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Organic micropollutants in Swiss sewage sludge

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ABSTRACT

Sludges from sixteen municipal and eleven industrial Swiss sewage treatment plants were analysed for adsorbable organic compounds (AOX), chlorinated pesticides, polychlorinated biphenyls and polycyclic aromatic hydrocarbons. Except for the AOX values, which were significantly higher ($p < 0.05$) in industrial sludges, there was no significant difference between industrial and municipal sludges. The AOX values did not correlate with any of the measured pollutants. The methods employed (capillary GC-MS and GC-electron-capture detection) proved to be suitable for monitoring organic micropollutants in industrial and municipal sewage sludges.

INTRODUCTION

In Switzerland, about 40% of the sewage sludge produced is used as a fertilizer in agriculture [1]. The heavy metal and enteric bacteria contents are monitored on a routine basis before use, in contrast to organic micropollutants [2]. However, it is not known if the load of organic micropollutants needs to be measured frequently, as its significance is still not well understood. The number of different organic compounds in sludge may be extremely high. Therefore, a selection of relevant xenobiotics has to be made. Selection criteria may include high production volume, widespread use, toxicity, carcino-

genicity, persistence and accumulation. Chlorinated pesticides, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are relevant groups of compounds [3–11], which have been selected for analysis, in addition to the overall value of “adsorbable organic halogen compounds” (AOX) [12–14].

Only a few European countries have proposed or established tolerance or limit values of organic micropollutants, e.g., Netherlands for soil [15], Germany for soil [16] and sewage sludge [17] (values for PCBs and AOX) and Switzerland for sewage sludge (value for AOX). Various results have been published for organic micropollutants in sewage sludges in Switzerland [18–23] (mainly PCBs) and elsewhere [24–32].

The methods used in this work are not new.

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However, it was the aim of this study to test if they are suitable for monitoring. Further, this study was intended to compare sludges from industrial and municipal treatment plants in relation to the concentration of organic micropollutants listed in Table I, to check AOX for correlation with specific micropollutants and to establish whether the ban on PCBs and the mentioned pesticides have had an effect on sludge contamination.

EXPERIMENTAL

Selection of sewage treatment plants

In April 1989, samples of digested sludge were taken from 27 Swiss sewage treatment plants. These plants are located in various areas of Switzerland (in parentheses are given abbreviations as in Tables II and III):

- 16 samples from municipal plants:
 - 2 plants from unpopulated areas (UNP)
 - 3 plants from little populated areas (LOWP)
 - 5 plants from large agglomerations with incinerators (BIGIN)
 - 4 plants from small agglomerations with incinerators (SMAIN)
 - 2 plants from large agglomerations without incinerator (BIG)
- 11 samples from industrial plants:
 - 6 plants from chemical industry (CHEM)
 - 2 plants from paper industry (PAP)
 - 3 plants from textile industry (TEX)

The capacities of municipal sewage treatment plants were in the range 130–620 000 biological equivalents of inhabitants. One equivalent corresponds to 25 kg of dry matter of sewage sludge per year. The capacities of industrial sewage treatment plants were in the range 22 000–415 000 equivalents. The number of inhabitants linked to municipal sewage treatment plants ranged from >100 to about 290 000; the number of inhabitants linked to industrial sewage treatment plants did not exceed 26 000. The wide size range of the treatment plants and the widespread geographic location throughout Switzerland represent a good coverage.

Sample storage

Wet samples of 3 l of digested sludge were collected on April 10th, 1989, and stored at 4°C until express delivery the next day. Immediately upon re-

ceipt, the samples were homogenized, divided into 500-ml portions and stored at -20°C. The origin of the samples was known only to the Federal Research Station for Agricultural Chemistry until the end of the measurements ("blind analysis").

Analysis

For the measurement of AOX an official method [33] was used. For the other organic micropollutants, published methods [34–36] were modified for sewage sludge. Recovery data are listed in Table I. No values have been corrected for losses during extraction.

