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Levels and profiles of PCBs and OCPs in marine benthic species from the Belgian North Sea and the Western Scheldt Estuary

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Abstract

Various benthic invertebrates (flying crab, common shrimp, and red starfish), small fish (sand goby), benthic flatfish (dab, plaice, and sole) and gadoids (bib and whiting) were collected in the Belgian North Sea and along the Scheldt Estuary, both representing areas impacted by various contaminants to different degrees. The levels of 25 polychlorinated biphenyls (PCBs) and 15 organochlorine pesticides (OCPs), which included penta- and hexachlorobenzene, α-, β-, and γ-hexachlorocyclohexane isomers, chlordanes, and DDT and metabolites, were determined. Sum of PCBs and OCPs in benthic invertebrates and goby ranged from 1.5 to 280 ng/g wet weight (ww) and from 0.27 to 23 ng/g ww, respectively. The fish livers revealed total PCB and OCP levels ranging from 20 to 3200 ng/g ww and from 6.0 to 410 ng/g ww, respectively. Levels of both contaminant groups were significantly higher in samples from the Scheldt Estuary compared to the Belgian North Sea. For most species a highly inverse correlation was found between the concentration of contaminants and the distance to Antwerp (r between 0.812 and 0.901, $p < 0.05$), pointing to a higher degree of exposure further upstream. PCB and OCP exposures are highly correlated (r between 0.836 and 1.000, $p < 0.05$), which suggests that the pollution can be classified as historical. However, because urban and industrial centres may still be emitting these compounds, more recent point and non-point sources cannot be ruled out.

Keywords: PCBs; Pesticides; Invertebrates; Fish; North sea; Scheldt estuary

1. Introduction

The use and/or production of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), such as 2,2-bis-(4-chlorophenyl)-1,1,1-trichloroethane (DDT), hexachlorobenzene (HCB) and lindane (γ-HCH) have been banned in most developed countries since the 1970s (UNEP, 2003). Despite this measure, these compounds are among the most prevalent environmental pollutants and they can be found in various environmental compartments, both biotic (from plankton to humans) (de Voogt et al., 1990; Covaci et al., 2002; Voorspoels et al., 2002) and abiotic (air, water, sediments, soil) (Fuoco et al., 1995; de Boer et al., 2001). Their widespread presence is due to their extremely persistant and lipophilic nature. These properties cause these persistent organic pollutants (POPs) to bioaccumulate in the adipose tissues of biota, resulting in the enrichment throughout the food chain (de Voogt et al., 1990).

Prolonged exposure to these pollutants can interfere with normal physiology and biochemistry (den Besten et al., 1989; Everaarts et al., 1998; Mills et al., 2001; Picard et al., 2003). The occurrence and severity of these interferences depend on various factors, such as the concentration of pollutants in the organism, susceptability of the species, and duration of exposure (Giesy and Kannan, 1998; Safe, 1994). Effects of these compounds can be seen at various levels of the food chain, including starfish (den Besten et al., 1990), shrimp (Key et al., 2003), crabs (Weis et al., 1992), fish (Mills et al., 2001; Khan, 2003; Boon et al., 1992; Sleiderink et al., 1995), porpoises (Jepson et al., 1999), and humans (Masuda, 2003).

Because humans readily consume seafood, such as shrimp, crab and various fish species, these organisms are of great scientific value to estimate the possible exposure to PCBs and OCPs through marine food

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sources. The area studied in this investigation covered both commercial fishing grounds (Belgian North Sea—BNS) and a recreational fishing area (Western Scheldt Estuary—SE). The drainage basin of the SE covers a very densely populated and highly industrialised region, polluted by POPs (Voorspoels et al., 2003; Van de Vijver et al., 2003; Chu et al., 2003; Steen et al., 2001), heavy metals (Coteur et al., 2003) and non-persistent pollutants, such as volatile organic compounds (Huybrechts et al., 2003).

In this work, PCBs and OCPs were determined in benthic invertebrates and different fish species from both BNS and SE in order to evaluate trends in levels, congener distribution, and geographical variation.

2. Materials and methods

2.1. Sampling

Seven locations were selected in the BNS and nine locations in the SE (Fig. 1). Selection of the species was based upon their availability at the sampling locations. Finally, three species of benthic invertebrate organisms were chosen: crab, starfish, and shrimp. These organisms are very suitable as sentinel species, since they tend not to migrate (Everaarts et al., 1998; Roose et al., 1998). Crabs have already been used extensively as sentinel organisms in monitoring studies of lipophilic contaminants on Canada's West Coast (Ikonomou et al., 2002), while starfish have been subject to many studies regarding levels and effects of POPs (Everaarts et al., 1998; Picard et al., 2003; den Besten et al., 2001). Furthermore, starfish hold a top position in the food chain as a predator of bivalves, but it may feed also on decaying organic material (e.g. fish) (Everaarts et al., 1998).

Three benthic flatfish, two gadoid fish species, and one goby species were also sampled at the same locations. An overview of all sampled species is presented in Table 1. Except for starfish and goby, all organisms in this study are suitable for human consumption.

The number of animals collected at each location varied between 3 and 10 for starfish, between 30 and 50 for shrimp, crab and goby, and between 1 and 5 for the other fish species. The sampling campaigns took place during October and November 2001. All organisms were collected using a 3 m beam trawl with fine-meshed net (6×6 mm), at a constant speed of 1.5 to 2.0 knots for about 30 min., using the research vessel *Zeeleeuw*, provided by the Flemish Marine Institute (VLIZ).

Preliminary sample pre-treatment steps were undertaken on board and they included species determination, recording of fish length and washing with distilled water. The flatfishes and gadoids were dissected on board immediately after capture and only the excised liver samples were collected for this study. The invertebrates and goby samples were stored entirely. All samples were kept in hexane pre-washed glass recipients at −20 °C until analysis.

2.2. Sample availability

All sampled species were available in large amounts at the BNS locations. Crab and shrimp were very abundant and available at each location, while starfish, goby and dab were very little abundant in the SE. Other flatfish and gadoids were caught in at least five locations on the BNS and three locations in the SE.

