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Determination of polychlorinated biphenyls in sewage sludges from Catalonia (N.E. Spain) by high-resolution gas chromatography with electron-capture detection[☆]

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Abstract

A study was carried out on the presence of polychlorinated biphenyls (PCBs) in sewage sludges from Catalonia (N.E. Spain) using high-resolution gas chromatography with electron-capture detection. Aroclor 1254 and 1260 were characterized. The concentrations were between 2310 and 69 $\mu\text{g}/\text{kg}$ (dry mass). High-resolution gas chromatography coupled with low-resolution mass spectrometry was used for screening the samples. No reports of the presence of PCBs in Spanish sewage sludges have been published previously. These analyses were performed in order to establish the availability of these sludges for disposal in agricultural soils.

1. Introduction

Polychlorinated biphenyls (PCBs) were once widely used as industrial chemicals, particularly as dielectric fluids in electrical transformers and capacitors, hydraulic fluids, lubricating and cutting oils, and as additives in sealants, plastics, paints, copying paper, adhesives and casting agents [1,2]. Their thermal stability and resistance to degradation contributed to their commercial usefulness, but also their long-term environmental effects. PCBs were extensively used commercially between the 1930s and 1970s, when their use was restricted because of their toxicity.

PCB residues have been detected in almost all compartments of the global ecosystem and the occurrence of these compounds in the environment has been extensively documented [3–9]. Over the years, PCBs have entered the environment following direct release from “open systems” and from industrial effluents, landfills, agricultural application of sewage sludges and the failure of electrical equipment. The PCBs enter the atmosphere by volatilization or in association with aerosols and can be transported over long distances before deposition on land or water surfaces. Consequently, PCBs and other organochlorine compounds (OCs) are now ubiquitous across the globe, even in remote polar regions. They come biomagnified through the food chain and may have adverse effects in aquatic and terrestrial organisms [10]. These often subtle ecotoxicological effects have sus-

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tained and stimulated research on the environmental importance of PCBs into 1990s.

Much attention has been drawn to the problem of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) and their environmental effects. More recently, however, research on other substances with similar toxic properties such as 2,3,7,8-TCDD (2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin) has increased [1]. Recent studies indicate that the levels of individual PCBs expressed as 2,3,7,8-TCDD toxic equivalents equals or precedes that of PCDDs and TCDDs [11,12].

Every year thousands of tons of sludge are produced in sewage treatment plants. Application to agricultural land, disposal in landfills and incineration are the most popular sludge disposal practices in Europe. Chemicals contained in the sludge have the potential to directly enter the biogeochemical cycle after application to land. This work was carried out in order to consider the presence and amount of PCBs in different samples of sludges from sewage treatment plants in Catalonia (N.E. Spain). The production of sludges in Catalonia is expected to be 0.25 million tons per year by the year 2000, and part of this can be used in amendment of agricultural soils. Sampling was performed in six different sewage treatment plants selected to give overall information about the quality of sludges.

Usually the analyses of these samples performed in Spain have given information about conventional agronomic parameters such as organic matter, nutrients, humic acids and other pollution parameters such as heavy metals, but very little information is known about specific organic contaminants. This paper reports a wide-ranging analysis of these selected pollutants, especially PCBs. Prior to analysis a procedure was established for the determination of PCBs in these particular samples.

2. Experimental

2.1. Chemicals

Aroclor 1242, 1248, 1254, 1260 and 1262 PCB standard mixtures and individual 28, 52, 101,

118, 138, 153 and 180 congener standards were purchased from Cromlab (Barcelona, Spain). The internal standard, 2,2',5-tribromobiphenyl, was purchased from Ultra Scientific (Hope, USA). Florisil for residue analysis (60–100 mesh, 0.15–0.25 mm) from Merck (Darmstadt, Germany) was used as a chromatographic adsorbent. It was activated at 500°C for 10 h and used immediately. Granular anhydrous sodium sulphate for residue analysis from Carlo Erba (Milan, Italy) was dried under the same conditions as Florisil. Copper for removal of sulphur was purchased from Merck. Glass-wool was cleaned by extraction in a Soxhlet apparatus with dichloromethane for 24 h.

