the beta-blockers sotalol, metoprolol, atenolol, and propranolol, the lipid-lowering agents clofibric acid and bezafibrate, the antibiotics roxithromycin and sulfamethoxazole, the metabolite anhydro-erythromycin (which has no antibiotic effects), and the X-ray contrast media iopamidol, iopromide, iomeprol, and amidotrizoic acid. Concentration levels of these compounds in surface waters range from few ng/l up to several hundreds of ng/l. For some compounds maximum concentrations of more than 1 µg/l were found. For the rivers Rhine and Neckar, for example, it was not possible to identify just one major source of pharmaceuticals, instead a large number of wastewater treatment plants along the river contribute to the overall load of pharmaceuticals.

Thus, from the results of this research project it can be concluded that with state-of-the art analytical methods and instrumentation it is possible to analyze pharmaceutical residues in the aquatic environment down to the low ng/l level. Using these sensitive analytical tools pharmaceuticals can be found in ground and surface waters if these are under the influence of wastewater. Additional studies proved that in most cases these compounds present in the raw waters are removed during drinking water preparation and, thus, most of the drinking waters are free of pharmaceutical residues.

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Table 2. Target list of chemicals

Pharmaceuticals	Hormones	Other Compounds
Gemfibrozil	Estrone	Bisphenol A
Ibuprofen	Ethynylestradiol	**Tris(3-chloropropyl)phosphate**
Ketoprofen	**Estradiol**	**Tris(2,3-dichloropropyl)phosphate**
Naproxen	Estriol	**N-butyl benzenesulfonamide**
Carisoprodol		**Caffeine**
Acetaminophen		*4-nonylphenol*
Propanolol		*4-octylphenol*
Primidone		Alkylphenol ethoxylates
Carbamazepine		*Alkylphenol ethoxycarboxylates*

Emerging Contaminants in Tertiary Treated Wastewater

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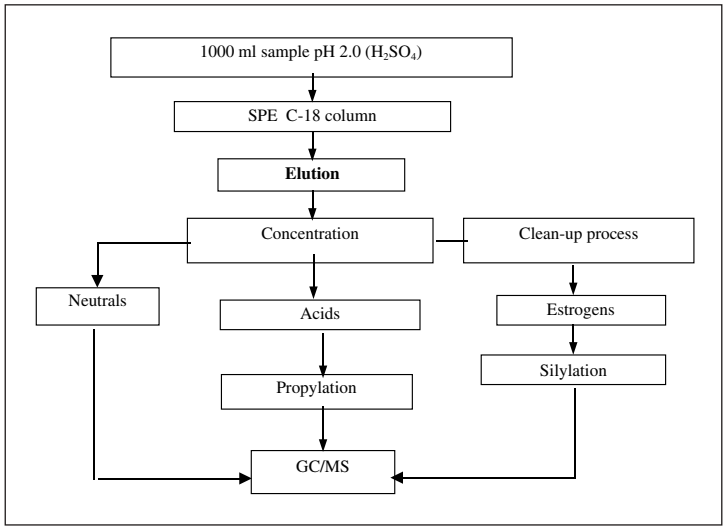
The widespread occurrence of emerging contaminants including pharmaceuticals, synthetic and natural hormones, alkylphenol ethoxylates (APEO) and their biological and chemical metabolites in surface and ground water [1] is receiving increasing attention for several reasons. Some of these contaminants are biologically active ingredients in drugs and personal care products, used as antibiotics in human or veterinary medicine, or industrial chemicals with endocrine-disrupting properties. Also included in this list are synthetic and natural hormones. Environmental concentrations range from the low ng/l level for hormones to the µg/l level for pharmaceuticals and APEO metabolites. Because concentrations are extremely low, there exists considerable uncertainty as to their ecotoxicological effects and no regulatory concentration limits have been set. Presently, analytical procedures are not standardized and published data comparisons can be difficult.

To address the environmental impact of these chemicals, it is necessary to know their sources, removal efficiencies during wastewater treatment, and their fate in the environment. The aim of this study was to develop and validate an analytical method for the detection of emerging contaminants in water. Preliminary data were presented from four municipal tertiary wastewater treatment plants that employ different tertiary treatment processes. The list of targeted chemicals (Table 2) was developed based on literature reports and analyses of wastewater effluent from a number of facilities around the country.