Determination of adsorbable organic halogen compounds (AOX)

The wet frozen sewage sludge samples were thawed to room temperature in a desiccator, cut into small pieces and homogenized. The dried sludge (10–100 mg) was suspended in 25 ml of nitrate solution (0.2 M NaNO₃–0.15 M HNO₃). Charcoal (20 mg) were added and the mixture was shaken for 1 h and filtered through a polycarbonate membrane filter (0.4- μ m pores). The solid residue in the filter was washed with 25 ml of nitrate washing solution (0.01 M NaNO₃–0.008 M HNO₃). The residue was combusted in a combustion apparatus at a temperature of at least 950°C in a stream of oxygen. The combustion gases were passed through an adsorber filled with concentrated sulphuric acid and were then delivered into a microcoulometer for measurement of halogens [33].

Determination of chlorinated pesticides

Doubly distilled water (20 ml) was added to 5 g of wet homogenized sewage sludge and the mixture was left at room temperature for at least 12 h. After addition of 1 ml of acetic acid, 20 ml of methanol, 0.4 g of potassium oxalate and 20 ml of light petroleum, the suspension was homogenized for 5 min with an electrical mixer and centrifuged for 5 min at 2500 rpm (radius = 21 cm). Subsequently the supernatant was separated. The aqueous layer was extracted twice more with light petroleum ether. The combined organic layers were dried over sodium sulphate, concentrated to a volume of 3–4 ml and mixed with cyclohexane–ethyl acetate (1:1, v/v) to a final volume of 10 ml.

The solution was passed through an Acrodisc fil-

TABLE I
MEAN RECOVERY OF MICROPOLLUTANTS IN SEWAGE SLUDGE SAMPLES

Compound ^a	Chemical Abstracts Registry Number	Abbreviation	Recovery (%) (<i>n</i> = 3) ^b			
			Rec ₁	SD ₁	Rec ₂	SD ₂
<i>Organochlorinated pesticides</i>						
<i>o,p'</i> -DDD	53-19-0	DDT&MET	88	11	65	4
<i>p,p'</i> -DDD	72-54-8	DDT&MET	95	22	111	10
<i>o,p'</i> -DDE	3424-82-6	DDT&MET	89	9	86	4
<i>p,p'</i> -DDE	72-55-9	DDT&MET	87	8	98	3
<i>o,p'</i> -DDT	789-02-6	DDT&MET	97	1	83	11
<i>p,p'</i> -DDT	50-29-3	DDT&MET	102	6	113	2
Hexachlorobenzene (HCB)	18-74-1	HCB	88	11	71	5
γ -Hexachlorocyclohexane (γ -HCH)	58-89-9	Lindane	90	11	121	5
<i>PAHs</i>						
Benzo[<i>b</i>]fluoranthene	205-99-2	Σ 6PAH	98	6	78	8
Benzo[<i>k</i>]fluoranthene	206-44-0	Σ 6PAH	88	9	90	4
Benzo[<i>g,h,i</i>]perylene	191-24-2	Σ 6PAH	103	13	100	4
Benzo[<i>a</i>]pyrene	50-32-8	Σ 6PAH/BaP	93	13	88	7
Fluoranthene	206-44-0	Σ 6PAH	87	16	102	8
Indeno[1,2,3- <i>cd</i>]pyrene	193-39-5	Σ 6PAH	82	27	96	3
<i>PCBs</i>						
PCB congener No. 28 (IUPAC: 2,4,4'-trichlorobiphenyl)	7012-37-5	K28	100	15	91	4
PCB congener No. 52 (IUPAC: 2,2',5,5'-tetrachlorobiphenyl)	35693-99-3	K52	90	7	85	13
PCB congener No. 101 (IUPAC: 2,2',4,5,5'-pentachlorobiphenyl)	37680-73-2	K101	105	7	88	7
PCB congener No. 138 (IUPAC: 2,2',3,4,4',5'-hexachlorobiphenyl)		K138	92	7	103	5
PCB congener No. 153 (IUPAC: 2,2',4,4',5,5'-hexachlorobiphenyl)	35065-27-1	K153	113	15	94	15
PCB congener No. 180 (IUPAC: 2,2',3,4,4',5,5'-heptachlorobiphenyl)	35065-29-3	K180	115	7	99	8

^a Limits of determination: organochlorinated pesticides, 2 μ g/kg wet matter; PAHs, 1 μ g/kg wet matter; PCBs, 1 μ g/kg wet matter.