The solvents, dichloromethane and acetone, were doubly distilled in glass to obtain residue analysis-grade materials. The purity of the solvents was tested by concentration of 100 ml to 100 μ l and injection of 1 μ l of the extract into a gas chromatographic–electron capture detector (HRGC–ECD) system. Isooctane and *n*-hexane were purchased from Merck. All glass materials were cleaned with Extran AP 13 alkaline soap (Merck) by sonification for 5 min and dried at 60°C overnight.

Standard solutions of PCB mixtures containing 1 ng/ μ l of individual Aroclors 1242, 1248, 1254, 1260 and 3.5 ng/ μ l of 1262 and 91 pg/ μ l of individual congeners 28, 52, 101, 118, 153, 138, 180 were prepared in isooctane for residue analysis (Merck).

2.2. Apparatus

Gas chromatography was carried out on a Model KNK-3000 gas chromatograph (Konik, Barcelona, Spain) equipped with a Tracor (Austin, TX, USA) electron-capture detector using nitrogen as make-up gas. A BP-5 (SGE, Ringwood, Australia) fused-silica capillary column (25 m \times 0.22 mm I.D.) with a 0.25- μ m film thickness was used with hydrogen as the carrier gas at a linear velocity of 35 cm/s. The temperature programme was from 70°C (held for 0.7 min) at 20°C/min to 125°C (held isothermally for 1 min) and then to 280°C (maintained for 10 min) at 4°C/min; the injector and detector temperatures were 250 and 310°C respectively. The

injection mode was splitless for 45 s. The chromatographic data were processed using a Merck–Hitachi Model D-2000 integrator.

For HRGC–low-resolution MS (HRGC–LRMS) a VG TS-250 mass spectrometer (VG Instruments, Manchester, UK) interfaced to a VG 11-250 data system with a KNK-3000 (Konik) was used. The column and conditions were the same as for HRGC–ECD.

2.3. Sampling and analysis

Six sewage plant sludges from Catalonia were selected to give overall information about the presence, type and levels of PCBs in this kind of setting. The samples were collected bimonthly for 1 year in each place. The analyses were carried out on a total of 29 samples. The towns selected were Sant Feliu de Guíxols, Vilafranca del Penedès, Cadaqués, Manresa, Girona and Reus (abbreviated to SF, VI, CA, MA, GI and RE in the tables and figures).

Samples were dried at 110°C for 18 h, ground

with a centrifuge mill and sieved to 750 µm. Two methods of extraction (sonification and Soxhlet) were compared. Soxhlet extraction was performed on 5 g of dried sludge in a solution of acetone–*n*-hexane (1:1) [13,14]. The sonification method, used extensively [15,16], was finally chosen because of the minimal amount of co-extracted impurities. It is less time consuming and good recoveries are obtained.

Five grams of homogenized dried sample were extracted with three 50-ml aliquots of dichloromethane–hexane (1:1) for 5 min. The organic extract was concentrated by rotary evaporation and solvent exchange with *n*-hexane (5 ml), then dried through anhydrous sodium sulphate. Subsequently, freshly activated copper was added to remove elemental sulphur (S₈) [17]. The sample clean-up was tested with different adsorbents, such as deactivated alumina and Florisil. Better results were obtained when 8 g of Florisil and 4 g of anhydrous sodium sulphate were used. A 5-ml volume of extract was cleaned up and eluted with 50 ml of *n*-hexane [18]. An internal stan-

Table 1
Congeners identified in samples (Ballschmiter and Zell's nomenclature [20])

