

Occurrence and temporal variations of the xenoestrogens bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol in two German wastewater treatment plants

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Abstract

Goal, scope, and background The xenoestrogens bisphenol A, 4-*tert*-octylphenol, and the technical isomer mixture of 4-nonylphenol (tech. 4-nonylphenol) belong to the group of chemicals which are called endocrine disrupters due to their property of causing hormonal dysfunctions in the endocrine system of organisms at very low concentrations. Bisphenol A, 4-*tert*-octylphenol, and the tech. 4-nonylphenol (mixture of isomers) were determined in water samples collected from the influent and effluent of two German wastewater treatment plants (WWTP) during a long-time sampling period from February 2003 till August 2005 to assess their occurrence and temporal variations in WWTPs.

Methods The compounds were extracted and concentrated from water by solid-phase extraction (SPE) using Bond Elut PPL cartridges and quantified by use of gas chromatography–mass spectrometry (GC–MS).

Results The influent concentrations were as follows: Bisphenol A < limit of detection of the method (< 1 dm)—12,205 ng L⁻¹, tech. 4-nonylphenol < 1 dm—10,186 ng L⁻¹, and 4-*tert*-octylphenol 39—1,495 ng L⁻¹. The measured effluent concentrations were lower with values in the range of < 1 dm—7,625 ng L⁻¹ for bisphenol A, < 1 dm—14,444 ng L⁻¹ for tech. 4-nonylphenol, and < 1 dm—392 ng L⁻¹ for 4-*tert*-octylphenol. All target compounds were largely eliminated during the wastewater treatment

process. The elimination efficiency varied between 73% and 93%.

Discussion All analytes show highly fluctuating influent concentrations with very high peak concentrations at particular sampling times. The variation of effluent concentrations is by far lower than the variation of influent concentrations. For tech. 4-nonylphenol, a significant temporal concentration variation has been detected with very high concentrations up to the microgram-per-liter level in the time from February 2003 till July 2003 and clearly decreasing concentrations in the time from June 2004 till August 2005. This corresponds well with the implementation of Directive 2003/53/EC (nonylphenol and nonylphenol ethoxylates in the European Union “may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0.1% by mass”) from January 2005 on. Bisphenol A is present in the effluent samples in a wide range of concentrations from below the detection limit to high concentrations up to the microgram-per-liter level. For 4-*tert*-octylphenol, no particular trend of concentration development has been observed.

Conclusions Combined SPE and GC–MS proved to be an efficient method to identify and quantify polar organic compounds in environmental samples. With respect to the concentrations measured in the present study, bisphenol A sometimes is the prominent compound in influent samples. Neither bisphenol A nor 4-*tert*-octylphenol or tech. 4-nonylphenol show seasonal variations. However, there was a significant general trend of decreasing concentrations of tech. 4-nonylphenol in influent and effluent samples from both WWTPs which probably reflects the implementing Directive 2003/53/EC.

Recommendations and perspectives Further research is needed to investigate whether the observed decrease of tech. 4-nonylphenol concentrations in German WWTPs

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since June 2004 will continue further on. The reason for the high effluent concentrations of bisphenol A in only a few samples has to be clarified in further research. The results from this study provide insight into the concentration development of the xenoestrogens bisphenol A, tech. 4-nonylphenol, and 4-*tert*-octylphenol in WWTPs in the time span between 2003 and 2005.

Keywords 4-*tert*-Octylphenol · Bisphenol A · Endocrine disruptors · Long-term study · Tech. 4-nonylphenol · Wastewater treatment plants · Xenoestrogens

1 Introduction

The property of chemicals which can act like hormones is discussed since the 1940s of the last century when the interference of the hormonal systems of humans and wildlife by chemicals was first recognized (Hegemann et al. 2002). These chemicals are called endocrine disruptors and were defined as “exogenous substances or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations” (International Program on Chemical Safety (IPCS 2005). Endocrine disruptors can cause hormonal dysfunctions in the endocrine system of organism at very low concentrations. Some known endocrine disruptors are nonnatural compounds which imitate estrogenic activity. These are synthetic estrogens (for example ethinylestradiol and diethylstilbestrol) and xenoestrogens (for example 4-*tert*-octylphenol, 4-nonylphenol, bisphenol A; Gülden et al. 1998). The present study is focused on these xenoestrogens.

Bisphenol A (2,2-*bis*-(4-hydroxyphenyl)propane) is a chemical substance manufactured mainly as an intermediate for the production of polycarbonates and epoxy resins. Its chemical structure is shown in Fig. 1. Furthermore, bisphenol A is used as a stabilizing material for some types of synthetic polymers like polyvinyl chloride, as reactant for the production of the flame retardant tetrabromobisphenol A and as an antioxidant in hydraulic fluids (BUA 1997). Bisphenol A is also used as a reactive agent in the production of temperature-sensitive paper with color-developing layers (Gehring 2004). Therefore, recycling paper products like toilet paper (contributing significantly to wastewater) have to be considered as a major source for bisphenol A in wastewater and sludge (Gehring 2004). In the year 2002, approximately 2.8 Mio t of bisphenol A were produced at a global scale (Global Industry Group 2004), in Germany 210,000 t of bisphenol A were produced in 1995 (Leisewitz and Schwarz 1997). Most of the bisphenol A (70%), produced in Germany, is processed to polycarbonate

(BUA 1997). Under anaerobic conditions, bisphenol A shows a potential for bioaccumulation and adsorption to sludge or sediments because of its moderate lipophilic character ($\log P_{ow}$ 3.32; Spengler et al. 2003). Bisphenol A is easily biodegradable under aerobic conditions in surface water and wastewater treatment systems (Staples et al. 1998). Several recent studies reported the detection of bisphenol A in different environmental compartments like surface water (Hegemann et al. 2002; Staples et al. 1998, 2000; Belfroid et al. 2002; Céspedes et al. 2005; Jin et al. 2004; Kolpin et al. 2004; Hollert et al. 2005), sediments (Heemken et al. 2001; Fromme et al. 2002; Stachel et al. 2003; Bolz et al. 2001), wastewater (Kuch and Ballschmiter 2001; Fürhacker et al. 2000; Voutsas et al. 2006), sewage sludge (Fromme et al. 2002; Bolz et al. 2001), and landfill leachates (Yamamoto et al. 2001). Furthermore, bisphenol A was shown to be present in marine and freshwater fish (Hegemann et al. 2002).

