Polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in sediment cores from the Western Scheldt river (Belgium): analytical aspects and depth profiles

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Abstract

A rapid and simple analytical method for the determination of organochlorines, such as polychlorinated biphenyls (PCBs) and selected organochlorinated pesticides (OCPs) and organobromines, such as polybrominated diphenyl ethers (PBDEs), in sediment samples was optimised using CRM 536 (PCBs in freshwater sediment). The method involved a hot Soxhlet extraction that reduced the extraction time to 2 h. Elemental sulphur, which is present in sediments and may interfere during the analysis, was removed by means of copper powder added to the sediment during extraction and into the clean-up cartridge. The analysis of PCBs and OCPs was accomplished by gas chromatography with electron capture or mass spectrometric detection. Similar quantitative results for PCB congeners in CRM 536 were obtained using a 50-m capillary column and a 10-m narrow bore column suited for fast analysis. The analysis of PBDEs was done by mass spectrometry in negative chemical ionisation mode.

Concentrations of organic pollutants in two sediment cores (approximately 50 cm depth) from the Scheldt river (south of Antwerp, Belgium) showed a relative steady state for PCBs and DDTs, with a slight decrease in the top layers, suggesting a slight decline in their concentrations due to restrictions in their usage. On the contrary, PBDEs were showing an increase in their concentrations in the top layers (up to 270 and 8400 ng/g dry weight for sum of tri- to hexa-BDE congeners and for BDE 209, respectively). This suggests an increasing trend in the concentrations of PBDEs in the Belgian environment.
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1. Introduction

Despite their ban or restricted use (UNEP, 2003), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are among the most prevalent environmental pollutants and can be found in various environmental compartments, as well abiotic (air, water, sediments, soil) (de Boer et al., 2001) as biotic (from plankton to humans) (de Boer et al., 2000; de Voogt et al., 1990; Jones and de Voogt, 1999).

In contrast to PCBs, the use and production of polybrominated diphenyl ethers (PBDEs) is still being continued, although recently some restrictions have been issued following risk assessment reports (EU, 2003). PBDEs are used as flame retardants to improve fire safety in both commercial and domestic applications, where they are sometimes added in concentrations up to 30% by weight (WHO, 1994). These chemicals have shown a rise in production since they were first introduced in the 1960s, with a substantial increase since the end of the 1970s due to

the growing popularity of personal computers and other electronic equipment (de Boer et al., 2000). Unfortunately, this has lead to their widespread presence in various environmental compartments (de Boer et al., 2001; de Wit, 2002; Ikonomou et al., 2002; Law et al., 2003).

Sediments, particularly estuarine sediments, are one of the major sinks for these contaminants in the aquatic environment (Allchin et al., 1999; de Boer et al., 2001; Voorspoels et al., 2004). The study of sediments is an important step in mapping possible exposure pathways to various aquatic organisms, since contaminants in the sediments may be bioavailable to sediment dwelling organisms (Pruell et al., 1993). Furthermore, dated sediment profiles have been used to estimate the historical deposition of PCBs and other organic pollutants in the river bed impacted by local and regional sources (Fox et al., 2001).

The drainage basin of the Scheldt river covers a very densely populated and highly industrialised area of northern France, western Belgium and the southwestern Netherlands (Baeyens et al., 1998), resulting in a high pollution level with POPs (Voorspoels et al., 2003, 2004), as well as heavy metals (Coteur et al., 2003). High concentrations of PBDEs (up to 500 ng/g dw for BDE 209) were already measured in sediment samples from the Scheldt river (de Wit, 2002), while de Boer et al. (2003) have reported high levels of BDE 209 (up to 4600 ng/g dry weight) in suspended particulate matter (SPM) from the Western Scheldt and attribute this to spillage during use further upstream.

The scope of this work was (1) to optimise a rapid and simple analytical method for the determination of organochlorinated and organobrominated pollutants in sediments and (2) to measure the concentrations of organic pollutants in two sediment cores (~50 cm) from the Scheldt river, near Antwerp, Belgium and to evaluate temporal trends in pollution of PCBs, OCPs and PBDEs.