No.	Structure	No.	Structure	No.	Structure	No.	Structure	No.	Structure
<i>DiCBs</i>									
5	2,3 ^a	49	2,2',4,5'	97	2,2',3',4,5'	156	2,3,3',4,4',5 ^a	190	2,3,3',4,4',5,6
7	2,4 ^a	51	2,2',4,6'	99	2,2',4,4',5'	158	2,3,3',4,4',6	191	2,3,3',4,4',5',6
15	4,4' ^b	52	2,2',5,5'	100	2,2',4,4',6	159	2,3,3',4,5,5' ^a	192	2,3,3',4,5,5',6
		53	2,2',5,6'	101	2,2',4,5,5'	163	2,3,3',4',5,6	193	2,3,3',4',5,5',6
<i>TriCBs</i>									
16	2,2',3	60	2,3,4,4' ^a	110	2,3,3',4',6	164	2,3,3',4',5',6	<i>OctaCBs</i>	
17	2,2',4	64	2,3,4',6	118	2,3',4,4',5 ^a	167	2,3',4,4',5,5' ^a	194	2,2',3,3',4,4',5,5'
18	2,2',5	66	2,3',4,4' ^a	<i>HexaCBs</i>		<i>HeptaCBs</i>		195	2,2',3,3',4,4',5,6
22	2,3,4' ^a	70	2,3',4',5 ^a	128	2,2',3,3',4,4'	170	2,2',3,3',4,4',5	196	2,2',3,3',4,4',5,6'
28	2,4,4' ^a	71	2,3',4',6	130	2,2',3,3',4,5'	171	2,2',3,3',4,4',6	197	2,2',3,3',4,4',6,6'
31	2,4',5 ^a	72	2,3',5,5' ^a	131	2,2',3,3',4,6	172	2,2',3,3',4,5,5'	198	2,2',3,3',4,5,5',6
32	2,4',6	74	2,4,4',5 ^a	132	2,2',3,3',4,6'	173	2,2',3,3',4,5,6	199	2,2',3,3',4,5,6,6'
33	2',3,4 ^a	76	2',3,4,5 ^a	134	2,2',3,3',5,6	174	2,2',3,3',4,5,6'	201	2,2',3,3',4,5,5',6
37	3,4,4' ^b	<i>PentaCBs</i>		135	2,2',3,3',5,6'	177	2,2',3,3',4',5,6	203	2,2',3,4,4',5,5',6
<i>TetraCBs</i>									
41	2,2',3,4	82	2,2',3,3',4	138	2,2',3,4,4',5'	178	2,2',3,3',5,5',6	205	2,2',3',4,4',5,5',6
42	2,2',3,4'	84	2,2',3,3',6	141	2,2',3,4,5,5'	179	2,2',3,3',5,6,6'	<i>NonaCBs</i>	
44	2,2',3,5'	87	2,2',3,4,5'	144	2,2',3,4,5,6	180	2,2',3,4,4',5,5'	206	2,2',3,3',4,4',5,5',6
45	2,2',3,6	89	2,2',3,4,6'	146	2,2',3,4',5,5'	182	2,2',3,4,4',5,6'	207	2,2',3,3',4,4',5,6,6'
47	2,2',4,4'	91	2,2',3,4',6	148	2,2',3,4',5,6'	183	2,2',3,4,4',5',6	208	2,2',3,3',4,5,5',6,6'
48	2,2',4,5	92	2,2',3,5,5'	149	2,2',3,4',5',6	185	2,2',3,4,5,5',6		
		94	2,2',3,5,6'	151	2,2',3,5,5',6	187	2,2',3,4',5,5',6		
		95	2,2',3,5',6	153	2,2',4,4',5,5'	189	2,3,3',4,4',5,5' ^a		

^a Mono-*ortho*-PCBs.

^b Non-*ortho*-PCBs.

dard, 2,2',5-tribromobiphenyl, was added and the final volume of extract was adjusted to 0.5 ml under a gentle flow of nitrogen. Samples were then analysed by HRGC–ECD.

In order to validate the method used, the recoveries of seven individual congeners added to a simple sewage sludge, PCB free, were determined; this sample was extracted in a Soxhlet apparatus with three aliquots of acetone–*n*-hexane (1:1) until PCBs were totally removed. In all instances the recoveries were >95%. The feasibility of the method was also tested in two intercalibration exercises with the BCR (Bureau Communautaire de Référence) [19].

2.4. Chromatographic analysis

Qualitative determination

Purified PCB extracts were analysed by HRGC–ECD. Compounds were assigned by their GC retention times compared with standard Aroclor mixtures and individual selected congeners. The determination of specific congeners was carried out using Aroclor 1242, 1248, 1254, 1260 and 1262. Identification of congeners was done following Ballschmiter and Zell's nomenclature [20] (see Table 1).

Quantitative determination

Quantification was done by comparing Aroclor standards and individual congeners. The results were compared using different methods. The detection level was 1–5 pg injected. The sensitivity of method was 10–50 pg/g. One system of quantitative analyses involved the congener-specific methodology using the Aroclor 1260. Sample chromatographic peaks were determined using an internal standard, 2,2',5-tribromobiphenyl. Seven recommended BCR congeners were analysed to obtain calibration graphs and response factors. The feasibility of this method was checked in a BCR intercalibration exercise.