4-*tert*-octylphenol (4-(1,1,3,3-tetramethylbutyl)phenol) and the isomer mixture of technical 4-nonylphenol (tech. 4-nonylphenol) belong to the group of alkylphenols. The chemical structure of 4-*tert*-octylphenol is shown in Fig. 1. Tech. 4-nonylphenol is a complex mixture of different isomers. Chemical structures of the isomers of tech. 4-nonylphenol are shown in Fries and Püttmann (2003). In this study, 16 isomers of 4-nonylphenol are used for quantification. These isomers could be divided into four predominating isomer groups. The structures of the different isomers and the mass traces used for quantification have been reported previously by Fries and Püttmann (2003). With respect to the annual production amounts, 4-*tert*-octylphenol and tech. 4-nonylphenol are the most important substances among the alkylphenols. In 1996, 450,000 t nonylphenol were produced globally (Leisewitz and Schwarz 1997). In Germany, 2,000 t 4-*tert*-octylphenol and 37,000 t 4-nonylphenol were produced in 2000. Furthermore, 785 t alkylphenol ethoxylates were supposed to be wastewater relevant in the year 2000 (Leisewitz et al. 2003). 4-*tert*-Octylphenol and tech. 4-nonylphenol (until 2005) are used mainly for the production of alkylphenol ethoxylates, and in minor amounts for the production of phenol resins, as antioxidants in synthetic polymers and as agents applied in the aluminium die casting process (Wichmann et al. 2005). Alkylphenol ethoxylates are used, among others, as nonionic surfactants in household and industrial detergents and reach the hydrosphere by household and industrial wastewater (Leisewitz et al. 2003). Alkylphenol ethoxylates consisted until 2002 mainly of nonylphenol ethoxylates (80%) and octylphenol ethoxylates (15–20%; Pedersen and Hill 2002). Tech. 4-nonylphenol and 4-*tert*-octylphenol are degradation products of related alkylphenol ethoxylates in wastewater treatment plants (WWTPs). Tech. 4-nonylphenol and 4-*tert*-octylphenol reached the aquatic environment with the release from

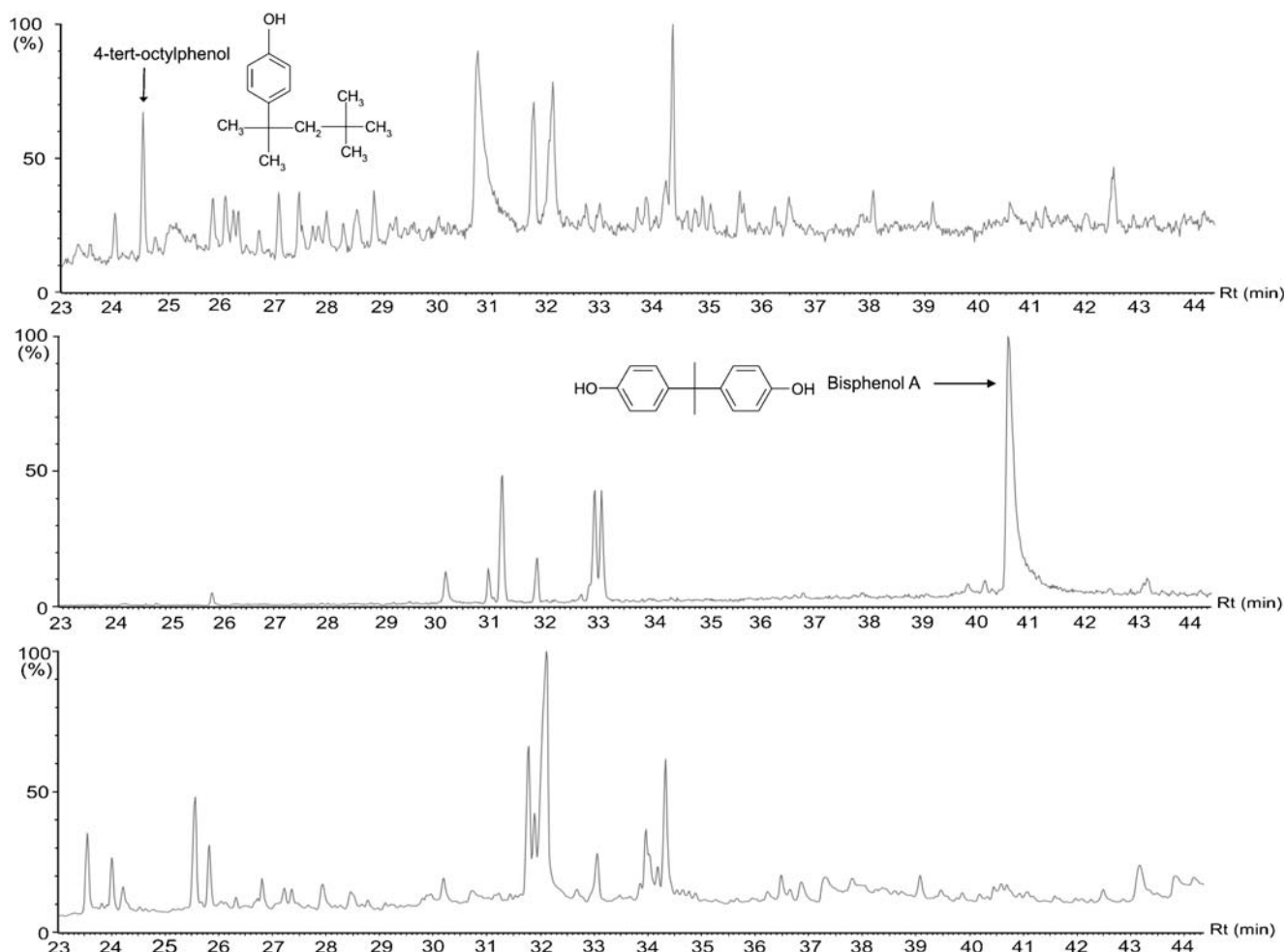


Fig. 1 Total ion chromatogram (TIC), mass trace (m/z) used for quantification and chemical structure of bisphenol A and 4-*tert*-octylphenol