2. Materials and methods

2.1. Samples

Sediment cores (~50 cm) were taken in March 2000 with a 2-cm-diameter gravity corer from two locations situated in the Scheldt river (near Kruibeke, south of Antwerp, Belgium) from zones with different flow characteristics. The two locations (A and B) were located within 100 m from each other. Subsamples were obtained by slicing the core in 1–5 cm intervals. Wet sediments were kept at +4 °C until further treatment. Prior to analysis, sediments were dried at room temperature for 48 h.

2.2. Reagents and standards

The following compounds were included: hexachlorobenzene (HCB), α-, β- and γ-hexachlorocyclohexane

(HCH) isomers (the sum expressed as HCHs), p,p'-DDE, p,p'-DDD, and p,p'-DDT (the sum expressed as DDTs) and 27 PCB congeners (IUPAC nos.: 18, 28, 31, 44, 52, 74, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 153, 156, 163, 170, 177, 180, 183, 187, 194, 196 and 199). PCBs 46 and 143 were used as internal standard (IS) for PCBs and pesticides. Additionally, 10 PBDE congeners were also measured and polybrominated biphenyl (PBB) 103 was used as IS for BDE 28, 47, 66, 85, 99 and 100, BB 155 was used as IS for BDE 138, 153 and 154, while ^{13}C-labeled BDE 209 was used as IS for BDE 209.

All solvents used for the analyses (n-hexane, acetone, dichloromethane and iso-octane) were of SupraSolv grade (Merck, Darmstadt, Germany). Individual analytical standards (CIL, Andover, MA, USA; Dr. Ehrenstorfer Laboratories, Augsburg, Germany) were used for identification and quantification. A certified material (CRM 536—PCBs in freshwater sediment—IRMM, Geel, Belgium) was used for the method optimisation.

2.3. Extraction and clean-up

The sediment sample (around 1 g) was placed into a hexane pre-washed extraction thimble. A triple amount of copper powder (<63 μm, Merck) was added and mixed with the sediment, followed by the addition of internal standards. Samples were extracted using a Soxhlet extractor B-811 (Büchi, Switzerland) operated in hot extraction mode. Several solvent mixtures (75 ml), such as hexane/acetone (3:1, v/v), hexane/acetone (1:1, v/v) and hexane/dichloromethane (3:1, v/v) were tested for different extraction times (2, 3 and 4 h). In each case, the extract was concentrated and transferred onto a solid-phase extraction (SPE) cartridge filled (from the bottom) with 8 g acidified silica (40% concentrated sulphuric acid, w/w), 0.5 g anhydrous sodium sulphate and 1 g copper powder. The elution of PCBs, OCPs and PBDEs was done with 15 ml hexane and 10 ml DCM. The eluate was concentrated to near dryness by a rotary evaporator and further by a gentle nitrogen stream. The final extract was re-solubilized in 80 μl iso-octane.

2.4. Instrumental analysis

The determination of PCBs and OCPs was performed by gas chromatography with electron capture detection (GC-ECD). An Agilent (Palo Alto, CA, USA) 6890 GC-μECD was equipped with a 50 m×0.22 mm×0.25 μm HT-8 capillary column (SGE, Zulte, Belgium). Helium was used as carrier gas at a constant flow of 1.0 ml/min and Ar/CH$_4$ (95:5) was used as make-up gas (40 ml/min). One microliter was injected in the pulsed splitless mode (pulse pressure=40 psi, pulse time=1.2 min) with the split outlet opened after 1.2 min. Injector and detector temperatures were set at 290 and 320 °C, respectively. The temperature program of the HT-8 column was set to 90 °C

for 1.2 min, then increased with 20 °C/min to 180 °C, kept for 1 min, then increased with 3 °C/min to 275 °C, kept 0.5 min and further ramped by 5 °C/min to 290 °C and kept for 18 min.

Additionally, an Agilent 6890GC-5793 quadrupole mass spectrometer (MS) equipped with a 10 m×0.10 mm×0.10 μm HT-8 narrow bore capillary column was tested for its ability of performing fast analysis of PCBs. The oven program started from 90 °C, for 1 min, then increased with 50 °C/min to 200 °C, kept for 0.5 min, then increased with 25 °C/min to 250 °C, kept for 0.2 min and finally ramped by 75 °C/min to 300 °C and kept 5 min. Total analysis time was 11 min. Helium was used as carrier gas at 0.4 ml/min. The MS was operated at 70 eV in electron impact ionisation (EI) mode with ion source, quadrupole and transfer line temperatures of 230, 150 and 300 °C, respectively. Dwell times were set to 10 ms and two ions from the molecular ion cluster of each PCB homologue group (M^+ and $[M+2]^+$) were monitored. The relative retention times to the nearest internal standard and ratios between the monitored ions were used as identification criteria. A deviation of ion ratios of less than ±20% from the theoretical value was considered acceptable for identification.