2.3. Targeted compounds

Based on their abundance in the samples, the following PCB-congeners (IUPAC numbering), were tar-

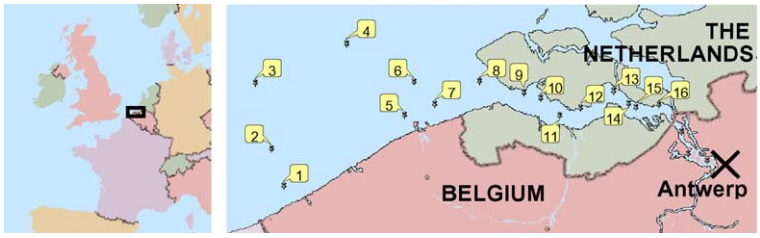

Fig. 1. Sampling locations.

Table 1
Overview of sampled species

Class	Species name
Benthic invertebrates	*Crangon crangon* (common shrimp), *Lyocarcinus holsatus* (flying crab), *Asterias rubens* (red starfish)
Benthic fish	*Pomatoschistus minutus* (sand goby)
Benthic flatfish	*Solea solea* (common sole), *Limanda limanda* (dab), *Pleuronectus platessa* (plaice)
Gadoid fish	*Merlangius merlangus* (whiting), *Trisopterus luscus* (bib)

geted for analysis: 28, 44, 52, 74, 95, 99, 101, 105, 110, 118, 128/174, 138, 149, 153, 156, 163, 167, 170, 177, 180, 183, 187, 194, 196, and 199. CB 44 and 110 were not measured in crab, starfish, and goby. Data of these two congeners were included in the sum of PCBs for the other species.

The following OCPs were also determined: pentachlorobenzene (QCB), α-, β-, γ-, and δ-hexachlorocyclohexane (hereafter refered to as ''HCHs''), hexachlorobenzene (HCB), *trans*-chlordane (TC), *cis*-chlordane (CC), *trans*-nonachlor (TN), oxychlordane (OxC) (TC, CC, TN, and OxC are hereafter referred to as ''Chlordanes''), 2,2-bis-(4-chlorophenyl)-1,1,1-trichloroethane (*p*,*p*′-DDT), 2,2-bis(4-chlorophenyl)-1,1-dichloroetylene (*p*,*p*′-DDE), 2,2-bis(4-chlorophenyl)-1,1-dichloroethane (*p*,*p*′-DDD), 2-(4-chlorophenyl)-2-(2-chlorophenyl)-1,1,1-trichloroethane (*o*,*p*′-DDT), and 2-(4-chlorophenyl)-2-(2-chlorophenyl)-1,1-dichloroethane (*o*,*p*′-DDT), (hereafter referred to as ''DDTs''). For crab, goby and starfish samples, no data are available for QCB, chlordanes, *o*,*p*′-DDT, and *o*,*p*′-DDD. These compounds contribute approximately 10% to the total OCP load determined in this study and are therefore not included in the sum of OCPs and in the statistical analyses to facilitate comparison between species. ε-HCH was used as internal standard (IS) for QCB, HCB, and HCHs whereas CBs 46 and 143 were used as IS for the PCBs, DDTs, and chlordanes.

2.4. Chemicals

All solvents used for the analysis (*n*-hexane, acetone, dichloromethane, and *iso*-octane) were of SupraSolv® grade (Merck, Darmstadt, Germany). Individual reference standards for each of the compounds were used for identification and quantification (CIL, Andover, USA; Dr. Ehrenstorfer Laboratories, Augsburg, Germany). Sodium sulphate was heated for at least 6 h at 600 °C and silica was pre-washed with *n*-hexane and dried overnight at 60 °C before use. Extraction thimbles were pre-extracted for 1 h and dried at 100 °C for 1 h.

2.5. Sample preparation and clean up

Prior to analysis, the samples were thawed and homogenised using a high-speed blade-mixing device, except for the shrimp and crab samples of which only the soft parts were taken. After homogenisation, two identical composite samples of each species, location and tissue were created. Thirty individual shrimp, goby and crabs were homogenised for each pool. The pools of starfish samples consisted of 3–8 equally sized individuals. The composite samples of gadoids and flatfish consisted of 3–6 individuals. Size was taken into account when fish samples were pooled.

The method used for the preparation and clean up of the samples has previously been described by Jacobs et al. (2002) and is briefly presented below. Between 1 and 10 g of homogenised sample was spiked with internal standards and extracted for 2.5 h by hot Soxhlet with hexane/acetone (3/1; v/v). After lipid determination, the extract was cleaned-up on acid silica and PCBs and OCPs were eluted with *n*-hexane followed by dichloromethane. The eluate was concentrated to near dryness and reconstituted in 80 μl *iso*-octane.

2.6. Chemical analysis

PCB quantification was performed using a Hewlett Packard 6890 GC (Palo Alto, CA, USA) coupled with a μ-ECD detector and equipped with a 50 m × 0.22 mm × 0.25 μm HT-8 (SGE, Zulte, Belgium) capillary column. One μl was injected in 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 °C and 320 °C, respectively. The temperature program of the HT-8 column was set to 90 °C for 1.2 min, then raised 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 raised by 5 °C/min to 290 °C and kept for 18 min.

OCP measurements of all extracts were performed using a Hewlett Packard 6890 GC equipped with a 25 m × 0.22 mm × 0.25 μm HT-8 capillary column and connected via direct interface with a Hewlett Packard 5973 mass spectrometer that was operated in Electron Capture Negative Ionisation (ECNI) mode. Methane was used as moderating gas and the ion source, quadrupole and interface temperatures were set at 150, 130 and 300 °C, respectively. The mass spectrometer was used in the selected ion-monitoring (SIM) mode. One μl of the cleaned extract was injected in pulsed splitless mode (injector temperature 280 °C, pressure pulse 30 psi, pulse time 1.50 min). The splitless time was 1.50 min. The temperature of the HT-8 column was kept at 90 °C for 1.50 min, then increased to 200 °C at a rate of 15 °C/min (kept for 2.0 min), further increased to 270 °C at a rate of 5 °C/min and kept for 1.0 min and finally raised to 290 °C at a rate of 25 °C/min and kept constant for 10.0 min.