3. Results

Aroclor 1260 was clearly identified in all samples, as a main constituent (Fig. 1 shows a sample containing Aroclor 1260 without other

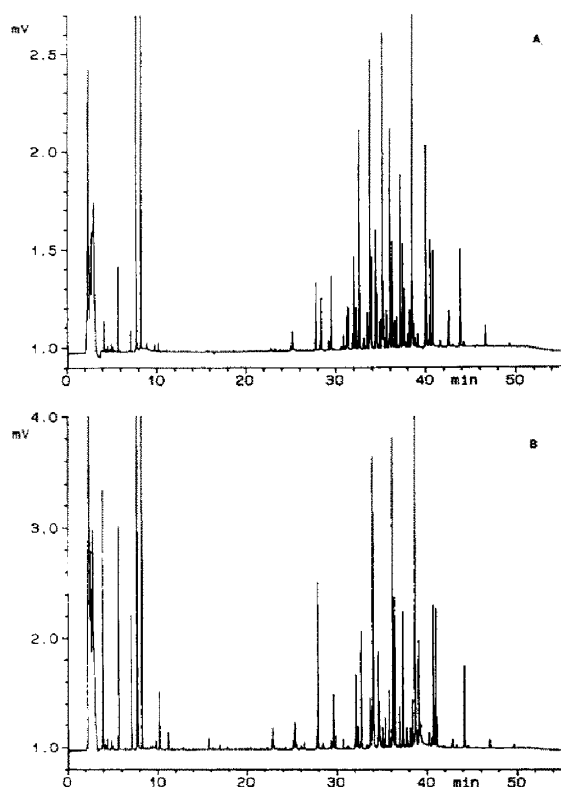


Fig. 1. HRGC–ECD (25-m BP-5 column) of (A) Aroclor 1260 and (B) sample VI (Vilafranca del Penedès).

Aroclor interferences). Other samples, however, showed complex mixtures with smaller retention times corresponding to Aroclors having a lower degree of chlorination (Fig. 2). Construction of a bar diagram (percentage of individual congener from total PCBs) proved the presence of Aroclor

Table 2

Results ($\mu\text{g}/\text{kg}$) obtained by BCR recommended method (seven individual congeners)

Congener	Sample					
	SF	VI	RE	CA	MA	GI
28	14	4	21	11	12	9
52	92	4	28	22	109	10
101	22	6	29	12	18	11
118	76	9	50	16	41	13
153	167	17	218	39	109	20
138	119	4	147	24	79	17
180	88	23	161	21	80	19
Total	578	69	653	143	447	100