The determination of PBDEs was performed with an Agilent 6890GC-5973MS equipped with a 25 m×0.22 mm×0.25 μm HT-8 capillary column and operated in electron capture negative ionisation (ECNI) mode. The ion source, quadrupole and interface temperatures were 250, 150 and 300 °C, respectively. Helium was used as carrier gas at constant flow (1.0 ml/min) with an initial pressure of 14.40 psi and with methane as moderating gas. The MS was operated in the selected ion monitoring (SIM) mode and the electron multiplier voltage was set at 2100 V. One microliter of the extract was injected in solvent vent mode (injector temperature at 90 °C, kept for 0.05 min, then increased with 700 °C/min to 280 °C, vent time 0.03 min, vent flow 100 ml/min). The splitless time was 1.50 min. The temperature of the HT-8 column was programmed from 90 °C, kept for 1.5 min, then increased with 30 °C/min to 180 °C, kept for 0.5 min, then increased with 5 °C/min to 270 °C, kept for 0.5 min and finally ramped with 25 °C/min to 290 °C and kept for 15 min. Dwell times were set to 25 ms. Ions *m/z* 79 and 81 were monitored for the entire run.

The analysis of BDE 209 was performed on a 12 m×0.18 mm×0.10 μm AT-5 capillary column (Alltech, Lokeren, Belgium). Helium was used as carrier gas at an initial flow rate of 1.0 ml/min (kept for 5 min) and then raised to 1.5 ml/min at 20 ml/min[2]. The oven temperature program started from 90 °C, kept for 1.35 min, and then increased with 25 °C/min to 290 °C, kept for 8 min. Methane was used as moderating gas and the ion source, quadrupole, and interface temperatures were 250, 150 and 300 °C, respectively. Dwell time was set to 50 ms. The ECNI-MS was operated in SIM mode at the *m/z* 484.7, 486.7 and 494.7, 496.7 for BDE 209 and ^{13}C-BDE 209, respectively.

2.5. Quality control

Quality for PCB and OCP analyses was assured through the analysis of procedural blanks, blind duplicate samples and certified material (CRM 536—PCBs in freshwater sediment). The obtained values for PCB congeners in CRM 536 were all within 10% of the certified values.

For PBDEs, an in-house reference material (a sediment sample used for the BROC interlaboratory feasibility study—BROC, 2003) was used for method validation. The concentrations of individual PBDE congeners did not differ with more than 15% from the mean values obtained in the BROC study (BROC, 2003). Recoveries of individual PBDE congeners, including BDE 209, obtained during BROC spiking experiments (BROC, 2003) are between 82% and 93% with a standard deviation less than 16%.

The limit of quantification (LOQ) for PCBs, OCPs and PBDEs was based on GC/ECD and GC/MS performance and on laboratory background levels, which were determined by analysing procedural blanks. Procedural blank levels were consistent (RSD<30%) and therefore the median blank value was used for subtraction. LOQs were established at three times the standard deviation of the procedural blank level, resulting in a certainty of more than 95% for results given for the samples. LOQs for PCBs and OCPs ranged between 0.1 and 0.4 ng/g when 1 g of sediment was analysed. Recoveries of internal standards were between 86% and 92% (RSD<9%). LOQs for tri- to hexa-PBDEs ranged between 0.05 and 0.1 ng/g dw, while for BDE 209 LOQ was 0.2 ng/g dw.

Additionally, the Toxicological Centre (University of Antwerp-UA, Belgium) has participated to several interlaboratory studies for PCBs, OCPs and PBDEs organised through the Quasimeme office. Sediment samples analysed for PCBs and OCPs (Table 1) and PBDEs (Table 2) showed good agreement between values obtained by UA and mean values of participating laboratories.