2.7. Quality assurance

Multi-level calibration curves in the linear response interval of the detector were created for the quantification and good correlation ($r^2 > 0.999$) was achieved. The identification of POPs was based on their relative retention times (RRTs) to the internal standard used for quantification on GC/ECD and was based on RRTs, ion chromatograms and intensity ratios of the monitored ions for quantification on GC/MS. A deviation of the

ion intensity ratios within 20% of the mean values of the calibration standards was considered acceptable.

The quality control was performed by regular analyses of procedural blanks, blind duplicate samples, certified reference material CRM 349 (PCBs in cod liver oil), and by random injection of standards and solvent blanks. The method was validated by participation in an interlaboratory comparison organised by the Institute for Reference Measurements and Materials (IRMM, Geel, Belgium). Seven PCB congeners (CBs 28, 52, 101, 118, 138, 153 and 180) were determined in non-spiked, medium- and high-level spiked pork fat (Bester et al., 2001). The results of the individual PCB congeners deviated less than 10% from the target values at all spiking levels.

Limit of quantification (LOQ) for PCBs and OCPs, based on GC/ECD and GC/MS performance, was dependent of the sample intake. The sample intake was therefore adapted to the expected pollution load of the sample. Results are reported as 'not detected' (N.D.) when the concentration is lower than 0.01 ng/g wet weight (ww). Procedural blank values were found to be very low for most OCPs (<5% of value found in samples), but *p*,*p*′-DDE and PCBs were clearly present and consistent (RSD < 30%) in procedural blanks and therefore the mean blank value for these compounds were used for subtraction.

Two PCBs of interest were co-eluting from the column, namely CB 128 and CB 174. However, after verification by GC/MS-EI, 90% of the CB 128/174 signal could be attributed to CB 128. The peak has therefore been interpreted as being CB 128.

2.8. Statistical analysis

For samples with concentrations below LOQ, zero was used in the calculations. Simple linear regression coefficient was used to test for correlations between the total PCB/OCP load and the distance to Antwerp. Simple linear regression was used also to test the correlation between PCBs, OCPs, CB 153, and *p*,*p*′-DDE. The Mann Whitney *U*-test was used to compare the mean concentrations in BNS and SE and to test the profile differences. Tests were considered significant if p was lower than 0.05. All statistical tests were performed using Statistica® v5.0 software (StatSoft Inc., Tulsa, OK, USA).

3. Results and discussion

3.1. Lipid content

Lipid determination was performed on an aliquot of the extract (1/5th) before clean up. This procedure allowed good lipid recoveries for lean and fatty fish during QUASIMEME interlaboratory exercises. The lipid percentage in benthic invertebrates ranged from 0.6 ± 0.1% in shrimp to 2.7 ± 1.1% in starfish. The whole-body lipid percentage in goby was 2 ± 1.1%. Lipid content in fish livers varied widely between species, with values ranging from 15 ± 9.4% in sole to 55 ± 7.8% in bib (Table 2).

The lipid content of fish tissue is influenced by several factors, such as sex, age, species, nourishment and spawning status (Larsson et al., 1993; Kozlova, 1997). In the present study, all samples were taken prior to spawning, resulting in maximum seasonal lipid levels. Nevertheless, wet weight based results are preferred and therefore, lipid based results are given only for comparison with other studies.

3.2. PCB levels

The congeners that could be detected and their frequency of detection were species and location dependent. Shrimp showed very low concentrations for all congeners analysed. The low extractable lipids of shrimp (0.6 ± 0.1%) were probably related to this observation (Roose et al., 1998). For the other benthic invertebrates and goby, most congeners could be measured in all samples. Total PCB levels in benthic invertebrates and goby ranged from 1.5 to 280 ng/g ww (from 330 to 24200 ng/g lipid weight (lw)).

In liver samples of gadoid fish all congeners could be measured. These samples also showed the highest lipid

Table 2
Lipid percentages (extractable lipids)

	N	Mean	SD	Median	Range
Crab	28	1.9	1.2	1.4	0.8–4.8
Goby	17	2.0	1.1	1.4	0.8–3.5
Starfish	21	2.7	1.1	2.5	1.3–5.3
Shrimp	23	0.6	0.1	0.6	0.5–0.8
Dab liver	7	35	7.1	37	21–42
Plaice liver	9	27	12	22	15–47
Bib liver	12	55	7.8	57	42–70
Sole liver	16	15	9.4	13	5.1–40
Whiting liver	12	34	14	36	9.8–50

content (Table 2). Although total PCB levels in dab were the lowest among all fish livers analysed, most congeners could be determined in dab and plaice liver, and only a few congeners were below LOQ (CBs 52, 74, 167, 194, 199) at some locations. In sole liver, more congeners were below LOQ at the BNS locations (Table 4). The congeners that were most often not detected in sole liver were CBs 28, 52, 167, 156, 194, and 199. All PCB levels in sole liver from the SE were above LOQ. The lipid content in sole liver was lower than in the other samples (Table 2), which can explain the high frequency of congeners below LOQ. In general, total PCB levels in the fish livers of this study ranged from 20 to 3200 ng/g ww (from 420 to 14400 ng/g lw). PCB data are summarised in Table 3. The concentration range of all congeners for each species is presented in Table 4.

Interspecies variation of PCB levels was rather limited. However, shrimp showed significantly lower levels at the BNS locations. These lower PCB levels in shrimp can be partially explained by their pelagic nature and feeding pattern. Shrimp live slightly above the seabed, resulting in less intense contact with the sediment compared to the other benthic species of the present study. Shrimp primarily feed on mysids and amphipods (Oh et al., 2001), that occupy a low trophic level. The other benthic invertebrates of the present study (crab and starfish) contained relatively higher PCB levels, that can also be explained by their feeding habit: crabs, and to a lesser extent starfish, are scavengers that feed partially on decaying organic material (such as carcasses of dead fish and other organisms), which can bear relatively high pollutant loads (Britton and Morton, 1994; Everaarts et al., 1998).

Goerke and Weber (2001) have shown that species-specific elimination of PCBs had a clear impact on residue patterns. In their study, white prawn (*Palaemon longirostris*), a species related to the common shrimp, eliminated all PCBs (the most chlorinated PCB tested was CB 153) at a faster rate compared to the other species, including flounder (*Platichus flesus*). In the present study, crab and whiting samples displayed significantly higher lipid normalised PCB levels at all locations than did the other species. For both species, the observations may be explained by their trophic position.