WWTPs due to both their use as free phenols in various products and through the degradation of alkylphenol ethoxylates. 4-*tert*-Octylphenol and 4-nonylphenol were detected in surface water (Jin et al. 2004; Kolpin et al. 2004; Heemken et al. 2001; Stachel et al. 2003; Bolz et al. 2001; Fries and Püttmann 2003; Isobe et al. 2001), sewage sludge (Bolz et al. 2001; Leisewitz et al. 2003), sediments (Heemken et al. 2001; Fromme et al. 2002; Stachel et al. 2003; Bolz et al. 2001; Isobe et al. 2001; Li et al. 2004), and wastewater (Leisewitz et al. 2003; Isobe et al. 2001; Rudel et al. 1998). In the federal state of Hesse, Germany, in 2000 and 2001 neither 4-nonylphenols nor 4-*tert*-octylphenol could be detected in surface and wastewater; however, the degradation products of nonylphenol, nonylphenoxyacetic acid and nonylphenoxyethoxyacetic acid, have been detected in surface water and wastewater (Leisewitz et al. 2003). In some studies, the detection of 4-nonylphenols and 4-*tert*-octylphenol in aquatic biota has been reported (Tsuda et al. 2000; Wenzel et al. 2004). Bennie (1999) gave a comprehensive review of the

environmental occurrence of nonylphenol. The $\log P_{ow}$ of 4-nonylphenol is slightly pH dependent and varies in wide range between 3.28 and 5.73 (Miyamoto and Klein 1998; Ahel and Giger 1993; Rastall et al. 2006). In more acidic environments, the potential of 4-nonylphenol for bioaccumulation and for accumulation on sludge or sediments will increase (Miyamoto and Klein 1998). For environmental modeling purposes, a $\log P_{ow}$ of 4.48 has been used (Hegemann et al. 2002). According to this value, tech. 4-nonylphenol should have a significant potential for accumulation to sludge or sediments. The octanol–water partition coefficient of 4-*tert*-octylphenol ($\log P_{ow}=4$) indicates also for this compound a rather high potential of bioaccumulation and for accumulation on sludge or sediments. Spengler et al. (2003) have shown with their experiments that tech. 4-nonylphenol belongs to the group of xenoestrogens which are eliminated from the wastewater largely by adsorption to sludge. Other authors came to the result that nonylphenol is readily but not completely adsorbed on surfaces of suspended particles in river water

(Li et al. 2004). The adsorption efficiency of nonylphenol at the suspended particle depends on water temperature and varies between 28% and 67% (Li et al. 2004).

The objective of the present study was the determination of the concentrations and removal rates of phenolic endocrine disrupters (4-alkylphenols and bisphenol A) in two wastewater treatment plants of Frankfurt am Main, Germany. These WWTPs are the WWTP Niederrad–Griesheim and WWTP Sindlingen. WWTP Sindlingen is designed for wastewater volume of 75,000 m³/day corresponding to 470,000 population equivalents. WWTP Niederrad–Griesheim is designed for a daily load of approximately 230,690 m³ of wastewater corresponding to 1,350,000 population equivalents. Sludge accruing from treatment of wastewater in both WWTPs is together about 41,864 t dry weight per year. Of this sludge, 74.5% comes from WWTP Niederrad–Griesheim and 25.5% from the WWTP Sindlingen. The retention time of wastewater in both WWTPs varies between 20 and 24 h. The mode of operation is the same in both WWTPs. Mechanical treatment is followed by two biological treatment steps with activated sludge for degradation of organic compounds and degradation of nitrogen compounds (nitrification). After final sedimentation, the effluent water is discharged into the receiving river Main.

The influent and effluent concentrations of bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol were measured during the sampling period from February 2003 till August 2005. The data are used to record temporal variations of concentrations and elimination rates.

2 Experimental section

2.1 Chemicals

Bisphenol A and 4-*tert*-octylphenol were purchased from Aldrich (Taufkirchen, Germany). Technical 4-nonylphenol was obtained from Dr. Ehrenstorfer (Augsburg, Germany).

2.2 Sampling and sample preparation

The whole sampling period consisted of two sections, first from February 2003 till July 2003 and second from June 2004 till August 2005. Samples were obtained from the WWTP Niederrad–Griesheim and the WWTP Sindlingen both located in the western part of Frankfurt am Main. Twin spot samples of influent and of treated effluent were taken nearly monthly at the same time of day. Thirty-four samples were taken from both influent and effluent from the WWTP Niederrad–Griesheim and 32 samples from both influent and effluent from the WWTP Sindlingen. Results of the duplicate samples were averaged. Due to logistical prob-

lems, effluent samples could not be collected throughput-proportional 24 h after sampling the influent of the WWTPs. Additionally, a 24-h composite sample was collected from WWTP Niederrad–Griesheim in February 2005. The analyte concentrations based on the 24-h composite sample from WWTP Niederrad–Griesheim were determined to see the difference between results obtained from spot sampling and 24-h sampling.

Water samples were collected in 1-L brown glass bottles. These bottles were precleaned by washing and flushing several times with distilled water and finally with methanol purified by distillation. The bottles were dried by heating to 125°C.

Water samples were filtered immediately after collection in the laboratory with fluted filters (597.5, Schleicher and Schuell, Dassel, Germany). Prior to this filtration, samples of influent were additionally filtered with fiberglass filters (589/2, Schleicher and Schuell, Dassel, Germany) to separate coarse components from the water samples. The filters were precleaned by ultrasonic extraction with dichloromethane. All samples were stored at 4°C and were analyzed within 1 week.

2.3 Extraction

Bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol were isolated from wastewater samples by solid-phase extraction using Bond Elut PPL cartridges (Varian, 100 mg mL⁻¹). The cartridges were washed with 1 mL methanol and then preconditioned with 1 mL methanol–acetonitrile (50:50), 1 mL methanol, and 1 mL distilled water. The analyzed sample volume was 1 L. Fourteen water samples were drawn at the same time through the cartridges all placed on top of the vacuum container. The flow rate was approximately 4 mL/min. The loaded cartridges were dried under a gentle high-purity nitrogen stream until dry and subsequently eluted with 1 mL methanol/acetonitrile (50:50). The extracts were collected in several glass vials (1.1 mL) and were concentrated with a gentle high-purity nitrogen stream until dry. The residue was dissolved in 100 µl acetonitrile and 4 µg squalane (1 µg µL⁻¹ in *n*-hexane) was added as an internal standard. The internal standard method was used for the quantification of all compounds.