The procedure employs solid-phase extraction using C-18 cartridges and extraction of three fractions and is schematically depicted in the Scheme.

The neutral fraction is analyzed by GC/MS as-is, the acid fraction after propylation [2], and the estrogens after silylation [3]. All fractions are analyzed using GC/MS after adding an internal standard. Reporting limits in tertiary treated wastewater range from 1 to 3ng/l.

The compounds that were detected at the four plants are underlined. APEO metabolites occur as complex mixtures and tend to be the among the most abundant anthropogenic contaminants. Concentrations were as high as 10 µg/l for the APECs. Of the APEO metabolites, the mono-carboxylated APEOs (APEC) and the carboxyalkylphenol ethoxycarboxylates (CAPECs) generally occur at the highest concentrations (up to approximately 10 µg/l per individual compound). Alkylphenols were found only in one case above 1 µg/l (Table 3).



Scheme. Analytical scheme used to characterize three groups of emerging contaminants by GC/MS: neutrals, acids, and estrogens.

Table 3. Alkylphenolethoxylate metabolites in four tertiary effluent in µg/l[a]

Site	Treatment	APEC +CAPEC	APEO	AP
1	Filtration-chlorination-dechlorination	5.7	0.23	0.01
2	Filtration-chlorination-dechlorination	11.4	0.66	0.04
3	Rapid infiltration-extraction-UV	5.8	0.8	3.9
4	Coagulation-sand filtration	1.6	0.08	0.03

[a] average of four analyses.

Of the pharmaceuticals, carbamazepine, gemfibrozil, ibuprofen, and naproxen were detected and were quantified (Table 4). The other contaminants were not detected.

Table 4. Concentration range of pharmaceuticals detected in tertiary treated effluent

Compound	Conc. Range µg/l
Carbamazepine	n.d. – 0.017
Gemfibrozil	n.d. – 0.069
Ibuprofen	0.005 – 0.063
Naproxen	n.d. – 0.094

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Determination of Cyanobacterial Hepato- and Neurotoxins in Water Samples by HPLC-ESI-MS-MS

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The occurrence of neuro- and hepatotoxins produced by cyanobacteria (blue-green algae) is a world-wide problem. The toxicological relevance of cyanobacterial toxins means that the unambiguous identification and accurate quantification of these compounds is becoming increasingly important.

A method for the simultaneous screening analysis of both cyanobacterial neurotoxins, such as anatoxin-a and saxitoxin, as well as hepatotoxins including microcystins and nodularin was developed. The cyanotoxins are determined in water samples by an analytical method consisting of ion-pair supported solid phase extraction (SPE) and reversed phase liquid chromatography coupled to ultraviolet and tandem mass spectrometry (RP-LC/UV, MS-MS, Fig. 13).

With quantification limits in water samples in the range of 50 ng l^{-1} for the microcystins (MC-LR, -YR, -RR, -LA), nodularin, and anatoxin-a and 630 ng l^{-1} for saxitoxin the method is well suited for the surveillance of the proposed WHO guidelines for cyanobacterial toxins. The mass spectrometric detection permits, in contrast to the commonly used UV detection, an unambiguous identification and an accurate quantification of the cyanotoxins even in highly matrix polluted water samples.

Depending on the availability of commercial standards further cyanobacterial toxins and their variants can be determined by the presented method without problems.

Acknowledgements
The financial support of the National Ministry of Education, Science, Research, and Technology of Germany is gratefully acknowledged.