3.3. OCP levels

OCP data are summarised in Table 5. α-, β-, and γ-HCH isomers, HCB, *p*,*p*′-DDT, *p*,*p*′-DDE, and *p*,*p*′-DDD were consistently analysed in all samples. Therefore only these compounds are included in the sum of OCPs and in the statistical data analysis. QCB, chlordanes (TC, TC, TN, and OxC), and *o*,*p*′-DDTs (*o*,*p*′-DDT and *o*,*p*′-DDD) are only reported and not extensively discussed. In general, the contribution of QCB, chlordanes, and *o*,*p*′-DDTs to the sum of OCPs in this study was around 10%. The concentration range of all compounds for each species is presented in Table 6.

Similar to PCBs, the lowest OCP concentrations were found in shrimp. Only QCB, HCB, *p*,*p*′-DDE, and γ-HCH could be detected in shrimp samples from both BNS and SE. OxC was the only chlordane that could be detected in shrimp from the SE (range 0.07–0.19 ng/g ww). All crab and most goby samples contained measurable concentrations of all OCPs.

Table 3
Total PCB levels for each species expressed in ng/g ww (in ng/g lw) at the different locations

Location	Benthic invertebrates			Benthic fish	Benthic flatfish liver			Gadoid fish liver	
	Crab	Shrimp	Starfish	Goby	Dab	Plaice	Sole	Bib	Whiting
BNS									
1	36 (2900)	1.5 (330)	26 (680)	25 (860)	310 (790)	190 (840)	200 (670)	810 (1400)	780 (2100)
2	29 (2200)		30 (1200)		250 (760)	110 (570)			730 (1800)
3	23 (2100)		30 (1200)		89 (420)		74 (480)		
4	53 (4400)	2.5 (430)	45 (2500)	25 (2100)			140 (1500)	1500 (2600)	1300 (2800)
5	32 (3100)	2.4 (380)	44 (2300)	27 (2200)			20 (1100)	940 (1600)	1600 (3500)
6	27 (2200)	1.8 (380)	30 (710)	23 (2400)	160 (420)	1100 (2300)	68 (1300)	650 (1200)	230 (1300)
7	47 (3100)	2.6 (360)	29 (1100)	13 (1700)	290 (810)	96 (640)	57 (910)		
8	47 (3400)	2.6 (420)	46 (1900)	97 (3200)				1700 (3100)	1700 (10 900)
SE									
9	210 (6200)	3.1 (470)					230 (2300)	1300 (2200)	
10	200 (11 700)							1400 (2900)	
11	190 (8600)	7.3 (1000)	83 (5200)			1400 (2900)	480 (3700)	2900 (4900)	
12	200 (6700)	6.5 (1200)		120 (4000)	260 (620)	980 (3900)	450 (3600)	2700 (4800)	3100 (10 100)
13	280 (24 200)	19 (3100)					300 (2100)	3200 (7300)	2800 (5400)
14	270 (5800)	37 (5300)				1200 (4300)	680 (5200)		1400 (14 400)
15		39 (6200)					800 (7700)		
16		34 (4800)							

Table 4
Concentration range of all PCB congeners in all samples (ng/g ww)

Congener	Benthic invertebrates			Benthic fish	Benthic flatfish liver			Gadoid fish liver	
	Crab	Shrimp	Starfish	Goby	Dab	Plaice	Sole	Bib	Whiting
CB 28	0.24–1.7	N.D.–2.1	0.19–0.60	0.06–0.59	0.80–3.0	0.96–9.3	N.D.–4.6	5.5–19	1.5–17
CB 52	N.D.–8.3	N.D.–1.5	0.63–2.4	0.29–3.3	N.D.–5.9	0.45–37	N.D.–30	10–120	4.7–79
CB 44	n.a.	N.D.–0.25	n.a.	n.a.	0.56–2.9	0.48–13	N.D.–6.9	5.2–28	2.2–23
CB 74	0.25–1.9	N.D.–0.58	0.13–0.53	0.05–0.35	0.44–2.5	N.D.–10	N.D.–3.3	4.0– 20	1.8–20
CB 95	0.08–10.2	N.D.–1.2	0.44–7.8	0.31–4.7	1.1–8.2	1.2–47	N.D.–26	5.4–85	7.2–92
CB 101	0.49–28	N.D.–0.36	2.3–7.3	0.86–12	4.6–20	3.5–120	1.5–71	41–240	17–260
CB 99	2.0–16	N.D.–0.84	1.8–4.2	0.86–6.6	4.2–16	4.7–81	1.8–32	39–160	11–160
CB 110	n.a.	N.D.–0.20	n.a.	n.a.	3.1–14	2.5–62	0.18–29	15–120	11–150
CB 149	0.25–23	N.D.–0.63	1.7–15	1.05–12	3.3–17	4.2–100	1.5–44	22–170	18–240
CB 118	2.2–17	0.18–2.5	1.8–4.4	0.80–7.2	7.2–21	7.3–86	1.6–49	54–230	15–210
CB 153	5.4–68	0.20–5.2	5.1–16	2.5–21	23–64	27–250	6.3–131	135–480	48–530
CB 105	0.57–4.5	N.D.–0.27	0.55–1.1	0.31–2.1	1.5–4.3	1.2–18	N.D.–9.8	9.5–48	2.9–48
CB 163	1.4–15	0.23–3.2	1.6–3.9	0.88–6.2	4.5–14	5.2–77	1.9–40	19–160	9.9–120
CB 138	3.8–35	N.D.–2.8	3.2–8.7	1.6–12	13–39	14–120	2.5–79	76–280	25–310
CB 187	1.7–16	0.20–3.7	1.5–3.7	1.2–7.1	6.7–24	7.8–97	1.3–54	27–190	16–150
CB 183	0.33–8.1	N.D.–0.73	0.12–0.46	0.18–2.1	0.52–2.7	0.92–19	N.D.–15	8.5–78	3.1–64
CB 128	0.68–6.8	N.D.–0.38	0.66–1.7	0.47–3.5	2.2–8.3	2.2–33	N.D.–12	15–61	4.8–77
CB 177	0.28–6.5	N.D.–0.94	0.48–2.1	0.39–4.6	0.86–6.1	1.8–30	0.29–9.1	6.3–39	4.9–21
CB 167	0.28–2.7	N.D.–0.46	0.22–0.73	0.25–1.7	N.D.–0.54	N.D.–6.6	N.D.–5.5	5.6–41	0.24–19
CB 156	0.32–4.2	N.D.–1.4	0.16–0.44	0.16–1.2	1.2–2.4	0.71–16	N.D.–15	9.3–86	1.4–45
CB 180	1.4–20	0.16–6.8	0.17–1.2	0.59–5.5	4.2–20	4.6–76	N.D.–97	45–300	8.3–230
CB 199	0.13–1.8	N.D.–0.44	N.D.–0.19	0.08–0.78	N.D.–2.7	0.18–8.4	N.D.–4.8	3.7–28	1.1–20
CB 170	0.60–5.7	N.D.–2.5	0.20–0.92	0.26–2.3	1.4–7.5	1.4–29	N.D.–35	19–130	3.3–83
CB 196	N.D.–0.78	0.08–2.8	N.D.–0.23	N.D.–0.15	4.1–20	5.3–48	0.49–38	34–200	12–141
CB 194	0.13–1.7	N.D.–0.50	N.D.–0.11	0.03–0.64	N.D.–2.0	N.D.–6.2	N.D.–30	5.3–32	0.48–20
Sum PCBs	23–280	1.5–39	26–83	23–120	89–310	96–1400	20–800	650–3200	230–3100