^b Rec₁: organochlorinated pesticides, addition of 10 μ g/kg wet matter; PAHs, addition of 3 μ g/kg wet matter; PCBs, addition of 2 μ g/kg wet matter. SD₁: standard deviation 1 (*n* = 3). Rec₂: organochlorinated pesticides, addition of 50 μ g/kg wet matter; PAHs, addition of 50 μ g/kg wet matter; PCBs, addition of 17 μ g/kg wet matter. SD₂: standard deviation 2 (*n* = 3).

ter (type Chromafil, 0.2- μ m pore diameter; Mache-rey–Nagel, Düren, Germany). Purification by gel permeation chromatography was performed on a column (30 \times 6 cm I.D.) filled with 33 g of Bio-Beads S-X3 (200–400 mesh) (Bio-Rad Labs., Richmond, CA, USA) and with a Model ABC Autorep 1002 B apparatus (Analytical Biochemistry Labs., Columbia, MO, USA) (carrier gas, 99.996% nitrogen; pressure 5 p.s.i.; 1 p.s.i. = 6894.76 Pa). Organochlorinated pesticides were eluted with cyclohexane–ethyl acetate (1:1, v/v) (load time 10 s, dump

time 14 min, collection time 20 min, wash time 6 min). The eluate was condensed to a volume of 1–2 ml and treated with 2 g of Celite.

The extract was further purified on a dual-column system. The precolumn (10 cm \times 2.5 cm I.D.) was filled with 0.5 g of Celite and the eluate–Celite suspension and covered with sand. The main column (25 cm \times 2.5 cm I.D.) was filled with 5 g of sodium sulphate, 10 g of aluminium oxide, 20 g of Florisil and 2 g of sand. Three 5-ml volumes of propylene carbonate were passed under slight pressure

through the precolumn into the main column, where it remained for 1 h. Chlorinated pesticides were eluted from the second column with 130 ml of cyclohexane. The eluate was condensed to 1–2 ml, diluted with cyclohexane to a final amount of 2 g (corresponding to 2.55 ml) and filtered through a Florisil–Sep-Pak cartridge (100 mg) (Waters, Milford, MA, USA) into a sample vial for analysis.

Capillary gas chromatography with electron-capture detection (cGC–ECD) was performed on a Hewlett-Packard Model 5890 gas chromatograph equipped with a Model 7673A autosampler (Figs. 1 and 2). The injection volume was 1 μ l (splitless mode) at an injector temperature of 250°C. A DB-1 and DB-17 capillary column (30 m \times 0.25 mm I.D.) was used (J&W Scientific; film layer 0.25 μ m; carrier gas, nitrogen at 5 ml/min). The temperature was programmed from 60°C to 280°C at 20°C/min with a final hold time of 30 min and a total run time of 41 min. The temperature of the electron-capture detector was set at 300°C. Peak measurement was performed with a Hewlett-Packard Pascal workstation (revision 4.0). The system was calibrated by four-point linear regression and peak heights were compared with an external standard. The limit of determination was 2 μ g/kg and the range of measurement was 2–500 μ g/kg [34,35].