Byproducts from Drinking Water Ozonation

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The application of ozone in drinking water treatment is widely distributed throughout the world. The main reasons for the use of ozone are disinfection and oxidation (*e.g.* taste and odor control, decoloration, elimination of micropollutants *etc.*) or a combination of both. Similar to other disinfectants for water treatment (*e.g.* chlorine or chlorine dioxide), ozone is unstable in water and undergoes reactions with some water matrix components. However, the unique feature of ozone is its decomposition into OH radicals which are the strongest oxidants in water. Whereas disinfection occurs mainly through ozone, oxidation processes may occur through both oxidants, ozone and OH radicals. In conjunction with the beneficial effects of disinfection and oxidation, undesired byproducts can be formed from the reaction of ozone and OH radicals with water matrix components. This problem has become even more prominent after recognizing the importance of microorganisms such as *Cryptosporidium parvum* oocysts which are more resistant against disinfection. This requires higher ozone exposures and in turn leads to higher byproduct formation. The byproducts include numerous organic and some inorganic compounds. The organic byproducts consist of aldehydes, ketones and carboxylic acids as well as some brominated compounds. Most of the organic byproducts are readily mineralized during biological filtration which typically follows an ozonation step. Chlorinated compounds are not formed because chloride cannot be oxidized by ozone or OH radicals. The inorganic byproducts are chlorate, bromate and iodate. Whereas chlorate is only formed if a chlorination is followed by ozonation, bromate and iodate are formed from ozonation of bromide- and/or iodide-containing waters. Bromate is classified as potential carcinogen and therefore strict drinking water standards are applied. Bromate is the only regulated ozonation byproduct and is difficult to remove after it has been formed. Therefore, bromate minimization strategies have been developed which allow bromate formation to be decreased during ozonation. Iodate, which is quickly formed from the oxidation of iodide, is non-problematic because it is quickly reduced to iodide after ingestion.

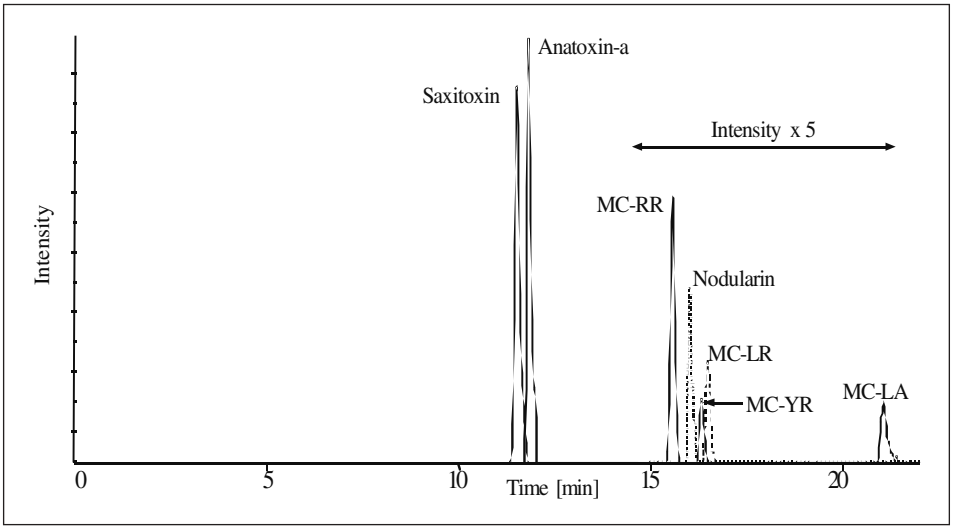

Fig. 13. HPLC/MS-MS (MRM mode) chromatogram of cyanotoxin

Abiotic Formation of Organohalogens in the Terrestrial Environment

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Introduction

To date more than 3650 organohalogen compounds are known to be naturally produced by biogeochemical processes [1]. The current understanding of the abiotic formation of organohalogens during early diagenetic processes in soils and sediments are reviewed. Next to volatile alkyl halides and polar organohalogens such as haloacetates there is evidence that even semivolatile organohalogens (*e.g.* polychlorinated dibenzodioxins) and halogenated humic substances are naturally formed by geochemical processes. The abiotic formation of halocarbons during diagenetic processes can be structured in three branches (see Fig. 14).

Biomass burning means radical chemistry of organic material in the presence of halides at elevated temperatures resulting in methyl halides [2–4]. Volcanoes are producing a whole bunch of volatile organohalogens including fluoro compounds *via* radical chemistry starting from methane, ethene and ethyne in the presence of halides on very hot mineral surfaces [5][6]. Early diagenetic processes in soils and sediments comprise radical chemistry of organic material in the presence of halides at ambient temperatures driven by redox-sensitive elements such as iron [7–13].