n.a.: not available; N.D.: not detected.

Table 5
Sum of OCPs for each species expressed in ng/g ww (in ng/g lw) at the different locations

Location	Benthic invertebrates			Benthic fish	Benthic flatfish liver			Gadoid fish liver	
	Crab	Shrimp	Starfish	Goby	Dab	Plaice	Sole	Bib	Whititng
BNS									
1	3.3 (270)	0.43 (91)	2.6 (67)	3.2 (110)	34 (86)	26 (120)	23 (76)	89 (160)	100 (280)
2	2.8 (220)		2.8 (110)		23 (72)	15 (79)			63 (150)
3	3.0 (270)		2.8 (120)		13 (59)		9.7 (62)		
4	4.6 (380)	0.27 (46)	4.5 (250)	3.4 (290)			16 (170)	270 (480)	160 (340)
5	3.0 (280)	0.61 (97)	4.4 (230)	3.6 (300)			6.7 (370)	120 (200)	280 (620)
6	2.6 (220)	0.28 (58)	3.3 (80)	3.0 (320)	31 (83)	160 (350)	7.5 (150)	75 (140)	22 (130)
7	4.4 (290)	0.47 (66)	2.6 (100)	1.8 (220)	38 (110)	8.7 (58)	6.0 (96)		
8	4.4 (320)	0.67 (110)	4.9 (200)	14 (460)				190 (350)	210 (1400)
SE									
9	18 (510)	0.60 (91)					23 (230)	150 (250)	
10	16 (920)							78 (160)	
11	14 (660)	0.71 (100)	10 (650)			130 (270)	51 (390)	280 (460)	
12	18 (600)	0.66 (120)		16 (550)	56 (130)	110 (440)	45 (370)	310 (540)	410 (1300)
13	21 (1800)	0.91 (150)					26 (180)	360 (810)	380 (750)
14	23 (480)	1.6 (230)				100 (370)	54 (410)		140 (1500)
15		1.3 (200)					57 (550)		
16		1.7 (240)							

Sum of OCPs includes: HCB, α-, β-, γ-HCH, and *p*,*p*′-DDTs.

All OCPs were consistently detected in liver samples of dab, plaice, bib, and whiting and most compounds were found in sole samples. Also *o*,*p*′-DDT and *o*,*p*′-DDD were analysed in the fish liver samples. *o*,*p*′-DDT could not be detected in most samples, except in dab and whiting. *O*,*p*′-DDD levels were above LOQ in most samples, except in sole liver. The highest concentrations measured for *o*,*p*′-DDT and *o*,*p*′-DDD were 2.1 and 8.0

Table 6
Concentration range of all OCPs in all samples (ng/g ww)

Compound	Benthic invertebrates			Benthic fish	Benthic flatfish liver			Gadoid fish liver	
	Crab	Shrimp	Starfish	Goby	Dab	Plaice	Sole	Bib	Whiting
QCB	n.a.	N.D.–0.69	n.a.	n.a.	0.31–1.3	0.03–0.96	N.D.–0.89	0.29–2.5	0.16–1.9
α-HCH	0.17–0.28	N.D.	0.13–0.18	0.09–0.42	0.24–1.1	0.14–0.93	N.D.–0.36	0.42–1.2	0.43–1.1
HCB	0.14–0.84	0.08–0.50	N.D.	0.05–0.48	1.9–4.4	0.59–3.7	N.D.–1.8	1.8–7.0	0.94–5.6
γ-HCH	N.D.–0.30	0.18–0.42	0.15–0.60	0.11–1.2	0.55–19	N.D.–11	N.D.–6. 7	5.1–17	3.4–18
β-HCH	0.08–0.40	N.D.	N.D.–0.11	N.D.–0.15	0.30–1.9	0.16–1.6	0.09–4.0	0.57–2.5	0.41–2.2
δ-HCH	n.a.	N.D.–0.01	n.a.	n.a.	0.01–0.26	N.D.–0.14	N.D.–4.7	0.07–0.36	0.02–0.30
OxC	n.a.	N.D.–0.19	n.a.	n.a.	0.24–0.58	0.19–1.8	N.D.–0.97	0.98–8.4	0.23–4.6
TC	n.a.	N.D.	n.a.	n.a.	0.12–0.75	0.01–2.0	0.01–0.57	0.56–5.4	0.10–3.4
TN	n.a.	N.D.	n.a.	n.a.	0.52–1.3	0.29–4.6	0.09–1.8	2.0–9.4	0.51–12
CC	n.a.	N.D.	n.a.	n.a.	0.35–1.1	0.09–2.3	0.07–0.64	1.1–6.5	0.24–5.0
o,p′-DDT	n.a.	N.D.	n.a.	n.a.	N.D.–0.61	N.D.–0.82	N.D.–0.61	N.D.–0.82	N.D.–2.1
o,p′-DDD	n.a.	N.D.	n.a.	n.a.	N.D.–0.86	0.19–5.0	N.D.	0.71–3.4	0.30–8.0
p,p′-DDT	0.17–5.1	N.D.	0.63–1.9	0.48–2.9	1.2–2.5	0.36–5.4	0.08–1.3	1.9–19	0.58–26
p,p′-DDE	1.3–11	N.D.–0.81	0.75–3.9	0.51–5.2	7.4–20	6.0–100	1.7–30	44–210	11–270
p,p′-DDD	0.26–5.9	N.D.	0.50–3.9	0.50–6.0	1.2–9.5	1.5–42	0.61–21	16–120	5.1–100
Sum OCPs	2.6–23[a]	0.27–2.6	2.6–10[a]	1.8–16[a]	14–63	9.5–140	6.4–61	83–390	25–440

n.a.: not available; N.D.: not detected.
[a] Sum of OCPs includes: HCB, α-, β-, γ-HCH, and *p,p′*-DDTs.

