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Original Paper

GC-MS analysis of organic compounds in wastewater and sewage sludge

A multimethod based on liquid–liquid extraction and solid–liquid extraction for the analysis of persistent organic pollutants in water and sludge from sewage treatment plants has been established. Traces of 22 organic compounds used in industry and personal care products (PCPs) were analyzed by GC/MS. The LODs for the analytes were less than 2.3 ng/L for wastewater and 31 μg/kg (dry weight matter) for sewage sludge. Satisfactory recoveries (70–130%) were achieved. The validated method permits the analysis of water and sludge samples at various stages of the treatment from different sewage treatment plants. Thus, the distribution between water and sludge as well as the dissipation of the compounds analyzed were balanced. By this means, the efficiency of different wastewater treatment plants (WWTPs) can be evaluated and measures can be taken to optimize the treatment process at different stages.

Keywords: Mass spectrometry / Multimethod / Persistent organic pollutants / Wastewater treatment plants

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1 Introduction

Municipal and industrial wastewater contains emerging organic pollutants in largely unknown multiplicity and in varying concentrations [1–3]. Many of these compounds were still detectable in the effluents of wastewater treatment plants (WWTPs) and enter the surface water, some of which is a source for drinking water. The main sources of organic pollutants in wastewater are industry (chemical and thermal waste), agriculture (animal waste, pesticides, and fertilizers), and private households (human waste, other organic waste, for example pharmaceuticals and detergents) [2, 4, 5].

Musks and phenols are commonly found in personal care products (PCPs). Most of the artificial fragrances, especially those found in perfumes and fragranced PCPs, contain phthalates [6]. These and other plasticizers are used to soften materials such as foams. The organic phosphates are used for flame proofing and plasticizing various plastics and as antiwear additives in lubricants. Compounds of all these classes enter the aquatic environment in contaminated wastewater or on application of sewage sludge onto fields [1]. These substances may be persistent, biologically active, and bioaccumulating. Hence, they exhibit a significant eco-toxicological relevance [1, 7–9]. Therefore, the necessary risk assessment needs a high precision analytical method to determine the occurrence and fate of these potentially hazardous compounds [10].

GC/MS has been proven for the analysis of organic trace compounds in environmental samples [11]. Many methods have been developed for the analysis of pesticides in water and soil and were later adapted for the sensitive determination of pharmaceutical residues and PCPs in sewage and sludge [12–15].

Our aim was to develop a GC/MS-based multiresidue method applicable to the determination of a large number of potentially hazardous compounds in wastewater and sewage sludge at the nanogram *per* liter level. To achieve this, we selected a representative set of commonly used organic compounds. With this method, water and sludge samples of municipal WWTPs were analyzed by GC/MS in order to valuate the elimination of the hazardous compounds of different stages of elimination.

2 Experimental

2.1 Instrumentation

The sewage sludge samples were dehydrated by freeze-drying in an Alpha 1-4 lyophilizer (Martin Christ, Oste-

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Abbreviations: IS, internal standard; **PCP**, personal care product; **SIM**, selected ion monitoring; **WWTP**, wastewater treatment plant rode, Germany) for later sample preparation. The samples were extracted by Accelerated Solvent Extraction (ASE200; Dionex, Sunnyvale, CA, USA) and if necessary centrifuged (Avanti J-25; Beckman Coulter, Fullerton, CA, USA). The solvents were evaporated by vacuum rotary evaporators (Laborota 4001; Heidolph, Schwabach, Germany).

Liquid–liquid and solid–liquid extractions were carried out using a magnetic stirrer (MR3000; Heidolph) and the organic phase was separated in a microseparator, as described in the EN 12673 [16]. A universal oven (Tv50u; Memmert, Schwabach, Germany) was employed for the derivatization procedure.

GC/MS analyses were performed using a Thermo Finnigan Trace gas chromatograph equipped with a PTV injector and coupled to a Trace MS^{Plus} (ThermoFisher Scientific, Waltham, MA, USA).