Table 1

Concentrations (ng/g dw) of PCBs and OCPs in two sediment samples (68MS and 69MS) used in the QUASIMEME 2002 interlaboratory test (UA—results of Toxicological Center, University of Antwerp versus mean of participating laboratories)

	68MS		69MS	
	UA	mean	UA	mean
PCB 28	0.20	0.21	1.30	0.90
PCB 101	0.50	0.56	1.10	1.37
PCB 105	0.18	0.17	0.53	0.44
PCB 118	0.48	0.43	1.30	1.36
PCB 138	1.15	1.23	2.65	2.71
PCB 153	1.28	1.21	2.98	2.71
PCB 180	0.87	0.72	1.59	1.59
p,p′-DDE	0.78	0.65	0.66	0.59
p,p′-DDT	0.37	0.30	0.76	0.41
HCB	0.17	0.11	1.36	0.94

Table 2
Concentrations (ng/g dw) of PBDEs in three sediment samples (1MS, 3MS and BROC) used in the QUASIMEME 2002 and 2003 interlaboratory tests (UA—results of Toxicological Center, University of Antwerp versus the mean of participating laboratories)

	1MS		3MS		BROC	
	UA	Mean	UA	Mean	UA	Mean
BDE 28	0.43	0.54	0.13	0.13	0.75	0.626
BDE 47	9.64	8.93	0.93	0.96	10.20	10.14
BDE 99	12.71	13.18	0.98	1.05	12.29	14.20
BDE 100	3.00	2.65	0.11	0.12	2.90	3.04
BDE 153	2.31	1.80	0.23	0.21	1.85	1.93
BDE 154	1.89	1.64	0.11	0.11	1.59	1.71
BDE 183	1.01	0.32	0.18	0.14	0.75	0.45
BDE 209	920	863	47.0	45.2	1234	1163

2.6. Statistical analysis

Statistical analysis was performed with SPSS 12.0 statistical software (Chicago, IL, US). The influence of extraction time and solvent mixtures on the recovery of PCBs from CRM 536 was analysed with univariate analysis of variance (ANOVA) using general linear model and Scheffe test for post hoc comparison. Values were considered significantly different when $p < 0.05$.

Principal components analysis (PCA) was performed with Statistical software Minitab Version 14.10 (Minitab Quality Plaza, 1829 Pine Hall Road, State College, PA 16801-3008, USA) using the correlation matrix. Results have been graphically displayed as score plot and loading plot.

3. Results and discussion

3.1. Method optimisation

The method described in the present paper was adapted from a previously described method for the extraction of organohalogenated pollutants from soils (Covaci et al., 2002).

For method optimisation, a certified material CRM 536 (PCBs in freshwater harbour sediment) was used and concentrations obtained during different method setups were compared with the certified values. For extraction, an automated Soxhlet was used in hot extraction mode, where the sample is permanently in contact with hot, but non-boiling solvent. No significant differences were observed between the PCB concentrations obtained from the certified material CRM 536 for different extraction times (2, 3 and 4 h, respectively), allowing thus a dramatic reduction in the extraction time compared with the 8–16 h usually needed for classical Soxhlet extraction (Smedes and de Boer, 1997).

Several solvent mixtures were tested for the extraction efficiency and it has been found that the mixtures hexane/acetone (3:1, v/v) and hexane/acetone (1:1, v/v) gave similar recoveries for the certified PCBs, while the use of a mixture hexane/dichloromethane (3:1, v/v) resulted in significantly lower values (Fig. 1). In order to increase the extraction efficiency, it is necessary to use a more polar solvent, such as acetone, which can penetrate the more polar core of sediment particles. A similar observation has already been reported for soil (Covaci et al., 2002). The hexane/acetone (3:1, v/v) mixture was preferred because the lower percentage of acetone in the extraction mixture results in a final raw extract free of acetone, which is necessary for clean-up on acidified silica.