ng/g ww, respectively. Levels of total chlordanes ranged from 0.27 to 25 ng/g ww.

3.4. PCB and OCP levels in other studies

Based on data provided by other studies, we can conclude that biota from the SE are highly contaminated. Levels of PCBs and OCPs found in dab, plaice, and sole liver from near the Norwegian coast (Green and Knutzen, 2003) were comparable with levels of the BNS livers from the present study, except for sole, which showed higher OCP levels in our study.

De Boer et al. (2001) reported CB 153 levels ranging from 270 to 1900 ng/g lw in fish liver from an area with high degree of industrialisation and harbour activities (Rotterdam habour, The Netherlands), while the levels in our study ranged from 79 to 3300 n/g lw. De Boer et al. (2001) concluded that flounder liver from their study could be considered as relatively highly contaminated, but these results were not exceptionally high for an harbour area. Levels of QCB, HCHs, and HCB in fish liver from the SE of the present study and in flounder liver reported by de Boer et al. (2001) were comparable, while DDTs were somewhat higher in the SE (1400 vs. 780 ng/g lw).

Most data on starfish are produced by analysis of the pyloric caeca and not of the whole body as in the present study, although it is not uncommon practice. Results of both analyses can be easily compared, since the difference between lipid-based PCB levels of pyloric caeca and of total body is approximately a factor 1.5 (den Besten et al., 2001). PCB concentrations found in starfish of the present study were similar to (Everaarts et al., 1998) or higher than (den Besten et al., 2001) those previously reported for starfish from the Southern North Sea. Similar levels were observed for α- and γ-HCH, *p,p′*-DDT, and *p,p′*-DDE, while levels of *p,p′*-DDD were slightly higher in the present study (40 vs. 10 ng/g lw) (den Besten et al., 2001).

In general, total POP levels of the BNS samples were almost one order of magnitude higher than those of Greenland (Cleeman et al., 2000), while fish livers from the SE surpassed the Greenland values by more than two orders of magnitude. The sum of *p,p′*-DDTs was higher in the present study (200 vs. 60 ng/g lw). HCHs levels were similar for sculpin and the fish of the present study (both around 25 ng/g lw), but levels in cod were higher. Compared to the Greenland study, the HCHs pattern was different in the fish livers of the present study. The major contributor to the sum of HCHs was clearly α-HCH in the Greenland study, while in the present study γ-HCH was the predominant isomer. This may be attributed to the higher long-range transport capability of α-HCH (Beyer et al., 2000).

3.5. PCB profiles

To visualise the PCB profiles in the different species, PCBs were divided into homologue groups (Table 7). Because homologue patterns did not vary between locations (mean RSD < 25), a mean profile for each species was calculated and is presented in Fig. 2.

Contribution of the lower chlorinated congeners (tri- and tetra-CBs) to the sum of PCBs was very low. Although the lower chlorinated biphenyls have an increased mobility from the substrate to water and are therefore more available to aquatic organisms (de Boer et al., 2001), they are very susceptible to metabolism and

Table 7
PCB homologue groups

Homologue	PCB congeners
Tri-CBs	28
Tetra-CBs	52, 44[a], 74
Penta-CBs	95, 99, 101, 105, 110[a], 118
Hexa-CBs	128/174, 149, 153, 156, 163, 167
Hepta-CBs	170, 177, 180, 183, 187
Octa-CBs	194, 196, 199

[a] Not measured for crab, goby, and starfish.

are eliminated rapidly in the marine environment. No statistically significant profile differences concerning tri-homologues could be observed between any of the species from this study and between the livers of the five large fish species analysed (flatfish and gadoids). Some species-dependant differences were seen concerning tetra- to octa-CB homologues between the small benthic organisms (crab, shrimp, starfish, and goby) and larger fish. The most obvious statistically significant deviating pattern was found in shrimp, where levels of tetra-, penta-, and hexa-CB congeners were relatively lower, while the concentrations for hepta- and octa-CB congeners were relatively higher (Fig. 2). The different levels of nearly all PCB homologue groups found in shrimp compared to the other benthic invertebrates are not likely to be solely dependent on the bioavailability, but probably also on metabolism and elimination. Being invertebrates, it was suggested that shrimp have a theoretical lower metabolic activity than marine vertebrates (Livingstone, 1992; Borgå et al., 2001), but they seem to be able to metabolise and eliminate certain PCBs faster than some fish species (Goerke and Weber, 2001). Because organochlorine patterns in an organism depend on both species dependent uptake and elimination processes (Mehrtens and Laturnus, 1999), deducting metabolic capacities from tissue profile should be done with great caution.

The contribution of hexa-CB congeners in crab, goby, and starfish was statistically higher than in the fish livers, while the contribution of octa-CB congeners was significantly lower. Also the hepta-CB congeners showed relatively lower concentrations in starfish.

Because contaminants in the sediments are bioavailable to sediment dwelling organisms (Pruell et al., 1993), four sediment samples from the SE have also been analysed to establish the PCB profile. The mean homologue pattern of the sediment is included in Fig. 2. The contribution of tri-, tetra-, and penta-CB congeners to the total PCBs is higher in the sediments than in the fish and benthic invertebrates, and the contribution of hexa-, hepta-, and octa-CB congeners to the total PCBs is higher in the organisms than in the sediment.