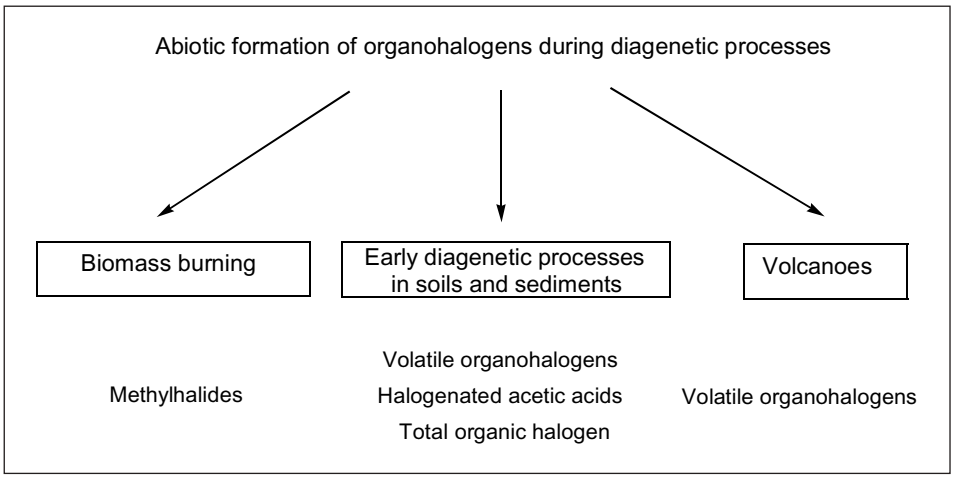

Fig. 14. Scheme of the abiotic formation of organohalogens in the terrestrial environment

Abiotic Formation of Organohalogens in the Terrestrial Environment

Halogenation processes taking place in the terrestrial environment are mostly ascribed to the omnipresence of biota [14]. Natural abiotic halogenation reactions are also known but have scarcely been investigated. From thermodynamic considerations it is possible that halide ions may form organohalide compounds naturally by purely chemical processes which are known to occur *in vitro*. There are reports that CH_3Cl may arise from CH_3Br or CH_3I by a simple nucleophilic substitution reaction involving chloride ions [15–19]. But recent findings from Coulter *et al.* [20] pointed out that this exchange reaction might be enzymatically mediated. Highly reactive compounds are necessary as prerequisite for the following reaction types, *e.g.* epoxy compounds or quinones. The first example is the synthesis of chlorogentisylol. The addition of chloride to the educt epoxidione leads to a halocarbon with a chlorohydrin structure that is further reduced to chlorogentisylol. This reaction scheme could be verified by Nabeta *et al.* [21]. Quinones exhibit chemical properties of an 1,4-unsaturated keto group that can be attacked by Cl^- at the 4 position. The nucleophilic addition of chloride to *p*-quinone leads to an intermediate resulting in chlorohydroquinone after re-aromatization [22]. This reaction type, repeated four times, was formerly applied in industry for the production of tetrachloro-*p*-quinone (*p*-chloranil) as a technical product. *p*-Chloranil was used as a herbicide until it came out that this compound was heavily contaminated by PCDD and its production was ceased immediately. Similar reactions might occur in the terrestrial environment that could be responsible for small PCDD concentrations in ancient sediment layers and archived soil samples.

A very similar reaction between humic acid and iodide was investigated by Rädlinger and Heumann [23][24]. They stirred an aqueous solution of humic acid and iodide for one hour and analyzed the reaction products by size exclusion chromatography and ICP-MS and found that iodide was chemically bound to the humic acid backbone, especially within the high molecular fraction. The reaction type is conceivable if quinonic moieties are an integral part of the humic acid structure.

Recently a new abiotic halogenation reaction was reported by Keppler *et al.* [7], that forms alkyl halides in the aerobic layer of soil. The thermodynamically labile organic matter is oxidized and the redox partner Fe(III) is reduced to Fe(II). Phenolic moieties of the natural organic matter containing alkoxy groups might be oxidized while Fe(III) is reduced. During this process halides (Cl, Br, I) present in soils are alkylated, and the alkyl halides (methyl, ethyl, propyl and butyl halides) formed represent degradation products of oxidized organic matter (Fig. 15).

As organic matter in soil displays a highly complex polymeric structure, it is difficult to describe chemical reactions taking place in soil. To reduce this complexity small molecules – so-called model compounds – are applied representing structural elements or redox features of the organic matter. Widely accepted model compounds for aromatic structures are catechol, hydroquinone, resorcinol, guaiacol, 2,3-dihydroxybenzoic acid and 2,3-dihydroxyphenylacetic acid. One of these natural monomeric constituents, guaiacol, was used as methyl-group donator for the oxidation reaction with dissolved Fe(III) or with the mineral ferrihydrite ($5Fe_2O_3 9H_2O$) and halides. Methyl halides, Fe(II) and *o*-quinone have been identified as reaction products.