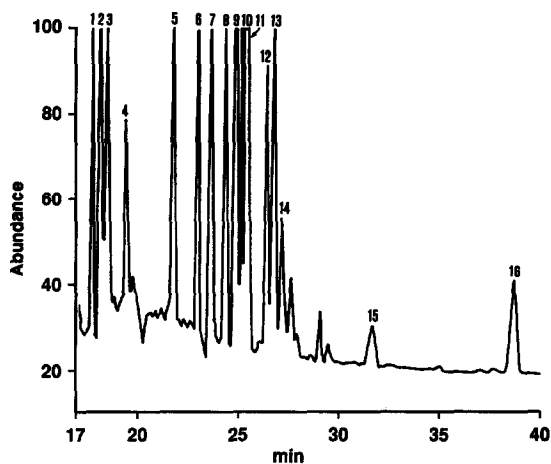


Fig. 1. GC–ECD of chlorinated pesticides for a spiked sewage sludge (recovery experiment, 50 μ g/kg). Peaks: 1 = α -HCH; 2 = HCB; 3 = lindane; 4 = δ -HCH; 5 = aldrin; 6 = HC epoxide; 7 = *o,p*-DDE; 8 = endosulfan; 9 = *p,p'*-DDE; 10 = *o,p*-DDD; 11 = dieldrin; 12 = endrin/*p,p'*-DDD; 13 = *o,p*-DDT; 14 = *p,p'*-DDT; 15 = methoxychlor; 16 = mirex.

Determination of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs)

Wet homogenous sewage sludge (30 g), 60 ml of saturated sodium chloride solution and 100 ml of cyclohexane were shaken (upside down) for 45 min. The phases were separated (after centrifugation, if necessary). The aqueous phase was extracted once more with 100 ml of fresh cyclohexane for 45 min. The combined organic layers were dried with sodium sulphate, evaporated to dryness and the residue dissolved in 5 ml of toluene–hexane (1:3, v/v).

Subsequent solid-phase extraction was performed with an ICT Bond-Elut bonded-phase SI cartridge (1000 mg; 3 ml; AL 601 406) (ICT, Harbor City, CA, USA). The cartridge was first washed with 5 ml of hexane and 3 ml of toluene–hexane (1:3, v/v) with the help of slight vacuum suction. The extract was passed through the cartridge, which was washed with two portions of 3 ml of toluene–hexane (1:3, v/v). The combined eluates were evaporated to dryness and the residue dissolved in 1 ml of cyclohexane [36].

PAHs and PCBs were measured with different aliquots from the same extracts by cGC–MS (electron impact ionization) (Fig. 3). A Hewlett-Packard system was used with a Model 5890 gas chromatograph equipped with a Model 7673A autosampler and an MSD 5971B mass spectrometer. The transfer line temperature was 280°C. The injection volume was 1 μ l (splitless mode) at 270°C. Helium

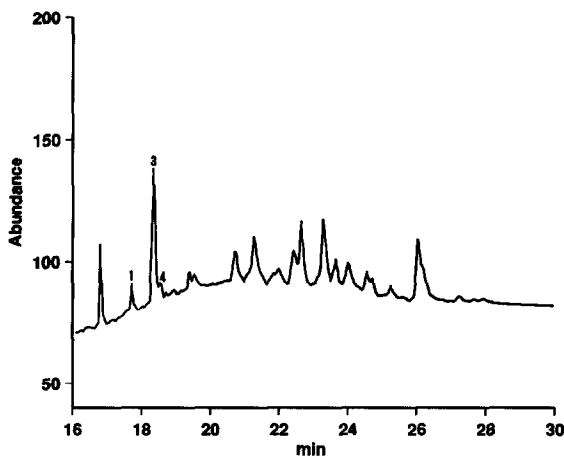


Fig. 2. GC–ECD of chlorinated pesticides in sewage sludge. Peak numbers as in Fig. 1.