3.6. OCP profiles

To visualise the OCP profile in the different species, OCPs were divided into three groups, namely HCHs, HCB, and DDTs. No location dependent profile differences were seen in neither species, except in shrimp. In the latter species the profile was slightly biased regarding DDTs contribution to the total OCP level. This was mainly because of very low total concentrations of DDTs (Table 6). The same bias was seen in the HCHs

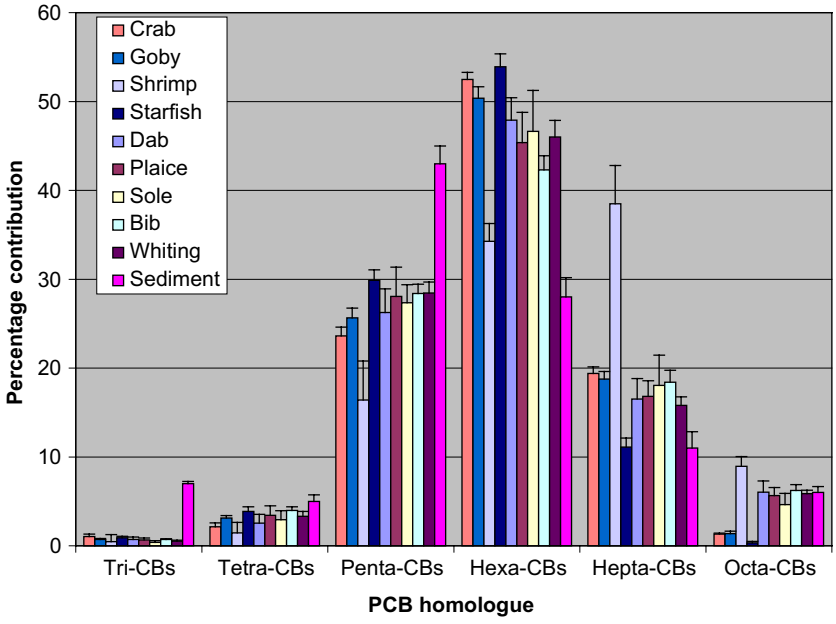

Fig. 2. PCB homologue profile (% ± 2 SE) in all species and in sediment from the SE.

profile of shrimp, since only the γ-HCH isomer could be measured (Table 6). Nevertheless, the mean of all profiles was taken for each species and is plotted in Fig. 3.

Figs. 4 and 5 give more detailed profile information on DDT metabolites and HCH-isomers, respectively. There are no significant profile differences in HCH-isomers and DDT-metabolites among the larger fishes of this study (flatfish and gadoids). Between the small benthic organisms and the larger fishes and among the small benthic organisms themselves, statistically significant

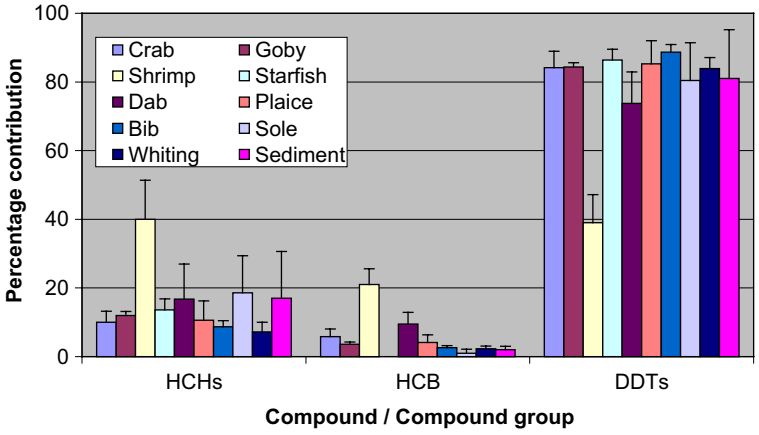

Fig. 3. OCP profile (%±2 SE) in all species and in sediment from the SE.

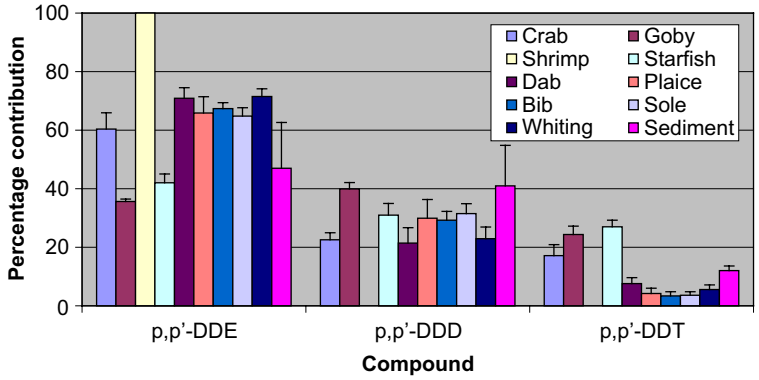

Fig. 4. Profile of *p,p′*-DDT metabolites (%±2 SE) in all species and in sediment from the SE.

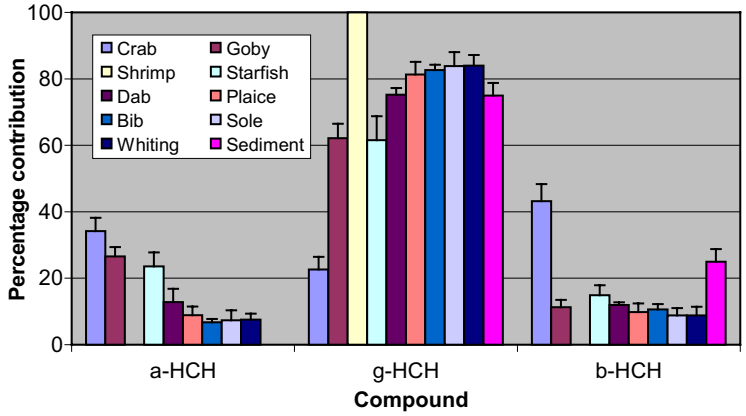

Fig. 5. HCHs profile (%±2 SE) in all species and in sediment from the SE.

profile differences were observed. The relative contribution of *p*,*p*′-DDD to the total OCP load was virtually equal in most species of this study. This metabolite is mainly formed in the environment by anaerobic degradation of *p*,*p*′-DDT (Walters and Aitken, 2001). The *p*,*p*′-DDD concentrations found in these samples are due to uptake from the environment (water, sediment, etc.) or by ingestion with food. Compared to flatfish and gadoids, the contribution of *p*,*p*′-DDT to the total sum of DDTs in the small benthic organisms was higher, while the contribution of *p*,*p*′-DDE was lower. Benthic invertebrates have a lower metabolic rate (Livingstone, 1992; Borgå et al., 2001), which can explain this observation.