2.2 Materials

The standards and internal standards (ISs) of triisobutyl phosphate, tri-*n*-butyl phosphate, tri-phenyl phosphate, tris(butoxyethyl) phosphate, tris(2-chloroethyl) phosphate, tris(2-chloroisopropyl) phosphate, tris(dichloroisopropyl) phosphate, ethylparathion-D10, Galaxolide®, Tonalide®, musk-xylene, musk-ketone, musk-xylene-D15, diethylhexyl phthalate, dibutyl phthalate, butylbenzyl phthalate, dioctyl phthalate, dibutyl phthalate-D4, butylbenzyl phthalate-D4, dicyclohexyl phthalate-D4, dioctyl phthalate-D4, 4-*tert*-butylphenol, 4-*tert*-octylphenol, nonylphenol (technical), pentachlorophenol, triclosan, 4-*n*-nonylphenol, bisphenol A, bisphenol A-D16, 3,4-di-chlorophenylacetic acid, and 2-(3-chlorophenoxy)-propionic acid were supplied by Merck (Darmstadt, Germany), Ehrenstorfer (Augsburg, Germany), Promochem (Wesel, Germany), and Fluka (Neu-Ulm, Germany). Toluene, acetone, hydrochloric acid, triethylamine (TEA), and ethyl acetate were obtained from Merck. Trimethylsulfonium hydroxide (TMSH) was purchased as a 0.25 M methanolic solution from Fluka. The water used in the liquid–liquid extraction was purified through a Milli-Q-Plus 185 system (Millipore, Bedford, MA, USA). The Isolute inert material (International Sorbent Technology, Hengoed, UK) for the ASE was purchased from Separtis (Grenzach-Wyhlen, Germany). IS solution (in acetone) contains ethylparathion-D10, musk-xylene-D15, dibutyl phthalate-D4, butylbenzyl phthalate-D4, dicyclohexyl phthalate-D4, dioctyl phthalate-D4, 4-*n*-nonylphenol, bisphenol A-D16 and 2-(3-chlorophenoxy)-propionic acid in concentrations of 1000 or 2000 ng/mL. The spiking solution contains all compounds from Table 1 at a concentration of 1000 ng/mL in 1 mL except the IS-substances.

All glasswares were decontaminated by washing with ethyl acetate and heating (4 h at 400°C) in an annealing furnace for glass in order to destruct the ubiquitous phthalates.

Table 1. Retention times and monitored *m*/*z* values of all analytes and ISs

	RT (min)	Target ion (*m*/*z*)	Qualifier ion (*m*/*z*)
Organic phosphates, musks, and plasticizers			
Tri-iso-butylphosphate	7.37	211	155
Tri-*n*-butylphosphate	9.07	211	155
Tris-(2-chloroethyl) phosphate	11.00	249	251
Tris-(2-chloroisopropyl) phosphate	11.45	277	279
IS-Musk-xylene-D15	12.28	294	312
Galaxolide	12.46	243	258
Musk-xylene	12.54	282	297
Tonalide	12.80	243	258
IS-Dibutyl phthalate-D4	14.54	153	227
Dibutyl phthalate	14.57	149	223
Musk-ketone	14.79	279	294
IS-Ethylparathion-D10	15.10	301	99
Tris(dichloroisopropyl) phosphate	18.44	381	191
IS-Butylbenzyl phthalate-D4	18.60	153	210
Butylbenzyl phthalate	18.62	149	206
Tris(butoxyethyl) phosphate	18.91	199	299
Tri-phenylphosphate	18.92	326	325
IS-Dicyclohexyl phthalate-D4	19.53	153	171
Diethylhexyl phthalate	19.59	149	167
IS-Dioctyl phthalate-D4	20.51	153	283
Dioctyl phthalate	20.52	149	279
Phenolic compounds			
4-*tert*-Butylphenol	5.74	164	149
IS-2-(3-chlorophenoxy)-propionic acid	7.75	155	214
4-*tert*-Octylphenol	8.52	121	149
3,4-Di-chlorophenylacetic acid	8.62	159	218
Nonylphenol (technical)	9.38–10.20	163, 234	121, 149
Pentachlorophenol	10.26	280	278
IS-4-*n*-Nonylphenol	11.38	121	234
IS-Bisphenol A-D16	14.03	252	270
Bisphenol A	14.13	241	256
Triclosan	14.77	304	302

2.3 Glass liner regeneration

The following procedure was applied for the GC-MS method 1: used glass liners were added to chromosulfuric acid for 24 h. The clean glass liners were washed with methanol and toluene and added to a mixture of MSTFA and 1% TMSCl for 24 h. After a second washing step with methanol and toluene, the glass liners could be used for the analysis.