2.4 GC–MS analyses

Gas chromatography–mass spectrometry (GC–MS) analyses of the dissolved residues were carried out using a Fisons GC 8000 series GC coupled to a Fisons MD 800 mass spectrometer. Mass spectra were recorded under electron-impact ionization (70 eV) in the full-scan mode (50–600 *m/z*). The GC was equipped with a 30 m×0.25 mm i.d. BP-X5

capillary column of 0.25- μm film thickness. The following oven temperature program was used: 80°C held for 1 min, then increased at 4°C/min to 300°C, and finally held for 20 min. A volume of 1- μL sample was injected splitless with an inlet temperature of 280°C. Helium was used as carrier gas.

Bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol have been identified by characteristic ions of their mass spectra shown in Table 1. Mass spectra were acquired in full-scan mode which allows recording of the complete mass spectrum of the compounds and is thus qualified for avoiding identification errors. The findings have been verified by comparing mass spectra and retention times with standard compounds. For quantification of the target compounds, the following characteristic ions were used: Bisphenol A *m/z* 213, 4-*tert*-octylphenol *m/z* 135, tech. 4-nonylphenol: isomer group 1 *m/z* 177, isomer group 2 *m/z* 149, isomer group 3 *m/z* 135, and isomer group 4 *m/z* 121 (see Table 1). In Fig. 1, chromatograms of bisphenol A and 4-*tert*-octylphenol are shown. Chromatograms of tech. 4-nonylphenol can be found in Fries and Püttmann (2003; 24). Bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol were quantified by comparing their peak areas with the peak area of the internal standard squalane. The peak area of internal standard squalane has been measured in the total ion chromatogram while the signals of bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol have been integrated in the respective mass traces as aforementioned. Therewith, quantification errors due to peak overlapping could be avoided. The peak areas of bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol were revised with correction factors and response factors as described in detail by Fries and Püttmann (2003). The correction factors and response factors have been determined before each measuring. To determine recovery rates, five distilled water samples were spiked with standard solutions of bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol and the spiked water samples were analyzed as described above. Limits of detection of the method were 20 ng L⁻¹ for bisphenol A, 13 ng L⁻¹ for 4-*tert*-

octylphenol, and 10 ng L⁻¹ for tech. 4-nonylphenol. Limit of detection of the method, recovery rates, and standard deviation of each compound are shown in Table 1.

3 Results and discussion

3.1 Influent and effluent concentrations

Measured analyte concentrations are shown in Table 2. 4-*Tert*-octylphenol was detected in all influent samples and 54 of 66 effluent samples. Bisphenol A could be measured in 64 of 66 influent samples but only in ten of 66 effluent samples. Tech. 4-nonylphenol was detected in 54 influent samples and in 22 effluent samples. The concentrations of tech. 4-nonylphenol are calculated from the sum of the 16 separated 4-nonylphenol isomers.

Tech. 4-nonylphenol could be measured with median (mean) concentrations of 164 ng L⁻¹ (2,736 ng L⁻¹) in WWTP Niederrad–Griesheim and 155 ng L⁻¹ (2,004 ng L⁻¹) in WWTP Sindlingen, respectively. The high differences between mean and median concentrations can be explained by the remarkable concentration decrease of tech. 4-nonylphenol in the time from June 2004 till August 2005. Division of the sampling period into the two sections leads to different median (mean) concentrations of tech. 4-nonylphenol in the influent samples comparing the first and the second sampling section. From February 2003 till July 2003, the median (mean) concentrations in influent samples were in the microgram-per-liter level in WWTP Niederrad–Griesheim and WWTP Sindlingen whereas from June 2004 till August 2005 the median (mean) influent concentrations were much lower and ranged from 57 ng L⁻¹ (114 ng L⁻¹) in WWTP Sindlingen to 72 ng L⁻¹ (285 ng L⁻¹) in WWTP Niederrad–Griesheim (Table 3). These decreases can be explained with the implementation of Directive 2003/53/EC (EU 2003). Since 17 January, 2005, in the EU, the application of nonylphenol and nonylphenol ethoxylates as an industrial or commercial cleaning agent, as an additive in textile, leather, and metal industry, or as an additive in

Table 1 Ions used for identification and for quantification, limits of detection of the method (ldm), recovery rates and standard deviation of bisphenol A, 4-*tert*-octylphenol and tech. 4-nonylphenol

	Ions used for identification	Ions used for quantification	ldm [ng L ⁻¹]	Recovery rate [%]	Standard deviation [%]
Bisphenol A	213, 228	213	20	86	20
4- <i>Tert</i> -octylphenol	107, 135, 206	135	13	107	14
Tech. 4-nonylphenol			10	90	18
Isomer group 1 (<i>m/z</i> 177)	107, 121, 149, 163, 177	177	10	90	18
Isomer group 2 (<i>m/z</i> 149)	107, 121, 149, 191, 220	149			
Isomer group 3 (<i>m/z</i> 135)	107, 135, 220	135			
Isomer group 4 (<i>m/z</i> 121)	107, 121, 163, 177, 220	121			

Table 2 Elimination rates, concentrations and number of samples (*n*) higher than ldm of bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol in influent and effluent of the WWTPs Niederrad–Griesheim and Sindlingen

		WWTP Niederrad–Griesheim			WWTP Sindlingen		
		Influent (ng L ⁻¹)	Effluent (ng L ⁻¹)	Elimination rate (%)	Influent (ng L ⁻¹)	Effluent (ng L ⁻¹)	Elimination rate (%)
Bisphenol A	Min	466	<20	93	<20	<20	73
	Median	4,451	<20		1,352	<20	
	Mean	4,761	456		2,520	583	
	Max	12,205	7,625		9,124	4,890	
	24-h composite sample	3,048	<20	100			
4- <i>Tert</i> -octylphenol	Min	302	<13	92	39	<13	85
	Median	700	37		253	38	
	Mean	745	68		363	86	
	Max	1,495	312		1,378	392	
	24-h composite sample	360	59	84			
tech. 4-nonylphenol	Min	<10	<10	73	<10	<10	79
	Median	164	<10		155	<10	
	Mean	2,736	1,918		2,004	696	
	Max	10,186	14,444		7,977	3,031	
	24-h composite sample	245	<10	100			