The sulphur originates under anaerobic conditions from microbial sulphate reduction (via sulphide) and the degradation of organic sulphur compounds (Riis and Babel, 1999). Smedes and de Boer (1997) have shown that the presence of elemental sulphur in the finale extract prior to GC analysis may have a bad effect on the performance of the ECD detector and on the correct peak assignment. For sulphur elimination, copper powder was added in the extraction thimble and on the top of the acidified silica gel cartridge, thus eliminating a tendentious additional step in the clean-up procedure. The sulphur removal by means of Cu was very efficient for all analysed samples and the
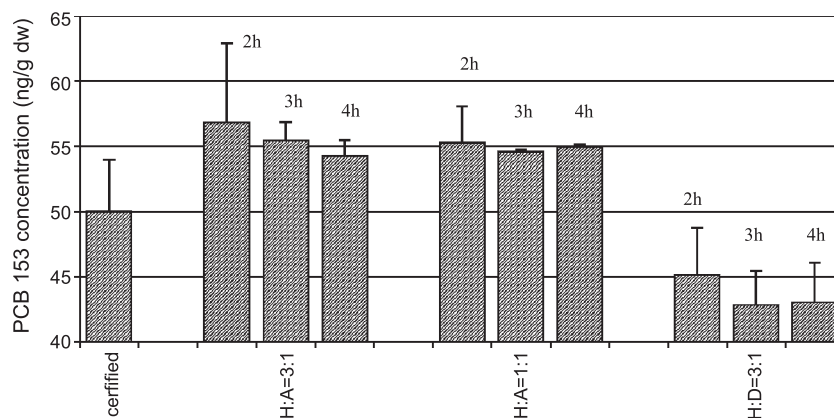

Fig. 1. Influence of extraction time and composition of extraction solvent mixture on the recovery of PCB 153 from CRM 536 (H—hexane, A—acetone, D—dichloromethane). Error bars represent $1.96\times$ standard error.

Table 3
Recoveries of certified PCB congeners from CRM 536

	Certified values (S.D.)	Recovered values (S.D.)	%
PCB 28	44 (5)	48 (3)	110
PCB 52	38 (4)	41 (2)	109
PCB 101	44 (4)	48 (0)	110
PCB 105	3.5 (0.6)	3.8 (0.4)	110
PCB 118	28 (3)	27 (1)	96
PCB 128	5.4 (1.2)	4.6 (0.5)	86
PCB 138	27 (4)	33 (2)	122
PCB 149	49 (4)	52 (2)	118
PCB 153	50 (4)	57 (4)	114
PCB 156	3.0 (0.4)	3.6 (0.2)	120
PCB 163	17 (3)	18 (3)	105
PCB 170	13 (1)	13 (1)	96
PCB 180	22 (2)	22 (1)	101

reduction of elemental sulphur (which may be up to 7–10 mg/g sediment) was done to a level at which it did not interfere with the GC analysis. Riis and Babel (1999) have already demonstrated that Cu powder reacts with elemental sulphur if the contact time is more than 30 min. Furthermore, the use of Cu powder results in a higher reaction surface than in case of Cu granules or Cu wire. They have also shown that the commercially available Cu powder (<63 mesh, Merck) can be used directly, without any additional pretreatment. Furthermore, no adsorption of organohalogenated pollutants has been observed on the Cu powder during the present work, in accordance with observations by Riis and Babel (1999).

The use of acidified silica for clean-up resulted in cleaner extracts than silica or Florisil, but some OCPs, such as dieldrin, heptachlor and heptachlorepoxide, are completely destroyed by the acidic treatment. The use of basic silica (33% KOH, w/w) in combination with acid silica might improve the extract cleanliness, but this should be applied when only PCBs and PBDEs are the target analytes. Several other OCPs, such as HCHs and DDTs, are labile in basic conditions.

Due to some co-elutions on the HT-8 column when ECD was used (such as PCB 110/o,p'-DDD, PCB 132/p,p'-DDD, PCB 128/PCB 174, PCB 156/PCB 172), the use of a confirmatory analysis by GC/MS was mandatory. It was previously shown (Covaci and Schepens, 2001) that narrow bore capillary columns could be successfully used in the determination of PCBs by GC/MS. Therefore, a narrow bore column with a similar stationary phase as the one used in the GC/ECD was used on GC/MS. Results for the certified material CRM 536 obtained on both columns agreed satisfactory (difference less than 10%) for PCBs which did not present co-elutions on ECD (such as PCB 118, 153, 180). Moreover, these concentrations (Table 3) were in agreement with the certified values (>90% for most congeners).

3.2. Presence of organic pollutants in sediments from the Scheldt river

3.2.1. Levels of pollutants

OCP levels were low, with HCHs being below LOQ, HCB values between 0.5 and 1.3 ng/g dw and with DDTs between 6.6 and 44.4 ng/g dw. p,p'-DDE (41%) and p,p'-DDD (41%) were the principal contributors to the sum DDTs (Table 4) in all samples, except for A2, where p,p'-DDT was the principal component (37%).