2.4 GC-MS method

The compounds were separated on an HP-5-MS fused-silica capillary column (30 m × 0.25 mm id, 0.25 μm film thickness; Agilent, Palo Alto, CA, USA). Helium 5.0 was used as a carrier gas at a constant flow rate of 1.5 mL/min. The GC was operated in splitless injection mode and the PTV injector was programmed from 60 to 285°C (1.1 min) at 14.5°C/s at an injection volume of 1 μL. The GC column temperature programs for different classes of compounds (see Table 1) are as follows:

Method 1: organic phosphates, musks, and plasticizers – 60°C (0.5 min), 22.5°C/min to 162°C, 4.0°C/min to 202°C, 20°C/min to 300°C (2.1 min).

Method 2: phenolic compounds – 60°C (0.5 min), 20.5°C/min to 110°C, 13.0°C/min to 180°C, 7.4°C/min to 250°C, 3.7°C/min to 260°C.

The Trace MS$^{\text{Plus}}$ detector was operated in selected ion monitoring (SIM) mode at the ionization energy of 70 eV. The transfer line between GC and MS was kept at 250°C and the ion-source temperature was kept at 200°C. The MS calibration was done by autotuning.

2.5 Sample preparation

2.5.1 Liquid–liquid extraction of all liquid samples

An IS solution (1 mL, 1000 ng/mL) was added to 1 L of acidified wastewater (2 mL HCl; pH < 2). Afterwards samples were extracted with 20 mL toluene for 30 min using a magnetic stirrer and glass bonded magnetic stirrer bars. The organic phase was separated with the help of microseparators, under addition of 175 mL deionized water and transferred to a 50 mL pear-shaped flask. To dry the organic phase, the pear-shaped flask was frozen at –20°C overnight. The organic phase was separated once again and transferred to another 50 mL pear-shaped flask. The extract was evaporated down to approx. 1 mL on a rotary evaporator and transferred into a vial suitable for derivatization and later for GC-MS measurement.

2.5.2 ASE of sewage sludge for the extraction of organic phosphates, musks, and plasticizers

The freeze-dried sludge (0.5 g) was weighed out into a 33 mL ASE extraction cell and 1 mL IS solution (2000 ng/mL) was added. The cell was filled up with Isolute inert material and locked. The extraction was made twice with 100% ethyl acetate at 130°C for 45 min. After addition of 2 mL toluene, the extract was evaporated up to approx. 1 mL on a rotary evaporator. This concentrate (100 μL) was transferred into a vial and diluted with 900 μL toluene.

2.5.3 Solid–liquid extraction of sewage sludge for the extraction of phenolic compounds

The freeze-dried sludge (0.5 g) was weighed out into a 250 mL Erlenmeyer flask. IS solution (1 mL, 2000 ng/mL) was added. After 15 min, a glass magnetic stir bar and 30 mL 1 M NaOH were added to the inoculated sample. The alkaline suspension was stirred for 30 min at 700 rpm. Subsequently, the suspension was centrifuged for 10 min with 3000 rpm (1351 × *g*). The clear solution was decanted into another 250 mL Erlenmeyer flask. The still alkaline solution was adjusted with 37% HCl to pH 2. After addition of 20 mL toluene and a glass magnetic stir bar, the solution was stirred for 30 min at 700 rpm.

With the help of microseparators (addition of deionized water), the organic phase was separated and transferred into a 50 mL pear-shaped flask. To dry the organic phase, the pear-shaped flask was frozen at –20°C, the organic phase was separated once again and transferred to another 50 mL pear-shaped flask. The extract was evaporated down to approx. 1 mL on a rotary evaporator and transferred into a vial.

2.5.4 Derivatization procedure

Standard solution (200 μL) or extracts from the LLE and SLE were mixed with 100 μL TMSH solution and 20 μL TEA solution. For derivatization, the vials were placed in an oven for 1 h at 70°C. The sample was then ready for GC-MS analysis and was injected within 3 days after derivatization.

2.5.5 Recovery experiments

The spiking solutions were added to wastewater and the freeze-dried sewage sludge. Each compound was spiked to a final concentration of 2000 ng/L and 4000 μg/kg, respectively. After a residence time of 15 min (water) or complete evaporation of the solvent (sludge), the samples were extracted as described above.