cosmetics, which can be discharged into wastewater, is forbidden in concentrations equal or higher than 0.1% by mass (Directive 2003/53/EC; EC 2003). The analytical data indicate that tech. 4-nonylphenol and nonylphenol ethoxylates have been eliminated from products or replaced by other chemicals largely already before January 2005 which might cause the decreasing concentrations observed in this study since June 2004. Another reason for the remarkable decrease of tech. 4-nonylphenol might be the elimination of one or several point sources in the area of investigation during the sampling period. In June 2003, tech. 4-nonylphenol was detected with a remarkable high effluent concentration in the WWTP Niederrad–Griesheim. The 24-h composite sample was taken in February 2005. The influent concentration of this composite sample (245 ng L⁻¹) is in good agreement with the concentration measured in the time span from June 2004 till August 2005. Data of 4-

nonylphenol concentrations in wastewater which are available from other recent studies show a high variability. In one study, concentrations of 4-nonylphenols in crude wastewater from WWTPs in UK ranging between 32 and 122 ng L⁻¹ have been measured in summer 2003 (Jiang et al. 2005). These values are in the same concentration range observed in the present study in the time from June 2004 till August 2005. On the other hand, some studies reported much higher concentrations in untreated wastewater with values between 11,900 and 44,800 ng L⁻¹ in the years 1996, 1997, and 2001 (Céspedes et al. 2005; Rudel et al. 1998).

Bisphenol A shows the highest median (mean) concentrations of all three analyzed substances in influent samples from WWTP Niederrad–Griesheim and WWTP Sindlingen, respectively, with median (mean) concentrations up to 4,451 ng L⁻¹ (4,761 ng L⁻¹). The influent concentration of the 24-h composite sample from WWTP

Table 3 Different concentrations and elimination rates of tech. 4-nonylphenol in WWTP Niederrad–Griesheim and WWTP Sindlingen in the time from February 2003 till July 2003 (section I) and from June 2004 till August 2005 (section II)

	WWTP Niederrad–Griesheim				WWTP Sindlingen			
	Section I		Section II		Section I		Section II	
	Influent (ng L ⁻¹)	Effluent (ng L ⁻¹)	Influent (ng L ⁻¹)	Effluent (ng L ⁻¹)	Influent (ng L ⁻¹)	Effluent (ng L ⁻¹)	Influent (ng L ⁻¹)	Effluent (ng L ⁻¹)
Min	5,866	2,515	<10	<10	2,470	1,084	<10	<10
Median	8,495	3,440	72	<10	5,471	1,801	57	<10
Mean	8,127	6,138	285	<10	5,155	1,855	114	<10
Max	10,186	14,444	2,196	<10	7,977	3,031	612	<10
Elimination rate	25		100		57		100	

Niederrad–Griesheim is lower compared to the median and mean concentrations of the spot samples but is still in the same order of magnitude (see Table 2). The concentrations of bisphenol A detected in the influent samples are slightly higher compared with data reported in other studies. Gehring (2004) detected influent concentrations of bisphenol A in 12 German WWTPs with values up to 7,220 ng L⁻¹ and median concentration of 1,280 ng L⁻¹. Jiang et al. (2005) measured influent bisphenol A concentrations between 378 and 890 ng L⁻¹ for two WWTPs in UK. Interestingly, higher median influent concentrations could be observed in the time from February 2003 till July 2003 (7,891 ng L⁻¹ in WWTP Niederrad–Griesheim and 4,964 ng L⁻¹ in WWTP Sindlingen) than in the time from June 2004 till August 2005 (3,486 ng L⁻¹ in WWTP Niederrad–Griesheim and 1,054 ng L⁻¹ in WWTP Sindlingen).

In comparison with bisphenol A, 4-*tert*-octylphenol was present at much lower concentrations in influent samples with median (mean) concentrations of 700 ng L⁻¹ (745 ng L⁻¹) in WWTP Niederrad–Griesheim and 253 ng L⁻¹ (263 ng L⁻¹) in WWTP Sindlingen. The measured 24-h composite sample from the influent of the WWTP Niederrad–Griesheim provided a concentration of 360 ng L⁻¹ for 4-*tert*-octylphenol. This value is much lower than the median and mean influent concentration and spot sample concentration from that day. The observed difference indicates that time of sampling influences the level of concentration. The results found for 4-*tert*-octylphenol in this study are in agreement with other recent studies carried out on WWTPs in UK and USA which provided similar contents (Rudel et al. 1998; Jiang et al. 2005).

Due to mixing of wastewater in the WWTP, the effluent concentrations are less influenced by concentration peaks. Bisphenol A has been detected in four effluent samples from WWTP Niederrad–Griesheim and in six effluent samples from WWTP Sindlingen with lower median (mean) concentrations than in influent samples from both WWTPs (see Table 2). Due to the high concentrations in the respective ten effluent samples, the high differences between mean and median concentration can be explained. Similar to most of the effluent samples, bisphenol A could not be detected in the 24-h composite effluent sample.

4-*tert*-Octylphenol was detected in 26 effluent samples in WWTP Niederrad–Griesheim and in 28 effluent samples in WWTP Sindlingen at comparable concentrations with mean values of 68 ng L⁻¹ in WWTP Niederrad–Griesheim and 86 ng L⁻¹ in WWTP Sindlingen (see Table 2). The effluent concentration of the 24-h composite sample from WWTP Niederrad–Griesheim with a value of 59 ng L⁻¹ is in good agreement with the concentrations measured in spot samples. The results found for 4-*tert*-

octylphenol and bisphenol A in this study are in agreement with other recent studies carried out on WWTPs in Spain, USA, and UK which provided contents between 29 and 150 ng L⁻¹ for 4-*tert*-octylphenol and 12 and 340 ng L⁻¹ for bisphenol A (Céspedes et al. 2005; Rudel et al. 1998; Jiang et al. 2005).