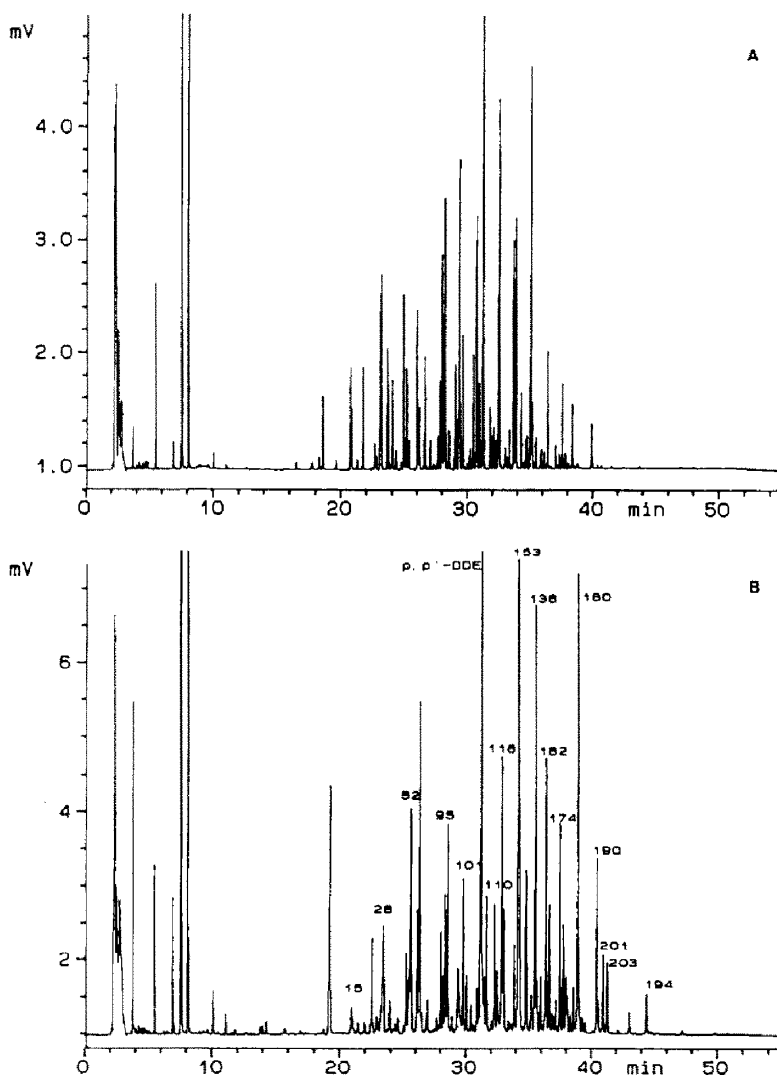


Fig. 2. HRGC-ECD (25-m BP-5 column) of (A) Aroclor 1254 and (B) sample SF (Sant Feliu de Guíxols). PCB congener numbers and *p,p'*-DDE are indicated.

1254 (Fig. 3). Fig. 4 shows the overall trends of the samples.

Aroclor 1260 is the most frequently identified compound because of its extensive commercial use and high degree of chlorination. As described [21–23], the degradation most frequently occurs in less chlorinated congeners (1–3 chlorine atoms) by photodegradation, microbiological action and volatilization. The degree of chlorination of the identified congeners was 4–8.

Other compounds identified were 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene and 1,3,5-

trichlorobenzene. These pollutants are ubiquitous and are also associated with PCBs because they are used commercially together in Askarel mixtures which are used as electrical insulating media in transformers and electric capacitors. The most common transformer Askarels showed 30% of trichlorobenzene–70% of Aroclor 1254 and 40% of trichlorobenzene–60% of Aroclor 1260 [1,2].

The results obtained with both methods are given in Tables 2 and 3. The application of the method to the seven BCR individual congeners

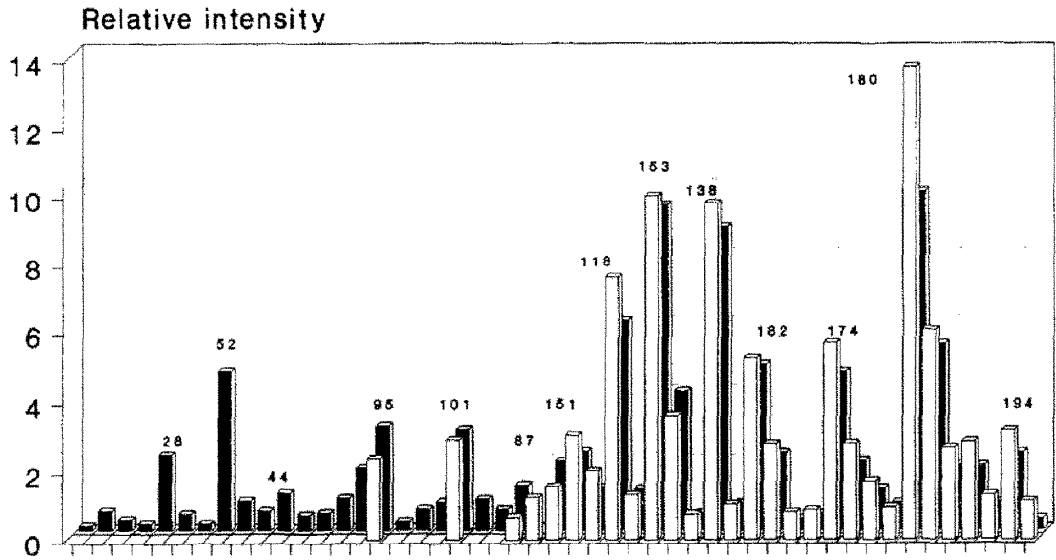


Fig. 3. Bar diagram showing relative intensities in percentages of SF sample (■; Sant Feliu de Guíxols) compared with an Aroclor 1260 standard mixture (□).