3 Results and discussion

3.1 Sample injection

It was vital to use only a deactivated glass liner, containing no glass wool, since the active sites on the surface of the liner could affect both the thermal stability as well as the detectability at low concentrations. Müller and Stan (1990) [17] and Husmann *et al.* (1990) [18] have discussed this problem. To analyze the derivatized phenolic compounds, a new untreated deactivated glass liner was applied. For analysis of the organic phosphates, musks, and plasticizers, a glass liner regenerated with MSTFA was used.

After about 200 injections, a new glass liner was always required.

3.2 GC separation

For the 22 analytes with their nine ISs, two different chromatographic runs with different column oven programs were selected (see Section 2.4). The retention times of all analytes are shown in Table 1. An adequate and a fast separation was the objective depending on the type of sample. The run time for the organic phosphates,

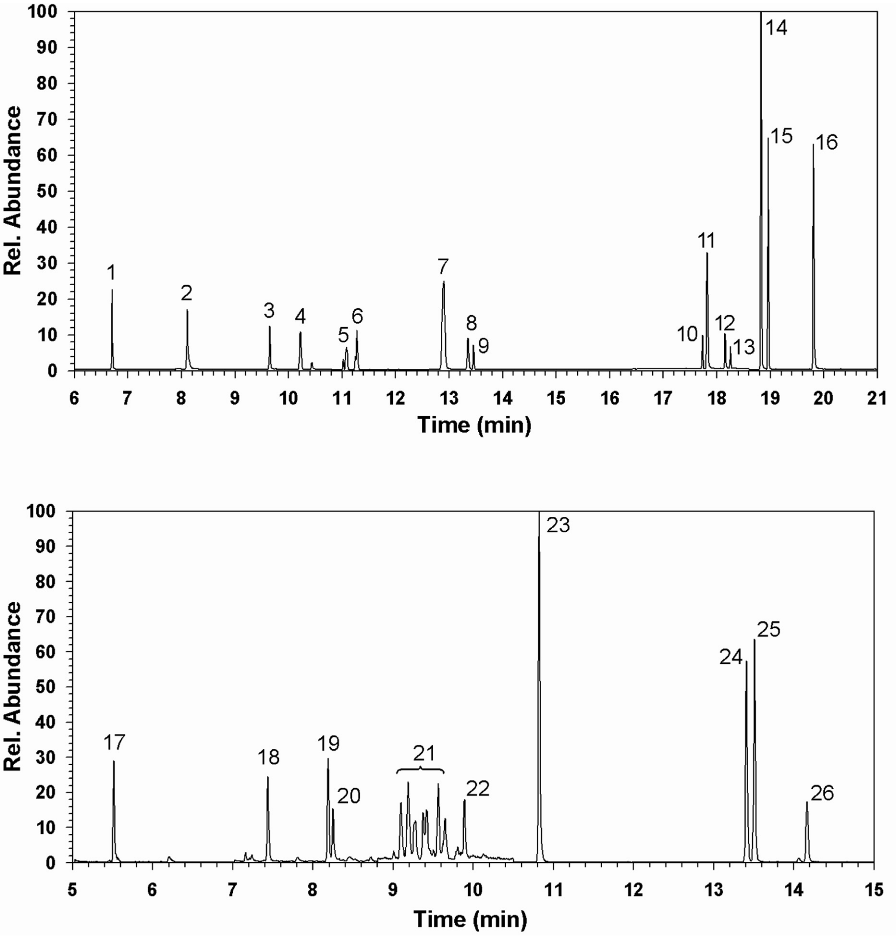

Figure 1. Total ion chromatograms of a standard solution (1000 ng/mL). Nonderivatized compounds: 1, tri-iso-butylphosphate; 2, tri-*n*-butylphosphate; 3, tris(2-chloroethyl) phosphate; 4, tris-(2-chloroisopropyl) phosphate; 5, musk-xylene-D15 and Galaxolide; 6, musk-xylene and Tonalide; 7, dibutyl phthalate and dibutyl phthalate-D4; 8, ethylparathion-D10; 9, musk-ketone; 10, tris-(dichloroisopropyl) phosphate; 11, butylbenzyl phthalate and butylbenzyl phthalate-D4; 12, tri-phenylphosphate; 13, tris(butoxyethyl) phosphate; 14, dicyclohexyl phthalate-D4; 15, diethylhexyl phthalate; 16, dioctyl phthalate and dioctyl phthalate-D4; derivatized compounds: 17, 4-tert-butylphenol; 18, 2-(3-chlorophenoxy)-propionic acid; 19, 4-*tert*-octylphenol; 20, 3,4-di-chlorophenylacetic acid; 21, nonylphenol; 22, pentachlorophenol; 23, 4-*n*-nonylphenol; 24, bisphenol A-D16; 25, bisphenol A; 26, triclosan.

musks, and plasticizers is 25.8 min and for the phenolic compounds 23.2 min.

In order to avoid carryover, an intermediate run with a toluene injection was necessary to clean the injector/column system after every sample.

3.3 MS detection

In the MS, every peak was collected with a minimum of 20 scans *per* second in the selected ion monitoring (SIM) mode. A smaller scan rate did not provide a sufficient integration of the peak areas. For quantitation, primarily the target ions were used (Table 1). The qualifier ions served for the confirmatory identification of the substances in the chromatogram.