The PCB concentrations in the upper layers of the two sediment cores are similar to levels (up to 200 ng/g dw) obtained in 1987–1988 from Western Scheldt estuary (Van Zoest and Van Eck, 1993), showing that the PCB pollution

Table 4
Concentrations (ng/g dry weight) of organochlorinated and organobrominated pollutants in sediment cores from two locations (A and B) from the Scheldt river

|	Depth (cm)	PCB 153	Sum PCBs	Tri- to hexa-BDEs	BDE 209	HCB	p,p'-DDE	p,p'-DDD	p,p'-DDT	Sum DDTs	Sum HCHs
A1	0–1	23.5	183	85.1	2842	0.7	4.4	4.4	3.0	11.8	<0.3
A2	2–3	32.3	238	179	7412	1.2	6.7	6.5	7.9	21.0	<0.3
A3	4–5	22.0	167	29.7	NA	1.1	5.4	4.9	1.9	12.2	<0.3
A4	6–7	28.2	201	3.7	1736	1.1	5.5	5.7	3.1	14.3	<0.3
A5	8–9	14.8	105	2.2	653	0.3	3.2	3.2	0.2	6.6	<0.3
A6	10–15	24.3	201	4.8	401	1.2	5.1	5.7	2.4	13.3	<0.3
A7	20–25	28.9	235	32.2	1370	0.8	6.8	8.0	2.8	17.6	<0.3
A8	35–40	46.4	400	11.8	1165	1.1	11.4	10.9	5.2	27.6	<0.3
A9	45–50	23.6	192	1.4	332	0.4	5.2	4.9	2.6	12.7	<0.3
A10	55–58	38.1	310	2.9	913	1.0	10.0	8.4	5.0	23.4	<0.3
B1	0–1	27.9	232	272	8413	0.8	6.6	7.0	2.8	16.4	<0.3
B2	2–3	30.6	232	180	5580	1.3	5.9	5.8	3.1	14.9	<0.3
B3	4–5	25.8	206	171	NA	1.0	6.6	6.4	2.1	15.1	<0.3
B4	6–7	21.2	173	47.5	NA	0.6	4.9	5.9	1.5	12.4	<0.3
B5	10–15	23.4	198	4.3	469	0.7	5.1	6.6	1.8	13.4	<0.3
B6	20–25	19.0	151	2.0	315	0.5	3.8	4.9	0.8	9.4	<0.3
B7	35–40	36.6	311	1.4	515	0.8	8.1	4.1	3.3	15.6	<0.3
B8	45–50	26.5	242	2.5	668	0.7	7.2	7.4	2.3	16.9	<0.3

NA—not available due to insufficient sample.
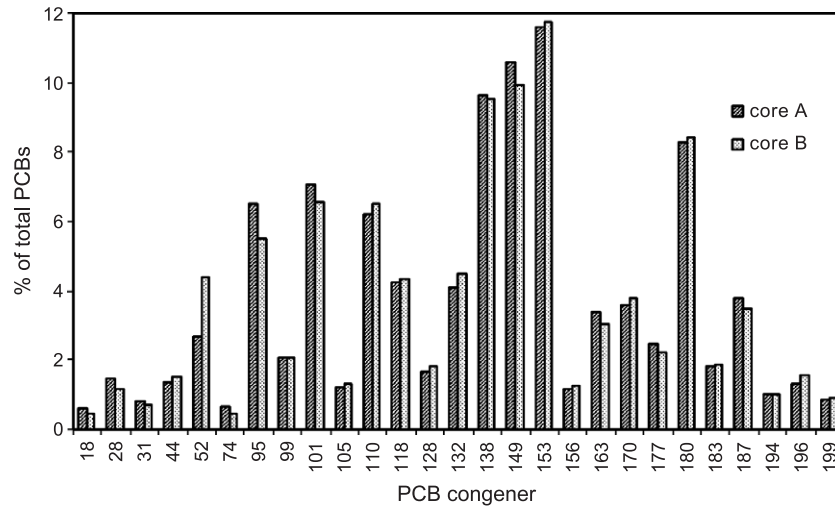
Fig. 2. Profiles of selected tri- to octa-CB congeners in two sediment cores from the Scheldt river.

has only slightly decreased in the last 15 years. This is probably due to the heavy industrialisation of the river's catchment area with continuous input of pollutants. The PCB concentrations found in the surface layers of the sediment cores were also similar to levels up to 120 ng/g dw found in sediments from the Amsterdam and Rotterdam harbour (de Boer et al., 2001). The PCB congener profile was similar between the two sediment cores (Fig. 2). Concentrations of tri- and tetra-CB congeners were low, while the predominant homologues were the penta- to hepta-CBs (Fig. 2), with a profile resembling to a mixture of Aroclor 1254 and 1260.