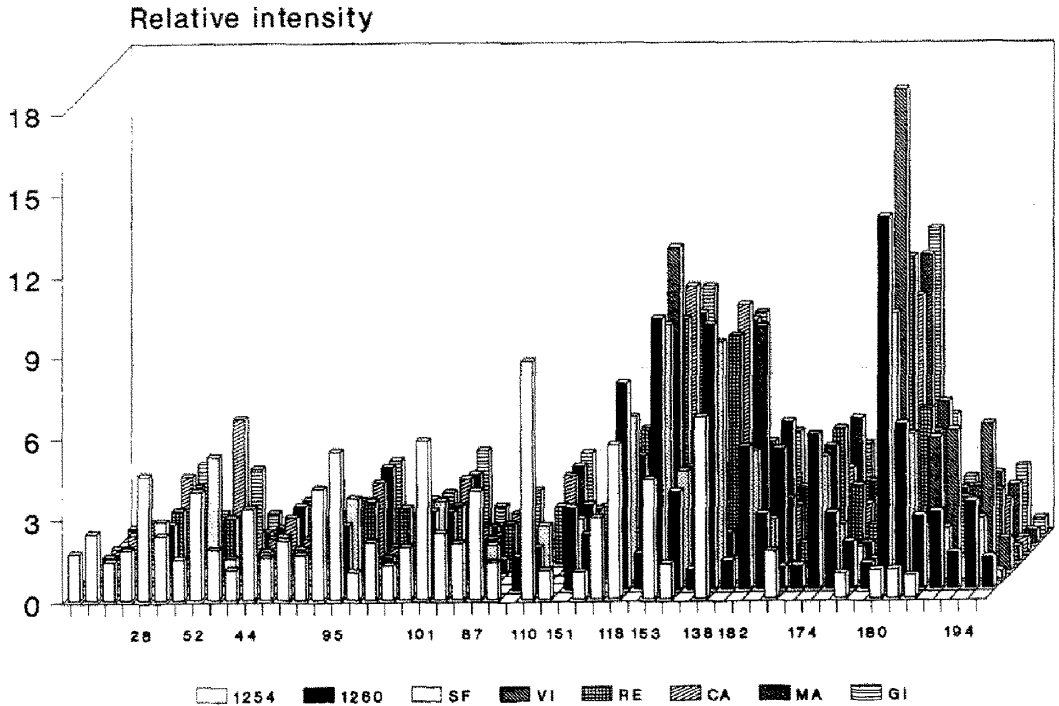


Fig. 4. Bar diagram showing relative intensities in percentages of all samples compared with the Aroclor 1254 and 1260 standard mixtures.

Table 3
Comparison of results obtained by two different methods

Sample	PCB level ($\mu\text{g}/\text{kg}$)	
	BCR congeners ^a	Aroclor 1260 ^b
SF	578	1421
VI	69	382
RE	653	2310
CA	143	623
MA	447	1239
GI	100	501

^a Quantification based on seven individual congeners recommended by BCR.

^b Quantification based on Aroclor 1260 mixture.

is presented in Table 2. Table 3 gives the quantitative results using Aroclor 1260, and a comparison with those obtained by the BCR method. The levels found are similar to published data [24–26].

The peak eluting between the 110 and 87 PCB congeners was identified as *p,p'*-DDE [1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene] by HRGC–LRMS; this compound was only found in some of the samples analysed. *p,p'*-DDE is one of the major metabolites of DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane]. In the environment, DDT is metabolized to DDD [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane] and DDE. In some samples DDD is the major metabolite whereas in others DDE predominates. Aliphatic hydrocarbons were detected together with PCBs in the same fraction. A background of aliphatic hydrocarbons, typically due to an unresolved complex mixture, did not allow the determination of PCBs using LRMS with selected ion monitoring. Other compounds identified in the screening, prior to the special clean-up for PCBs, were polycyclic aromatic hydrocarbons (PAHs), fatty acids and sterols.

4. Conclusions

PCBs from several municipal sewage sludge treatment plant were characterized and quantified. The analysis revealed PCBs in all these samples. Prior to analysis a procedure was estab-

lished for the determination of PCBs in these particular samples. The recovery of the extraction procedure was >95% and the feasibility of this method was tested in a BCR intercalibration programme.

The PCBs levels found were similar to those already published. Aroclor 1260 was detected most frequently in the commercial mixture. The specific sources of these pollutants in the samples analysed are still unknown, but extensive commercial use of these compounds, their ubiquitous presence, high resistance to degradation, sediment uplift and suspended particulate permitted detection.