Chromatograms of a standard solution are shown in Fig. 1.

3.4 Calibration curves

The IS method was applied for the quantitation of the 22 analytes. The ratio of the peak area of the analyte peak to that of the IS served as the analytical parameter. The calibration curves were constructed using the standard solution at concentrations of 5, 10, 50, 100, 500, 1000, 5000, and 10 000 ng/mL, each containing 1000 ng/mL IS. The results showed that these ratios were linearly correlated with the injected amount from the LOQ up to 10 000 ng/mL, with R^2 ranging between 0.92 and 0.99 for all compounds.

3.5 Recovery studies

The recovery experiments were carried out with not less than four spiked wastewater and sewage sludge samples.

Table 2. Recovery rates (Rec), detection limits (LODs), and quantification limits (LOQs)

Compound	Influent	Effluent	Wastewater		Sewage sludge		
	Rec (%)	Rec (%)	LODs[a] (ng/L)	LOQs[a] (ng/L)	Rec (%)	LODs[a,b] (μg/kg)	LOQs[a,b] (μg/kg)
Organic phosphate							
Tri-iso-butylphosphate	85 ± 2	88 ± 3	1.4	4.8	90 ± 3	5.7	19.0
Tri-*n*-butylphosphate	68 ± 1	81 ± 4	0.6	1.9	96 ± 2	2.3	7.7
Tris-(2-chloroethyl) phosphate	31 ± 10	35 ± 4	0.9	2.9	66 ± 5	3.4	11.4
Tris-(2-chloroisopropyl) phosphate	50 ± 12	72 ± 9	0.7	2.4	84 ± 6	2.8	9.5
Tris(dichloroisopropyl) phosphate	66 ± 9	101 ± 4	0.5	1.6	78 ± 8	2.0	6.5
Tris(butoxyethyl) phosphate	62 ± 10	72 ± 4	2.1	7.0	93 ± 4	8.3	27.6
Tri-phenylphosphate	86 ± 10	96 ± 6	0.2	0.6	58 ± 6	0.7	2.3
Musks							
Galaxolide	94 ± 7	98 ± 8	0.1	0.4	127 ± 3	0.5	1.7
Tonalide	76 ± 3	89 ± 3	0.1	0.2	96 ± 1	0.2	0.7
Musk-xylene	76 ± 4	80 ± 3	0.3	0.9	91 ± 3	1.1	3.6
Musk-ketone	66 ± 3	75 ± 3	0.2	0.6	92 ± 2	0.8	2.5
Plasticizer							
Dibutyl phthalate	84 ± 9	83 ± 6	0.04	0.1	82 ± 4	0.2	0.6
Butylbenzyl phthalate	86 ± 13	87 ± 6	0.12	0.4	94 ± 4	0.5	1.6
Diethylhexyl phthalate	79 ± 10	88 ± 5	0.03	0.1	92 ± 4	0.1	0.4
Dioctyl phthalate	83 ± 8	83 ± 6	0.04	0.1	91 ± 5	0.2	0.6
Phenols							
4-*tert*-Butylphenol	74 ± 8	79 ± 4	1.5	4.9	88 ± 13	5.8	19.5
4-*tert*-Octylphenol	64 ± 7	74 ± 3	2.2	7.4	94 ± 7	8.9	29.6
Nonylphenol	58 ± 14	99 ± 8	2.3	7.7	48 ± 12	9.2	30.8
Pentachlorophenol	69 ± 17	90 ± 8	1.2	3.9	86 ± 14	4.7	15.7
Bisphenol A	73 ± 4	94 ± 2	0.3	0.6	92 ± 6	0.7	2.2
Others							
3,4-Di-chlorophenylacetic acid	163 ± 16	131 ± 16	1.0	3.2	678 ± 62	3.9	12.9
Triclosan	67 ± 9	68 ± 3	0.3	1.1	116 ± 8	1.4	4.5