Similar as for PCBs, four sediment samples from the SE were analysed for their OCP content to establish the OCP, DDTs, and HCHs profiles (Fig. 3). Levels of OCPs in the sediments were very low, with concentrations ranging from 2.2 to 7.7 ng OCPs/g dry weight. Contribution of *p*,*p*′-DDT to the total DDTs was higher in the sediments than in the fishes, while contribution of *p*,*p*′-DDE was lower (Fig. 4). This DDT-metabolite profile in the sediments supports the explanation of the interspecies differences that were observed. For small benthic species, the profile differences between sediment and the tissues were less pronounced (Fig. 4), which supports the lower metabolic ability of the smaller benthic organisms.

Crab showed significantly higher contribution of *p*,*p*′-DDE, which seems contradictory to the above proposed explanation (Livingstone, 1992; Borgå et al., 2001). The relatively higher *p*,*p*′-DDE levels in crab may however be explained by the species' feeding habit. Being scavengers, crab accumulates a substantial part of its *p*,*p*′-DDE load from its preys, which might have much higher pollutant load than crab themselves. This can explain the relatively higher than expected *p*,*p*′-DDE contribution to the total DDTs-load.

The HCHs profile also displays variation between certain samples (Fig. 5). The contribution of the β-HCH isomer was quite similar for most species. However, in the small benthic species the α-isomer contribution was higher and γ-isomer contribution was lower compared to the flatfish and gadoids. The HCHs profile of the sediments was slightly biased because α-HCH could not be detected (Fig. 5). The high contribution of α-HCH, which was in the HCH technical mixture, to the total sum of HCHs in the benthic invertebrates from this study is consistent with the limited metabolic abilities of these organisms.

Selective organ distribution may also explain the profile differences between the small benthic organisms and fish (Inomata et al., 1996; Feroz and Qudduskhan, 1979). For the crab, goby, shrimp, and starfish samples, the whole bodies or soft parts were used, while for fish, only liver tissue was analysed.

Table 8
Correlation between CB 153 and *p*,*p*′-DDE levels

	N	*r*	*p*
Crab	14	0.9893	0.000
Shrimp	13	0.9526	0.000
Starfish	10	0.9653	0.000
Goby	7	0.9996	0.000
Dab	6	0.8783	0.021
Plaice	7	0.8952	0.006
Sole	12	0.9713	0.000
Bib	10	0.8359	0.003
Whiting	9	0.9063	0.001

Significant if $p < 0.05$.

3.7. Correlations between compounds

Levels of PCBs and OCPs were significantly correlated in all species. This correlation was greatly influenced by CB 153, which constituted almost 20% of the total PCB load, and by *p*,*p*′-DDE, which contributed approximately for 50% to the total OCPs. Details of correlations between CB 153 and *p*,*p*′-DDE are given in Table 8. The high correlation between these compounds (mean $r > 0.93$; $p < 0.05$) indicates that they are likely to originate from the same source and that they represent the background pollution in this area; the presence of a point-source of one of the compounds is highly unlikely.

3.8. Geographical variation

In addition to the inter-compound correlation, there was also a significant correlation between contaminant levels and sampling locations. The BNS and the SE were considered as two separate areas, as it was more likely to find higher concentrations in the estuary than in the North Sea, where the impact of dilution is rather high. The Mann–Whitney *U*-test was applied to compare the mean concentrations of PCBs and OCPs in both areas. Only species of which more than 3 sampling locations for each area were available were included in the calculations. Of these species (crab, shrimp, sole, bib, and whiting), the difference in concentration between BNS and SE was statistically significant. It could be concluded that concentrations were clearly area dependent and that they were significantly higher in the SE for both PCBs and OCPs (Tables 3 and 5). Recently the same conclusions were drawn concerning levels of polybrominated diphenyl ether (PBDE) in biota from these two areas (Voorspoels et al., 2003).

Apart from the concentration difference between BNS and SE, a correlation was observed between pollutant concentration and the distance to Antwerp. Considering samples from location 7 to 16, a statistically significant inverse correlation between the distance to Antwerp and concentration was observed for both PCBs and OCPs (Table 9). This correlation was highly significant for both

Table 9
Correlation between concentration of PCBs/OCPs and distance to Antwerp

		PCBs		OCPs	
	N	*r*	*p*	*r*	*p*
Crab	8	0.8801	0.004	0.8778	0.004
Shrimp	9	0.8934	0.001	0.8727	0.002
Starfish	4	0.6697	0.330	0.7087	0.291
Goby	3	0.7857	0.425	0.7474	0.463
Plaice	4	0.8404	0.160	0.8095	0.191
Sole	7	0.8924	0.007	0.8186	0.024
Bib	6	0.8496	0.032	0.7675	0.075
Whiting	4	0.1676	0.832	0.1182	0.882

Note: only samples with $N > 3$ have been taken into account; significant if $p < 0.05$.

PCBs and OCPs in crab, shrimp, sole, and bib (r between 0.850 and 0.893; $p < 0.05$). For starfish, goby, and plaice, the correlation did not reach statistical significance. No correlation could be found for whiting samples. This can be possibly explained by the small sampling size of whiting combined with the lesser sedentary character of gadoids. The results of all other samples clearly indicated that pollution was higher more upstream. Recently the same inverse correlation with the distance to Antwerp was observed concerning PBDE levels in biota (Voorspoels et al., 2003). Although PCBs and OCPs are mostly banned products, the levels found in BNS and SE might reflect not only "historical" exposure, but also present contamination due to the vicinity of the highly urbanised and industrialised area of Antwerp.

3.9. Conclusion

Levels of PCBs and OCPs in benthic invertebrates and in benthic flatfish and gadoid liver samples from the BNS were comparable with those found in other parts of the North Sea. The same species sampled at various locations in the SE could be considered as highly contaminated.

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