The PCB content of municipal sewage sludges is a critical point concerning their treatment, management and agricultural use. Further developments in the analysis of these compounds and a quantitative normalization procedure in sludges are necessary to allow an integrated assessment of the behaviour and impact of these contaminants according to the type of processing techniques and use of the sludges.

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References

- [1] R.D. Kimbrough and A.A. Jensen (Editors), *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products*, Elsevier, Amsterdam, 1989.
- [2] D. Erickson, *Analytical Chemistry of PCBs*, Butterworth, Guildford, 1986.
- [3] S. Jensen, A.G. Johnels, M. Olsson and G. Olterlind, *Nature*, 224 (1969) 247.
- [4] M. El-Dib, *Bull. Environ. Contam. Toxicol.*, 34 (1985) 216.
- [5] S. Georgii, G. Bachour, K. Failing, U. Eskens, I. Elmadfa and H. Brunn, *Arch. Environ. Contam. Toxicol.*, 26 (1994) 1.

- [6] M.C. Kennicutt, T.L. Wade, B.J. Presley, A.G. Raquejo, J.M. Brooks and G.J. Denoux, *Environ. Sci. Technol.*, 28 (1994) 1.
- [7] J.R. Kucklick, T.F. Bidleman, L.L. McConnell, M.D. Walla and G.P. Ivanov, *Environ. Sci. Technol.*, 28 (1994) 31.
- [8] Y. Ohsaki and T. Matsueda, *Chemosphere*, 28 (1994) 47.
- [9] F.F. Daelemans, F. Mehlum and J.C. Schepens, *Bull. Environ. Contam. Toxicol.*, 48 (1992) 828.
- [10] G. Sanders, K.C. Jones, J. Hamilton and H. Dörr, *Environ. Sci. Technol.*, 26 (1992) 1815.
- [11] J. Tarhanen, J. Koistinen, J. Paasivirta, P.J. Vuorinen, J. Koivusaari, I. Nuuja, N. Kannan and R. Tatsukawa, *Chemosphere*, 18 (1989) 1067.
- [12] U. Järnberg, L. Asplund, C. de Wit, A.K. Grafström, P. Haglund, B. Jansson, K. Lexén, M. Strandell, M. Olsson and B. Jonsson, *Environ. Sci. Technol.*, 27 (1993) 1364.
- [13] J. Japenga, W. Wagensar, F. Smedes and W. Salomons, *Environ. Technol. Lett.*, 8 (1987) 9.
- [14] B.G. Oliver and A.J. Niimi, *Environ. Sci. Technol.* 22 (1988) 388.
- [15] A.L. Alford-Stevens, W.L. Buddle and T.A. Bellar, *Anal. Chem.*, 57 (1985) 2452.
- [16] V. López-Ávila, J. Benedicto, E. Baldin and W.F. Beckert, *J. High Resolut. Chromatogr.*, 15 (1992) 319.
- [17] N.I. Rubinstein, R.J. Pruell, B.K. Taplin, J.A. Livolsi and C.B. Norwood, *Chemosphere*, 20 (1990) 1097.
- [18] A.C. Alder, M.M. Häggblom, S.R. Oppenheimer and L.Y. Young, *Environ. Sci. Technol.*, 27 (1993) 530.
- [19] X. Santos and M. Galceran, *Certification of Chlorobiphenyls in Waste Fuel Oil, Intercalibration Exercise*, BCR, Brussels, 1990.
- [20] K. Ballschmiter and M. Zell, *Fresenius' Z. Anal. Chem.*, 302 (1980) 20.
- [21] K. Furukawa and F.J. Matsumara, *Agric. Chem.*, 24 (1976) 251.
- [22] R. Moolenaar, in R. Davenport and B. Bernard (Editors), *Advances in Exposure, Health and Environmental Effects Studies of PCBs, Symposium Proceedings*, US Environmental Protection Agency, Washington, DC, 1983, pp. 67–96.
- [23] P. Moza, J. Scheunert, W. Klein and F.J. Korte, *Agric. Food. Chem.*, 27 (1979) 1120.
- [24] P. Brunner, U. Weberrub and H. Hagemayer, presented at the *18th International Symposium on Environmental Analytical Chemistry, 4th International Congress on Analytical Techniques in Environmental Chemistry, Barcelona, 1988*.
- [25] S. Wild and K. Jones, *Chemosphere*, 19 (1989) 1765.
- [26] R.E. Alcock and K.C. Jones, *Chemosphere*, 26 (1993) 2199.