[a] Confidential interval of 95%.
[b] Dry weight matter (dwm).

The level of spiking was 2000 ng/L for the influent and for the effluent, and 4000 μg/kg for the freeze-dried sludge sample. The samples were extracted and the contents were determined, according to the analytical procedure described above. The recoveries for the majority of all 22 analytes ranged from 70 to 100% (Table 2). These results were considered satisfactory for a single step extraction.

3.6 LODs and LOQs

The organic phosphates, musks, plasticizers, phenols, and other compounds of interest were prepared as standard solutions in acetone at different concentrations in order to determine their LODs (injection volume of 1 μL). For each compound, a concentration of 10, 5, and 1 ng/mL was injected. In the corresponding SIM chromatogram, the S/Ns of two characteristic masses of each compound were determined. The LODs were calculated by extrapolation to an S/N of 3. The data for the LODs and LOQs (S/N of 10) for treated and untreated wastewater and sewage sludge are listed in Table 2. Most of the compounds investigated were detectable at absolute amounts of 0.03 – 1.4 pg at an injection volume of 1 μL.

3.7 Quality assurance

Phthalates and bisphenol A are ubiquitous. Therefore, special attention was paid to avoid contamination. Only glass flasks or vessels were used for sampling. In addition, all glass flasks or vessels and vials were heated to 400°C for 4 h. All plastic materials were removed from the laboratory, as far as possible, in order to avoid cross contamination by the laboratory air. Fittings of the caps of vials may contain phthalates and bisphenol A. Therefore, a thin aluminum film (baked out) was added between septum and glass vial.

To avoid phthalates bleeding from the septum of the GC injector, septa preconditioned for a high inlet temperature was used. The calibration and analysis were performed with material from the same batch, avoiding differences between different batches. At regular intervals, a blank control was performed to check the proper conditions of GC/MS system and of the reagents used.