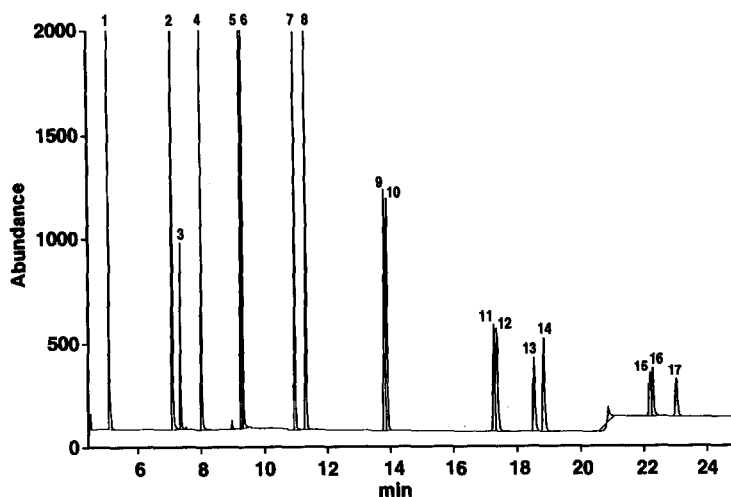


Fig. 3. GC-MS (SIM mode) of PAHs for a spiked sewage sludge (recovery experiment, 50 $\mu\text{g}/\text{kg}$). Peaks: 1 = naphthalene; 2 = acenaphthylene; 3 = acenaphthene; 4 = fluorene; 5 = phenanthrene; 6 = anthracene; 7 = fluoranthene; 8 = pyrene; 9 = benzo[*a*]anthracene; 10 = chrysene; 11 = benzo[*b*]fluoranthene; 12 = benzo[*k*]fluoranthene; 13 = benzo[*a*]pyrene; 14 = perylene; 15 = indeno[1,2,3-*cd*]pyrene; 16 = dibenz[*a,h*]anthracene; 17 = benzo[*ghi*]perylene.

(99.996%) was used as the carrier gas at a flow-rate of 40 ml/min and a head pressure of 12 p.s.i. A 30 m \times 0.25 mm I.D. glass capillary column coated with DB-1 (methylsilicone; J&W Scientific; layer thickness 0.25 μm) was used with the following temperature programme: 4 min at 60°C (solvent delay), increased at 20°C/min to 250°C, then at 5°C/min to 270°C, held for 5 min at 270°C, increased at 25°C/min to 300°C, with a final hold for 16 min at 300°C. Quantification was achieved by single-ion monitoring (SIM) during a run time of 35.7 min. For PAHs, ions at m/z 128, 152, 166, 178, 202, 228, 252, 276, 278 were monitored, and PCBs were monitored in the second analysis with ions at m/z 256, 291, 326, 360, 394. The system was calibrated automatically by three-point linear regression. Quantification was done by comparison of peak heights with that of an external standard. The limit of determination was 1 $\mu\text{g}/\text{kg}$, the detection limit was 0.5 $\mu\text{g}/\text{kg}$ and the range of determination was 1–100 $\mu\text{g}/\text{kg}$ for each compound.

Statistical analysis

The water content of the samples was determined with an aliquot of the sewage sludge and the results were calculated with respect to dry matter.

It was not possible to calculate an arithmetic mean, because some values were below the limit of

determination. Instead, two means were calculated: mean 1, values below the limit of determination were set equal to zero; mean 2, values below the limit of determination were set equal to the limit of determination. Mean 2 was not calculated for sum parameters.

The signed rank test (two-sided Wilcoxon test) was used for comparison of values within this study and for comparison of values obtained in this study with those given elsewhere [37]. $P < 0.05$ was regarded as statistically significant.

RESULTS AND DISCUSSION

Adsorbable organic halogen compounds (AOX)

AOX is an overall parameter for the content of non-volatile, halogenated organic hydrocarbons in sewage sludge and other environmental samples. It is now frequently used for an initial ecological assessment of sewage sludge in relation to halogenated organic compounds [31]. Germany has adopted a limit of 500 mg/kg AOX (500 mg Cl/kg dry matter) in the amendment of the ordinance on sewage sludge, and Switzerland has established a guide value for the same limit [38].