In the present study, PBDEs were also found in the sediment layers from the Scheldt river (1.4–270 ng/g dw for the sum of tri- to hexa-BDE congeners) (Table 4). The PBDE profile in these samples (Fig. 3) was very similar to the profile of penta-BDE technical mixture (Sjödin et al., 1998). High concentrations of BDE 209 (up to 8400 ng/g dw) were found also in the top layers of the cores from the present study (Table 4).

Previously, lower concentrations of tri- to hexa-BDE congeners (32 ng/g dw) and BDE 209 (1200 ng/g dw) were found in the Western Scheldt, near the Belgian–Dutch

border (BROC, 2003). However, this sample was collected with a Van Veen grab sampler which mixes deeper sediment layers with surface layers. This results therefore in a "dilution" of pollutant's concentrations.

3.2.2. Core distribution of pollutants

The depth profiles of PCBs and DDTs were similar in the two sediment cores (depths of 58 and 50 cm, respectively), while the concentrations of PCBs and DDTs showed a slight, but non-significant increase with the depth (Table 4). This suggests that the pollution of the Scheldt river has only slightly decreased in the past years, a phenomenon which was already reported for other polluted rivers, such as the Rhine (de Boer et al., 2001). In contrast, PCB levels in cores from marine or lake sediments show an evident decline in the past years, since their sources are mainly from fall out and atmospheric deposition (Isosaari et al., 2002).

For each sediment layer, the ratios between the levels of p,p'-DDE and p,p'-DDD were close to the unit (1.01 ± 0.10 and 1.04 ± 0.39 for cores A and B, respectively). This indicates that aerobic and anaerobic degradations of p,p'-DDT occurred at equal rates. Similar values for the ratio
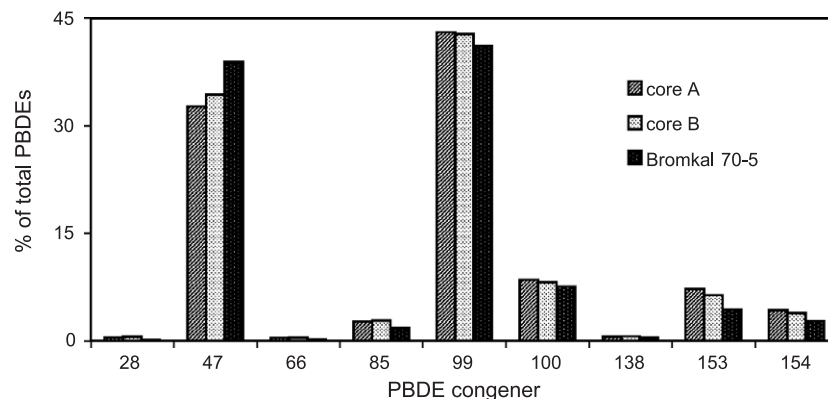
Fig. 3. Profiles of selected tri- to hexa-BDE congeners in two sediment cores from the Scheldt river and in the technical mixture Bromkal 70-5.
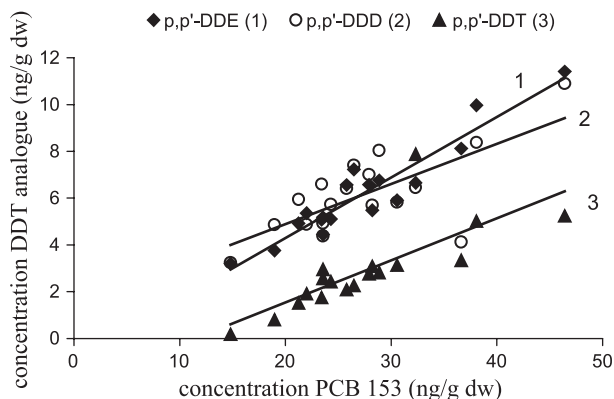
Fig. 4. Correlations between concentrations of DDTs analogues and concentration of PCB 153. (p,p'-DDE: $y=0.259x-0.877$, $R^2=0.894$, $p<0.001$; p,p'-DDD: $y=0.172x+1.451$, $R^2=0.514$, $p<0.001$; p,p'-DDT: $y=0.180x-2.048$, $R^2=0.586$, $p<0.001$).

p,p'-DDE/p,p'-DDD were found in bed sediment from urban sites sampled between 1992 and 2001 from United States river and streams (NAWQA, 2003).