In a recent paper of Keppler *et al.* [11] natural formation of the highly reactive chlorinated compound vinyl chloride (VC) in soil is described. In this case, they consider the redox-sensitive functional aromatic groups of soil organic matter as catechol and the corresponding *o*-quinone as precursors for vinyl chloride. Catechol also plays a key role within the biochemical degradation pathway of aromatic compounds. Previous laboratory experiments with catechol have shown that it can be oxidized by Fe(III) producing CO_2 [8] and, if halides are added, alkyl halides [13] (Fig. 16).

The CH_3Cl/VC ratio was about 8. There was no VC and CH_3Cl formation of when Fe(III) was absent. Moreover, no VC pro-

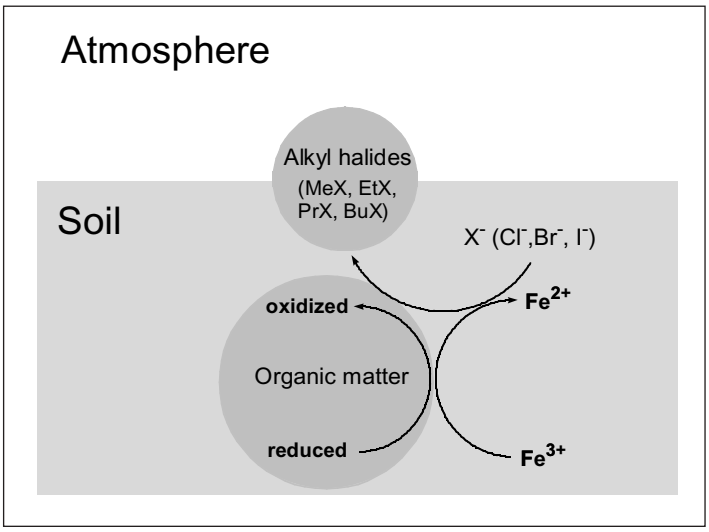

Fig. 15. Model for alkyl halide formation by the reaction of Fe(III) and organic matter in the presence of halide ions

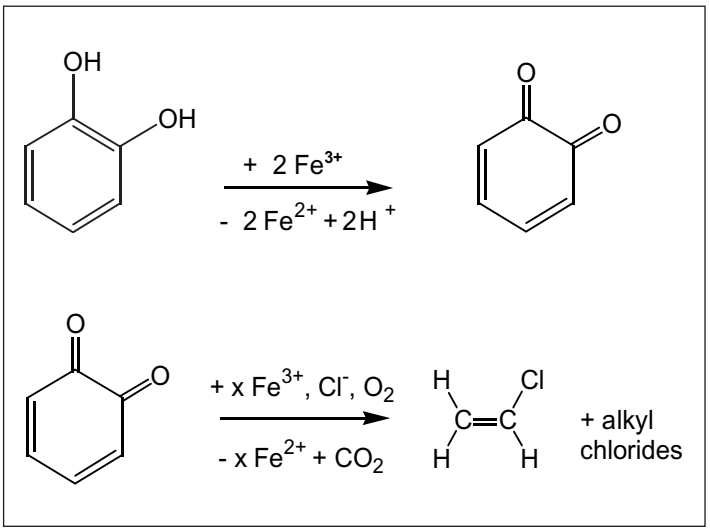

Fig. 16. Reaction scheme for the catechol oxidation with Fe(III) producing vinyl chloride, alkyl chlorides and CO_2

duction was observed by using H_2O_2, another naturally occurring oxidant. When both oxidants Fe(III) and H_2O_2 were applied the VC production increased significantly, probably caused by the Fenton reaction by which H_2O_2 and Fe(II) generate hydroxyl radicals. The prerequisite Fe(II) is provided by the reaction of catechol with Fe(III). OH radicals are powerful oxidants and could be responsible for the augmented formation of VC and CH_3Cl.

Most of the reported reaction schemes for the abiotic halogenation in the terrestrial environment are linked to radical chemistry by two essential redox-sensitive constituents of soil: iron and organic matter. Perhaps there is a third reaction partner: oxygen. It seems to be that by chance halides are involved in those radical reactions. Halides are natural soil constituents and interfere with those soil processes by their mere presence.

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