AOX were found in all samples in this study (Tables II and III). The AOX concentrations were significantly higher ($p < 0.05$) in industrial sludge

TABLE II
ORGANIC MICRO POLLUTANTS IN SWISS MUNICIPAL SEWAGE SLUDGE

No.	Origin ^a	AOX (mg/kg)	Lin- dane (µg/kg)	HCB (µg/kg)	DDT & MET ^b (µg/kg)	PCB congeners (µg/kg)				PAHs (µg/kg)		Water content (%)		
						C28	C52	C101	C138	C153	C180		Σ6PAH ^c	BaP
1	UNP	220	nd	nd	340	nd	nd	nd	20	11	nd	118	18	90.7
2	UNP	240	144	25	149	nd	nd	nd	nd	nd	nd	nd	nd	92.0
3	LOWP	210	nd	47	nd	nd	nd	16	32	26	nd	258	40	84.9
4	LOWP	270	nd	nd	nd	nd	18	nd	15	nd	nd	467	74	92.5
5	LOWP	400	nd	13	376	16	41	nd	89	12	nd	1833	16	87.4
6	BIGIN	360	93	73	nd	nd	19	nd	nd	nd	nd	747	128	90.1
7	BIGIN	410	nd	nd	nd	nd	nd	19	29	25	nd	233	20	92.7
8	BIGIN	2000	nd	nd	nd	nd	17	29	42	48	15	347	47	92.5
9	BIGIN	400	nd	60	nd	25	66	nd	25	15	nd	537	105	91.8
10	BIGIN	150	nd	nd	nd	16	86	nd	73	41	26	862	nd	91.3
11	SMAIN	280	95	nd	nd	14	43	nd	37	14	nd	202	31	90.1
12	SMAIN	360	nd	118	nd	nd	nd	nd	38	24	nd	39	nd	92.4
13	SMAIN	220	nd	nd	nd	nd	14	nd	13	nd	nd	114	nd	91.2
14	SMAIN	230	nd	nd	89	25	46	nd	18	nd	nd	767	nd	88.4
15	BIG	130	nd	nd	159	17	41	37	66	56	17	338	nd	92.0
16	BIG	300	nd	nd	nd	9	24	nd	41	26	12	583	101	88.5
Min.		130	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	84.9
Max.		2000	144	118	376	25	86	37	89	56	26	1833	128	92.7
Median		275	nd	nd	nd	nd	19	nd	31	15	nd	343	19	91.3
MV ₁ ^d		390	21	21	70	8	26	6	34	19	4	465	36	90.5
SD ₁ ^d		440	46	35	125	9	25	12	24	17	8	451	43	2.2
MV ₂ ^e		390	39	35		14	29	14	35	22	13		40	90.5
SD ₂ ^e		440	37	27		5	23	8	22	14	4		40	2.2

^a For abbreviations of sewage treatment plants, see Experimental.

^b Sum of *o,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE, *p,p'*-DDT and *p,p'*-DDT. Single values below the limits of determination were set equal to zero before addition.

^c Sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, benzo[*a*]pyrene, fluoranthene and indeno[1,2,3-*cd*]pyrene. Single values below the limits of determination were set equal to zero before addition.

^d Single values below the limits of determination were set equal to zero for calculation of mean value 1 (MV₁) and standard deviation 1 (SD₁); nd = 0.

^e Single values below the limit of determination were set equal to the limit of determination for calculation of mean value 2 (MV₂) and standard deviation 2 (SD₂); nd = limit of determination.