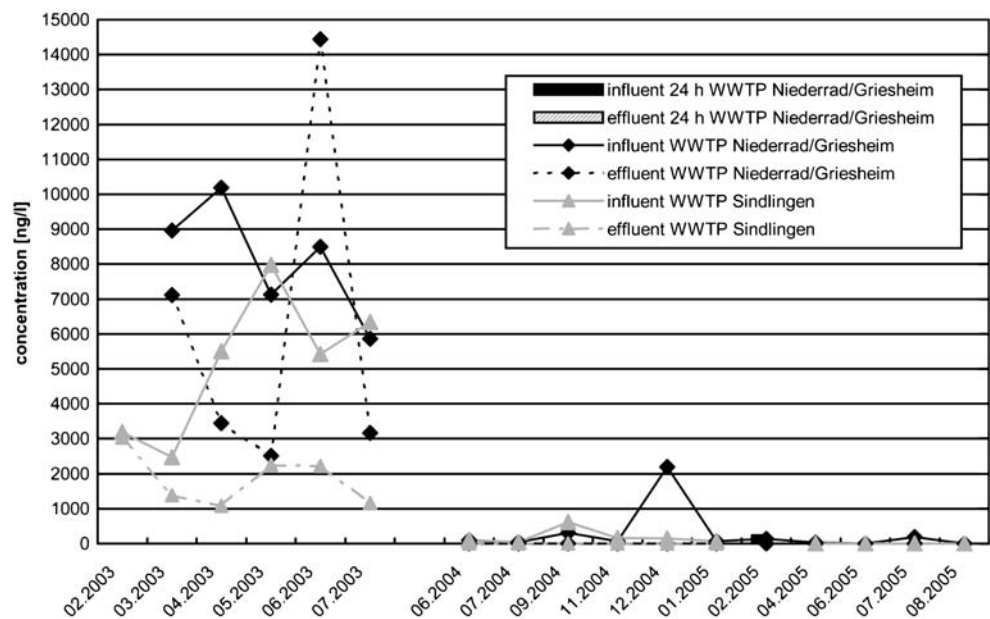
Comparable to bisphenol A, tech. 4-nonylphenol could also be detected in only ten effluent samples with median (mean) concentrations < 1 μm (1,918 ng L⁻¹) in WWTP Niederrad–Griesheim and in 12 effluent samples in WWTP Sindlingen with median (mean) concentrations < 1 μm (696 ng L⁻¹). The reason for the high differences between mean and median concentrations in the effluent samples is the remarkable decrease of tech. 4-nonylphenol during the sampling period, similar to the influent samples. From February 2003 till July 2003, the median (mean) concentrations in effluent samples were in the microgram-per-liter range in WWTP Niederrad–Griesheim and WWTP Sindlingen whereas from June 2004 till August 2005 4-nonylphenol could not be measured in both WWTPs (see Table 3). Also in the 24-h composite effluent sample, 4-nonylphenol was not detectable. The reason for these decreasing effluent concentrations is probably the same as described above (Directive 2003/53/EC; EC 2003). The effluent concentrations tech. 4-nonylphenol measured in the time from February 2003 till July 2003 (see Table 3) are in good agreement with data reported elsewhere (Isobe et al. 2001).

3.2 Temporal variation

The results show that the influent concentrations of bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol are dependent on the time of sampling while the effluent concentrations are less influenced by time of sampling. In consideration of day-to-day variations, long-term trends could be observed.

The concentrations of tech. 4-nonylphenol have shown a remarkable variation during the sampling period. Between February 2003 and July 2003, tech. 4-nonylphenol is detectable in all influent and effluent samples with concentrations up to the microgram-per-liter level. After the sampling break, since June 2004, tech. 4-nonylphenol was measured with much lower concentrations in the influent of both WWTPs and was absent in the effluent samples (Fig. 2, see Table 3). Due to unchanged analytical conditions, the reason for the elimination of tech. 4-nonylphenol in effluent and the remarkable decrease of the concentrations in influent of both WWTPs could be the decrease of entry of tech. 4-nonylphenol into wastewater treatment plants as a consequence of the prohibition of the application of tech. 4-nonylphenol or the elimination of one or several point sources as explained in “Section 2.1”. The

Fig. 2 Time series and 24-h composite sample concentration of tech. 4-nonylphenol in the WWTP Niederrad–Griesheim and WWTP Sindlingen through the sampling period from February 2003 till August 2005

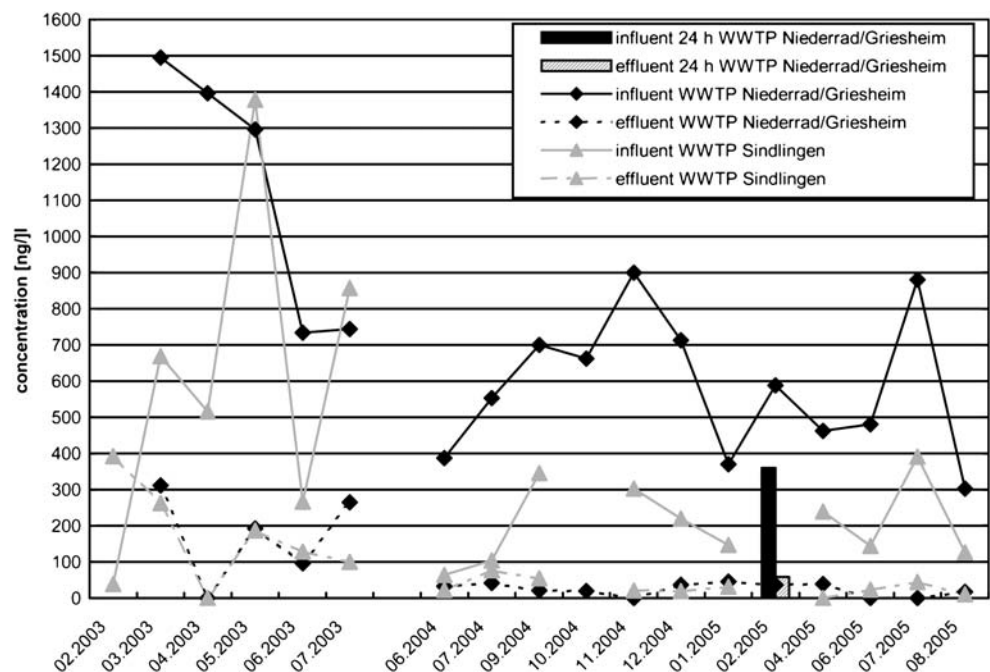


remaining occurrence of tech. 4-nonylphenol in influent samples from both WWTPs can probably be explained with leaching of 4-nonylphenol from phenol resins or other products into water or might come from the remaining allowed application in products equal or lower than 0.1% by mass.