High significant correlation coefficients were found between the concentrations of DDT analogues (p,p'-DDE, p,p'-DDD and p,p'-DDT) and the concentration of PCB 153 (Fig. 4), suggesting a similar trends in pollution changes for the two classes of pollutants.

The depth profiles of PBDEs in the sediment cores were completely different from those of PCBs, showing a steep increase in the surface layers compared with deeper core layers (Table 4). This is in accordance with the increase in the production and use of PBDEs in the last decades and with the high PBDE levels observed in surface sediments from other PBDE-polluted rivers, such as river Tees (Allchin et al., 1999).
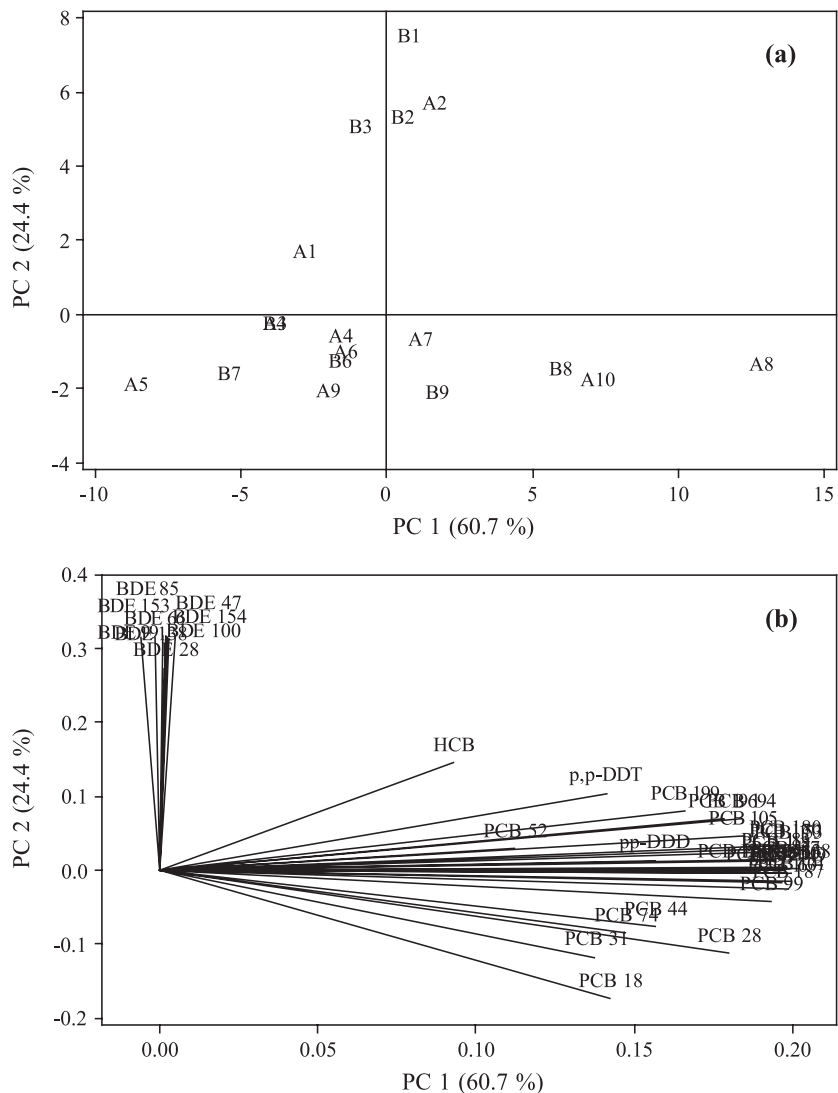
Fig. 5. Score plot (a) and loading plot (b) of PCA analysis based on concentrations of POPs (except of BDE 209) in two sediment cores from the Scheldt river.

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