TABLE III
ORGANIC MICROPOLLUTANTS IN SWISS INDUSTRIAL SEWAGE SLUDGE

No.	Origin ^a	AOX (mg/kg)	Lin- dane (µg/kg)	HCB (µg/kg)	DDT & METS ^b (µg/kg)	PCB congeners (µg/kg)					PAHs (µg/kg)		Water content (%)	
						C28	C52	C101	C138	C153	C180	Σ6PAH ^c		BaP
17	CHEM	810	nd ^f	nd	nd	nd	17	nd	nd	nd	nd	184	45	92.4
18	CHEM	2200	177	nd	164	15	nd	nd	7	nd	nd	336	nd	86.6
19	CHEM	110	nd	11	119	nd	10	nd	11	8	nd	105	20	82.8
20	CHEM	420	nd	46	nd	nd	34	nd	16	nd	nd	897	154	93.2
21	CHEM	310	nd	nd	125	nd	nd	nd	nd	nd	nd	1031	nd	90.2
22	CHEM	1000	25	28	1030	nd	27	nd	nd	nd	nd	nd	nd	92.7
23	PAP	540	nd	29	118	nd	nd	20	38	31	nd	nd	nd	94.5
24	PAP	7600	19	nd	159	nd	21	23	54	39	nd	nd	nd	92.4
25	TEX	2700	188	303	579	nd	nd	nd	nd	nd	nd	377	nd	92.3
26	TEX	420	nd	33	472	nd	26	nd	32	17	nd	802	153	90.9
27	TEX	750	nd	nd	nd	10	32	nd	25	13	nd	412	63	90.3
Min.		110	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	82.8
Max.		7600	188	303	1030	15	34	23	54	39	nd	1031	154	94.5
Median		750	nd	11	125	nd	17	nd	11	nd	nd	336	nd	92.3
MV ₁ ^d		1500	37	41	251	2	15	4	17	10	0	377	40	90.8
SD ₁ ^d		2200	72	89	319	5	13	8	18	13	0	377	60	3.4
MV ₂ ^e		1500	52	51		13	20	13	21	15	12		46	90.8
SD ₂ ^e		2200	65	84		3	9	5	14	10	3		56	3.4

^{a-e} See Table II.

^f nd = Not detected (below the limit of determination).

(median 750 mg Cl/kg dry matter; mean 1533 mg/kg) than in municipal sludge (median 275 mg/kg; mean 386 mg/kg). Only one out of sixteen municipal samples yielded an AOX value higher than 500 mg/kg, in contrast to seven out of eleven industrial sludges. PCBs and organochlorinated pesticides did not correlate with the AOX concentrations. This is not surprising, as there is a difference of three orders of magnitude between their concentrations.

Leschber *et al.* [32] measured a median value of 280 mg/kg in 170 samples of German sewage sludge (suitable for agricultural use). This is in the range of the present study and is almost identical with our median value (275 mg/kg) in municipal sludges.

Chlorinated pesticides

The concentrations of aldrin, dieldrin, endosulfan, endrin and heptachlorepoxide were all below the limit of determination of 2 µg/kg (wet matter) and are not discussed further. Values for other chlorinated pesticides are given in Tables II and III. Mean value 1 and mean value 2 showed a difference only at low values (of the order of one standard deviation). None of the compounds determined were found in all the samples tested. In municipal sewage sludges all median values were below the limit of determination. In contrast, the mean concentration of lindane was the only one below the limit of determination in industrial sewage sludges. There was no significant difference between municipal and industrial sludges.

Lindane was detected in three out of sixteen municipal and in four out of eleven samples of industrial sewage sludge. Mean value 2 for the municipal samples (39 µg/kg dry matter) was similar to corresponding concentrations in 57 German samples (27 and 56 µg/kg dry matter [28]) and the values for the industrial samples of this study (52 µg/kg).

HCB was found in six municipal and six industrial sewage sludge samples at concentrations comparable to values found by Witte *et al.* [28]. The measured values are significantly lower than those found by Müller [19] in nine Swiss sludges in 1982 (mean value 50 µg/kg).

DDT and metabolites were measured in five municipal (70 µg/kg, mean value 1) and eight industrial (251 µg/kg) sludge samples. Witte *et al.* [28] found 80 µg/kg dry matter for DDT (without measuring its metabolites). Clevenger *et al.* [29] reported a

mean value of 100 µg/kg dry matter for DDT. Drescher-Kaden *et al.* [39] and Witte *et al.* [28] considered the contamination of sewage sludge in Germany by chlorinated pesticides not to be important compared with other sources of contamination.