4-*tert*-Octylphenol is present with highly fluctuating concentrations in the influent of both WWTPs and with less fluctuating concentrations in almost all effluent samples of both WWTPs during the sampling period (Fig. 3). Apart from one sample, the concentrations are always higher in influent than in effluent samples indicating

an elimination of 4-*tert*-octylphenol in the WWTPs. The variations of effluent concentrations, especially in the time from June 2004 till August 2005, are lower than the variation of influent concentrations. In contrast to tech. 4-nonylphenol, a trend for 4-*tert*-octylphenol with respect to increasing or decreasing concentrations in both influent and effluent samples during the sampling period is not visible. The measured concentrations argue for a continuous and seasonal-independent but apparently time-of-day-dependent input of 4-*tert*-octylphenol into both WWTPs. Furthermore, different from tech. 4-nonylphenol, 4-*tert*-octylphenol is not affected by a prohibition of application.

Fig. 3 Time series and 24-h composite sample concentration of 4-*tert*-Octylphenol in the WWTP Niederrad–Griesheim and WWTP Sindlingen through the sampling period from February 2003 till August 2005



In nearly all influent samples, bisphenol A is present with highly variable concentrations (Fig. 4). It is noticeable that bisphenol A is either not detectable or present with relatively high concentrations in effluent samples. The reason for this behavior is not clear. A similar observation has previously been reported by Fürhacker et al. (2000) for a WWTP in Austria. The mean and median influent concentrations showed a decreasing tendency during the sampling period as described above but in consequence of day-to-day variations the decrease is not significant. Therefore, a clear temporal trend for bisphenol A with respect to increasing or decreasing concentrations is not observable.

3.3 Elimination during treatment process

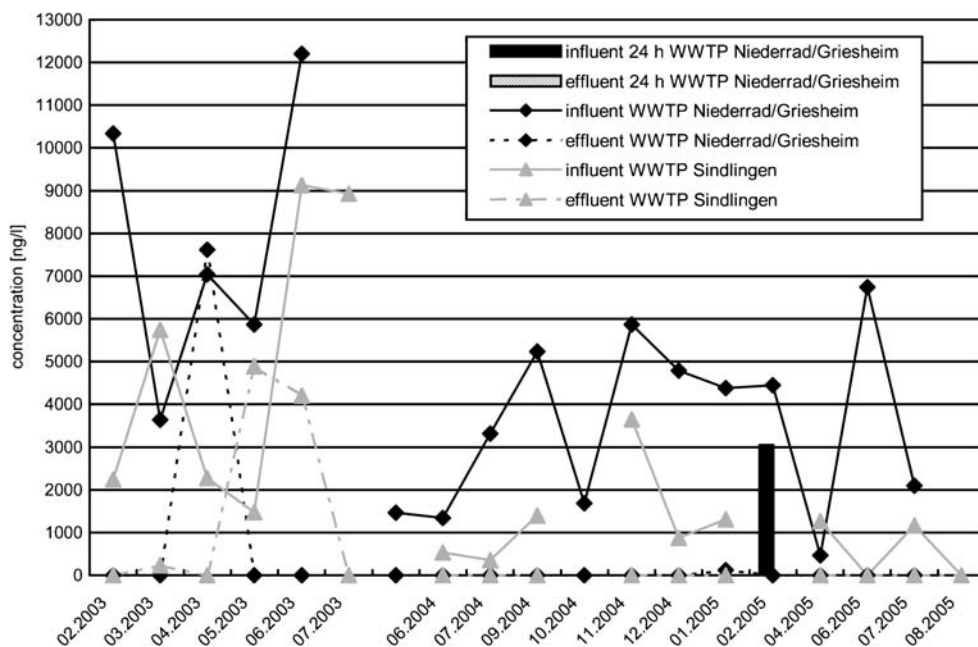
Due to removal rates calculated for the sampling period, an estimation of the removal capacity within both WWTPs is possible. All compounds were largely removed during the wastewater treatment process. The results are summarized in Table 2. The elimination rates are calculated using the results from the spot samples; therefore, the calculated efficiencies might carry some error due to diurnal variation in concentrations. The elimination rate based on the 24-h composite sample from WWTP Niederrad–Griesheim is used to validate the elimination efficiency calculated from spot samples. Complete elimination of 100% means elimination below the limit of detection of the method.

The calculated mean elimination rate of tech. 4-nonylphenol is 73% in WWTP Niederrad–Griesheim and 79% in WWTP Sindlingen. Dividing the sampling period into the two parts from February 2003 till July 2003 and June 2004 till August 2005 provides different elimination

rates. The elimination efficiency for tech. 4-nonylphenol from February 2003 till July 2003 was much lower than in the time from June 2004 till August 2005 and was estimated to be 25% in WWTP Niederrad–Griesheim and 57% in WWTP Sindlingen. In the second part, from June 2004 till August 2005, tech. 4-nonylphenol was eliminated until below the limit of detection of the method in both WWTPs. The 24-h composite sample was taken in February 2005 and gave 100% of the removal efficiency for tech. 4-nonylphenol in WWTP Niederrad–Griesheim which corresponds to the calculated removal efficiencies based on the spot samples from WWTP Niederrad–Griesheim. According to Isobe et al. (2001), the degradation of tech. 4-nonylphenol in WWTPs takes place mainly by adsorption to sludge. Furthermore, the lower elimination rates in the time from February 2003 till July 2003 can be explained by a competition between formation of 4-nonylphenols through degradation of 4-nonylphenol ethoxylates and further degradation and/or adsorption of free *n*-nonylphenols. The complete degradation of tech. 4-nonylphenol in the time from June 2004 till August 2005 is probably not caused by improved cleaning mechanism in the WWTPs but rather by much lower influent concentrations, which were already close to the limit of detection of the method. In the time from February 2003 till July 2003, a degradation rate of 100% was therefore easier to reach than in the time before with much higher inflow concentrations (see Fig. 2).

The elimination efficiency for 4-*tert*-octylphenol was estimated to be 92% in WWTP Niederrad–Griesheim and 85% in WWTP Sindlingen on average. The separate 24-h composite sample in WWTP Niederrad–Griesheim provided a removal efficiency of 84% for 4-*tert*-octylphenol

Fig. 4 Time series and 24-h composite sample concentration of bisphenol A in the WWTP Niederrad–Griesheim and WWTP Sindlingen through the sampling period from February 2003 till August 2005 Metadaten ESPR (11356), Beitrag Püttmann (ESS-ID 8427)



which supports the results obtained from spot samples. The high elimination rate of 4-*tert*-octylphenol can be explained mainly by accumulation to sludge and its assumed persistence against biodegradation (Isobe et al. 2001). The results are in good agreement with another study which provided elimination rates of 98.3% for 4-*tert*-octylphenol for WWTPs in Germany (Fahlenkamp et al. 2007).