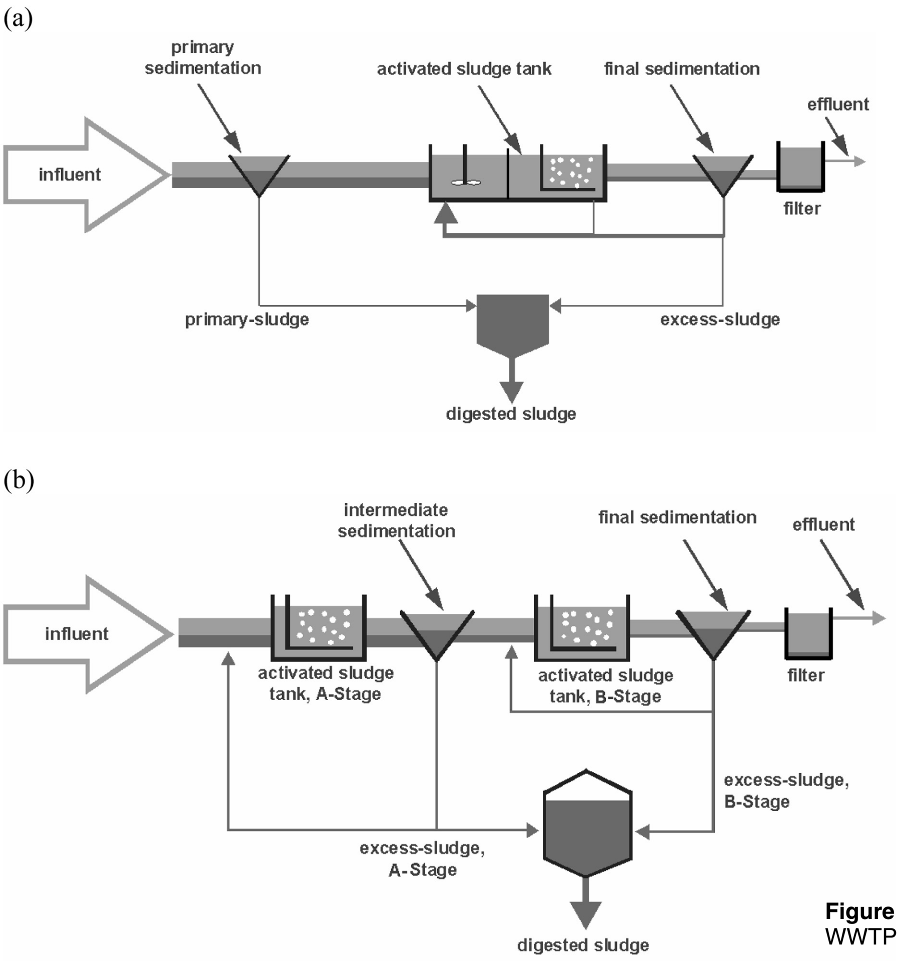

Figure 2. Flow chart of the investigated WWTP at (a) Duesseldorf and (b) Cologne.

The main focus was put on the chemicals (toluene, acetone) and the deionized water. The latter is very susceptible to contamination with phthalates and bisphenol A.

Analyses of the solvents toluene and acetone revealed that no contamination of the analytes above the LOD was detectable. The concentrations of DEHP and BPA in deionized water were 75 and 15 ng/L. The deionized water (175 mL) was only used to separate the organic phase from the water phase with the help of a microseparator. For this reason, the contamination was negligible, because only marginal extraction occurred.

3.8 Application to real samples

The effectiveness of this multiresidue method in measuring trace levels of organic phosphates, musks, plasticizers, and phenols has been proven by analyzing samples from two WWTPs situated in Duesseldorf and Cologne (Germany). The WWTP Duesseldorf is a single-stage and the WWTP Cologne a two-stage activated sludge plant. Both WWTPs have a downstream filtration unit. The arrangement of the process steps and the flow ways of the sludge and water route are schematically diagrammed in Fig. 2. The behavior of the trace compounds examined in the WWTPs could be explored on the basis of the sampling at all process steps of the water route, the sludge path as well as the processed water [19]. Former studies [20, 21] pointed out the need for mass balancing of organic trace compounds. The Duesseldorf and Cologne WWTPs investigated treat both household and industrial sewage by mechanical and biological sewage treatment, they also apply biological nitrogen and chemical phosphorus removal. 24 h composite raw and treated sewage and grab sludge samples were sampled during dry weather conditions. The WWTP Duesseldorf was sampled on 10 consecutive days from 06/06/2004 and the WWTP Cologne from 08/15/2004.

The complete mass balance of the plasticizer dibutyl phthalate is shown in Fig. 3 as an example for our study. Very good elimination, >95%, was observed, caused by sorption *via* sludge and biological degradation.

The elimination of DBP is brought about by sorption to the sewage sludge and by biological degradation in the activated sludge. The biological degradation predominates with 70–75% for the WWTP Duesseldorf, while for the WWTP Cologne the same distribution of the elimina-