The chlorinated pesticides measured in this study are banned in Switzerland [40], with the exception of lindane, which used for seed dressings. The concentrations of lindane and HCB in the River Rhine (16 and 219 ng/l in 1974) and in the ground water (9 and 6 ng/l in 1974) near Basle have been falling since 1980 (river, 5 and 3 ng/l; ground water, 0.5 and 2 ng/l in 1989) [41–43].

Polychlorinated biphenyls (PCBs)

The concentrations of PCB congeners 28, 52, 101, 138, 153 and 180 are given in Tables II and III. There was no significant difference between municipal and industrial sludges for any PCB congener. The values obtained in this study are lower than data published by Kampe *et al.* [27] and Witte *et al.* [28] (median values for the sequence of the above mentioned congeners = 22, 20, 40, 70, 70 and 43 µg/kg).

Drescher-Kaden *et al.* [39] mentioned a mean overall PCB concentration of 500 µg/kg dry matter in German sewage sludge, which is comparable to our results if it is taken into consideration that the six congeners measured correspond to about 20% of all PCB congeners found in sewage sludge [44].

In 1980, Burgermeister *et al.* [23] reported a median value of 1200 µg/kg dry matter as Aroclor in nine Swiss samples. Müller [19] found 2900 µg/kg “PCBs” as a median value for nine samples in 1982. Although it is difficult to compare these values, a decrease in PCB contamination can be discerned.

Germany introduced a limit value of 200 µg/kg dry matter for each of the PCB congeners 28, 52, 101, 138, 153 and 180 in an amendment of its ordinance for sewage sludge [17]. In this study no PCB congener exceeded a concentration of 200 µg/kg in any sample.

Kampe *et al.* [27] estimated that a maximum application rate of sewage sludge of 5 tons/hectare and within 3 years (with PCB concentrations markedly higher than measured in this study) will not raise the PCB concentration within 100 years in the treated soils. Losses were shown to be due to biodegradation and volatilization [45]. In another

study, decomposition of higher chlorinated PCB congeners could not be observed within the error of analysis (about 20%) in 1 year [22]. Therefore, no decomposition rate can be calculated from this study.

Polycyclic aromatic hydrocarbons (PAHs)

The concentration of the marker xenobiotic benzo[*a*]pyrene (BaP) and the summed concentrations (Σ 6PAH) of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, benzo[*a*]pyrene, fluoranthene and indeno[1,2,3-*cd*]pyrene are given in Tables II and III.

Benzo[*a*]pyrene was found in 15 of 27 sewage sludge samples, with similar concentrations in municipal and industrial sludge. The concentrations of benzo[*a*]pyrene found in our study are significantly (one order of magnitude) lower than the values published by Witte *et al.* [28]. Switzerland has no coal-fired electric plants, thermal energy production by burning coal or coke production, which may be one reason for the low concentrations of PAHs found in this study.

Degradation of PAHs has been demonstrated [46]. However, especially if concentrations are low, adaptation of microorganisms may not be possible. In one instance no measurable degradation at all was found [47].

CONCLUSIONS

The extraction procedures and the chromatographic methods used in this study proved to be suitable for monitoring organic micropollutants in industrial and municipal sewage sludges.

Except for AOX values there are no significant differences between industrial and municipal sludges. The elevated AOX values are an indicator of xenobiotic contamination and support the present ban on the use of industrial sludges in agriculture owing to high concentrations of heavy metals [48]. The AOX values do not correlate with any of the other measured micropollutants and therefore cannot be used to assess contamination by these compounds.

It is encouraging that the PCB and HCB levels have decreased in the last decade and that PAH concentrations are relatively low. However, further studies of organic micropollutants in selected sam-

ples of sewage sludge should be carried out in the near future; hazardous ecological effects cannot be fully excluded. Other groups of xenobiotics not analysed in this study may become relevant. A better knowledge of the concentrations of organic micropollutants in selected samples of sewage sludge is necessary in order to assess further the risk of xenobiotics in the environment.

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