Bisphenol A has been eliminated to concentrations below the detection limit in 55 of 66 analyzed samples (see Fig. 4). The elimination rate calculated on the spot samples is 73% in WWTP Sindlingen and 93% in WWTP Niederrad–Griesheim and 100% calculated on the 24-h composite sample (see Table 2). A similar observation has previously been reported by Fahlenkamp et al. (2007) for WWTPs in Germany. Bisphenol A is easily biodegradable under aerobic conditions and has a moderate $\log P_{ow}=3.32$ indicating that elimination mainly should occur by biodegradation. Spengler et al. (2003) also assumed that bisphenol A is eliminated by biodegradation and not by adsorption to sludge but the authors could not identify degradation products in their experiments.

4 Conclusions

With the applied analytical method consisting of SPE followed by GC–MS, it was possible to determine bisphenol A, 4-*tert*-octylphenol, and 16 isomers of tech. 4-nonylphenol in influents and effluents of two WWTPs in Frankfurt, Germany. The present study has shown that the endocrine-disrupting chemicals bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol were found in influent samples with concentrations up to microgram-per-liter level. 4-*Tert*-octylphenol could be detected in 54 effluent samples whereas bisphenol A could be measured only in ten and tech. 4-nonylphenol in 22 of 66 effluent samples. All three compounds provided highly fluctuating influent concentrations recognized by spot sampling. Bisphenol A was the prominent compound in influent samples. The variation of effluent concentrations is in general lower than the variation of influent concentrations due to mixing of concentration peaks in the influent during treatment of the water in the plant. Bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol were shown to be largely eliminated in the WWTPs during wastewater treatment processes. The elimination efficiency varied between 73% and 92%.

On the basis of the long observation period, differences between concentrations and elimination rates the year round could be observed. Neither bisphenol A nor 4-*tert*-octylphenol or tech. 4-nonylphenol has shown seasonal concentration variations. However, there was a remarkable general trend of decreasing concentrations of tech. 4-

nonylphenol in influent and effluent samples from both WWTPs. Between February 2003 and July 2003, the median concentrations of tech. 4-nonylphenol in influent samples from both WWTPs were approximately hundred times higher than in the time from June 2004 till August 2005 (see Table 3). From June 2004 till August 2005, tech. 4-nonylphenol was below the detection limit in the effluent samples in contrast to the measured effluent concentrations up to the microgram-per-liter level in the time from February 2003 till July 2003. This trend probably reflects the implementation of Directive 2003/53/EC (EC 2003) which prohibits the application of nonylphenol and nonylphenol ethoxylates in Germany as an industrial or commercial cleaning agent since January 2005. Furthermore, the elimination rate is much higher in the time from June 2004 till August 2005 with low influent concentrations compared to the time from February 2003 till July 2003 with higher influent concentrations (see Table 3). The acute aquatic toxicity of tech. 4-nonylphenol is considerably high with a predicted no effect concentration (PNEC) in surface water of $0.33 \mu\text{g L}^{-1}$ (EU 2002). The PNEC is calculated on the basis of all available toxicity data and should be protective for estrogenic effects on fish (EU 2002). The measured tech. 4-nonylphenol effluent concentrations were higher than the PNEC in the time from February 2003 till July 2003. The tech. 4-nonylphenol effluent concentrations were below the PNEC when only data obtained from sampling in June 2004 till August 2005 are considered.

Bisphenol A could be detected in nearly all influent samples up to the microgram-per-liter level but in only ten effluent samples. Elimination rates between 73% and 93% have been reached. Bisphenol A is present in the effluent samples in a wide concentration range from below the limit of detection of the method up to a very high concentration of $7,625 \text{ ng L}^{-1}$. The reason for the high effluent concentrations in a few of the analyzed samples is not clear yet. The PNEC for bisphenol A for aquatic organism is, at the moment, set to $1.6 \mu\text{g L}^{-1}$ but might change in the future depending on results from ongoing studies (EU 2003). This PNEC should be protective for estrogenic effects on fish. The concentrations measured in the effluent of both WWTPs were sometimes higher than the PNEC value but due to the dilution of effluent water in rivers, the concentrations in the river water can be expected to be below the PNEC value. The influent concentrations of bisphenol A showed a decreasing value pattern during the sampling period, but in consequence of day-to-day variations this decrease is not remarkable.

4-*Tert*-Octylphenol has shown the lowest influent concentration of all three analyzed xenoestrogens. However, in contrast to bisphenol A and tech. 4-nonylphenol, 4-*tert*-octylphenol is present in nearly all effluent samples

throughout the whole sampling period. The PNEC of 4-*tert*-octylphenol is set to 0.6 µg L⁻¹ (IPCS 2006). Due to the much lower measured effluent concentrations and due to further dilution in the rivers, no adverse effect for aquatic organism has to be expected based on the current knowledge. The measured 4-*tert*-octylphenol concentrations argue for a continuous and seasonal-independent but apparently time-of-day-dependent input of 4-*tert*-octylphenol into both WWTPs.

The results from this study provide insight into the concentration development of the xenoestrogens bisphenol A, tech. 4-nonylphenol, and 4-*tert*-octylphenol in WWTPs in the time from 2003 to 2005 and should be continued to control the further development.

5 Recommendations and perspectives

By looking at the observed concentrations and temporal concentration variations of the three xenoestrogens bisphenol A, 4-*tert*-octylphenol, and tech. 4-nonylphenol, some new questions arise. Bisphenol A is present in the effluent samples either < ldm or with high concentrations up to the microgram-per-liter level. Due to the unknown reason for this behavior, these chemical should be measured in future monitoring programs to clarify this observation. Also, only little is known about the sources of bisphenol A in wastewater and sludge which is needed to be clarified in further studies.

Furthermore, tech. 4-nonylphenol has shown remarkable decreasing influent and effluent concentrations since June 2004. Further research is needed to investigate whether the observed decrease of tech. 4-nonylphenol concentrations in German WWTPs will continue further on. Moreover, it has to be clarified whether the decrease is only caused by implementation of Directive 2003/53/EC (EC 2003) or additionally by the elimination of point sources in the area.

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