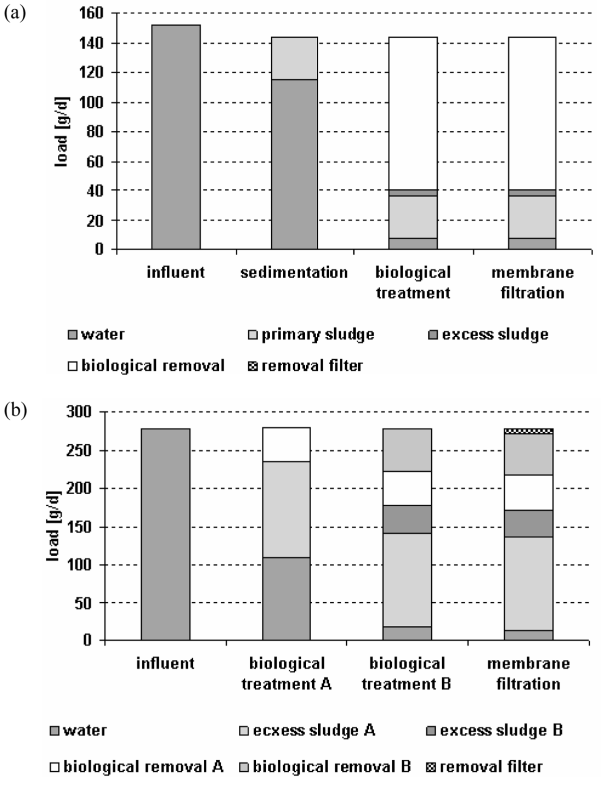

Figure 3. Mass balance of the plasticizer DBP in the (a) WWTP Duesseldorf and (b) WWTP Cologne.

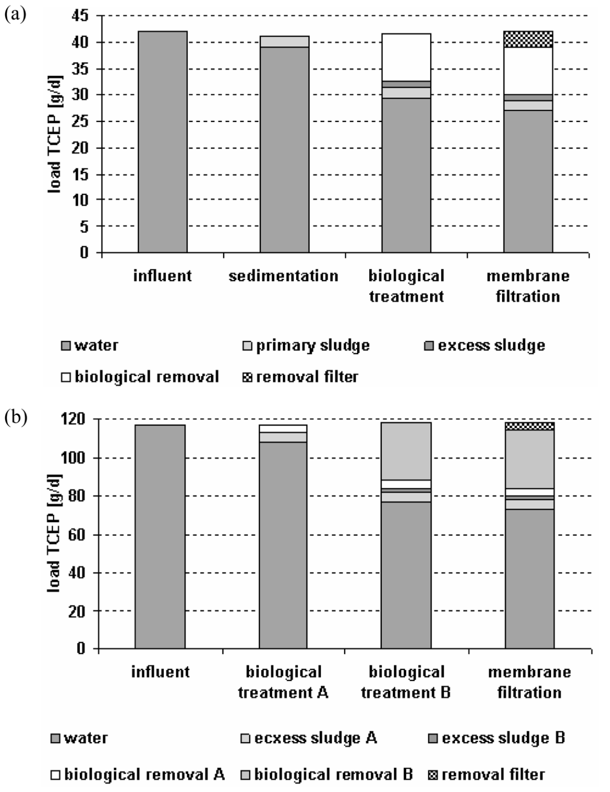

Figure 4. Mass balance of the chlorinate organic phosphate TCEP in the (a) WWTP Duesseldorf and (b) WWTP Cologne.

tion on sorption and biological degradation was found. The elimination in the phosphorus removal filtration plants of the WWTPs amounted to less than 5%. Small proportions of TCEP and other chlorinated organic phosphates were removed from the aqueous phase than was the case for DBP (Fig. 4). In Cologne the biological degradation of TCEP (25–35%) predominates in relation to the elimination on sorption (10–25%). The degradation in the activated sludge tank primarily occurs in the B-stage, the removal by the sludge is higher in the A-stage. The available results clarify that the elimination of the chlorinated organic phosphates, though not complete, takes place as a result of the combination of sorption and degradation in the activated sludge tank.

The poor degradability of the chlorinated organic phosphates and the tendential increase of the influent concentrations mean that they are a group of substances to be watched, even though the present values in the effluent of the WWTPs are still below the PNEC values (for instance TCEP: 65 μg/L [22]). Additionally, a couple of industrial chemicals spiked into biologically treated wastewater were analyzed after granulated activated carbon dosage (GAC). By this means, information was obtained for the compounds concerning their adsorption isotherms on GAC and the experimental data were modeled with the ideal adsorbed solution theory (IAST) [23].

4 Concluding remarks

A multicompound method based on liquid–liquid extraction or solid–liquid extraction and the measurement at GC/MS system has been established for the analysis of emerging contaminants in wastewater and sewage sludge. Traces of 22 organic trace compounds used in industry and PCPs have been accurately identified and quantified by GC/MS. Satisfactory LODs, recoveries, and SDs were determined for the complete sample preparation and measurement. Samples from various stages of different WWTPs were analyzed. The results of the precise analytical method were used for complete mass balancing of the 22 compounds in water and sludge as well as their dissipation.

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