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Congener-specific Data of PCBs in Some Species of Fish from the Gulf of Gdańsk, Baltic Sea

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Abstract

In 1992 a several species of fish were collected at Gdynia site from the western part of the Gulf of Gdańsk and analysed for polychlorinated biphenyls (PCBs). The results show that the actual concentrations of PCBs in fish from the southern part of the Baltic Sea are still relatively high and from 1700 to 11000 ng/g lipid weight was noted in the species such as flounder, eelpout, round goby, perch, pikeperch, sand eel, lamprey and cod.

Key words: Polychlorinated biphenyls, PCBs, fish, seafood, pollution, Baltic Sea.

Introduction

Polychlorinated biphenyls are a ubiquitous environmental toxins and become a synonym of synthetic chemicals considered to exert toxic effects in environmentally exposed marine mammals and human [1-3].

PCBs, PCNs, DDTs and dieldrin are still found in relatively high concentrations in biota from the Baltic proper, and those chemicals seem to be responsible for impaired reproduction observed in elderly pairs of white-tailed sea eagles nestling in coastal areas around the southern part of the Baltic proper [4-6]

Experimental Methods

Fish were collected at site Gdynia in the western part of the Gulf of Gdańsk in 1992. A pooled samples of a whole fish were subjected for analyses.

The samples were homogenised with an excess of anhydrous sodium sulphate, which was baked at 550°C for 2 days, and a powdered mixture was packed into a wide bore glass column (1-1.5 m x 4 cm i.d.). Before extraction a powdered mixture was spiked with [$^{13}C_{12}$] - labelled internal standards, consisting of 100 ng PCB no 80 and 200 ng PCB no 153. The samples were extracted with 500 ml mixture of acetone and *n*-hexane (2.5 : 1) and 500 ml mixture of acetone and diethyl ether (9:1) to obtain a fat extract. After evaporation of the solvents used for extraction, the residue was weighed to determine the amount of extractable lipids. Bulk lipid removal was performed by means of polyethylene film dialysis method [7]. By dissolving the

extracts in cyclopentane, dialysis through the polymeric membrane was accomplished by changing the outer cyclopentane (dialysate) after 12, 40 and 64 h. The three dialysate fractions, containing about from 1 to 20% of the original lipids, were combined and evaporated to a few ml. The extract was split into two parts of which 9/10 was used for analysis of planar contaminants not described here, and 1/10 was used for the analysis of PCBs. The 10% port of the extract was further fractionated by polarity on a glass column (40 cm x 10 mm i.d.) packed with 8 g of methanol-washed, activated (130°C, 48h) and deactivated (1.2% w/w water) Florisil gel [8]. The extract was eluted from the Florisil column with solvents of increasing polarity and collected in three fractions. The fraction 1 was eluted with 32 ml *n*-hexane and 38 ml 15% (v/v) methylene chloride in *n*-hexane, fraction 2 was eluted with 56 ml 50% (v/v) methylene chloride in *n*-hexane, and fraction 3 with 66 ml methanol. The PCBs were eluted in fraction 1 and 2, to which 30 μl tetradecane was added as a keeper before evaporation down to this volume. After the Florisil column, a recovery standard containing 100 ng [$^{13}C_{12}$]- labelled PCB no 101 and 200 ng of octachloronaphthalene was added to the final volume of 30 μl. PCB analyses were carried out by high resolution gas chromatography and low resolution mass spectrometry (HRGC/LRMS) using selected ion recording (SIR). The MS instrument used was a VG 12-250 coupled to a HP 5890 GC. A sample introduction was achieved by splitless injection at 250°C using helium as a carier gas. A PTE-5 capillary column (60 m x 0.32 i.d., 0.25 μm film thickness, Bellafonte, PA, USA) or a J & W DB-5, capillary column (60 m x 0.32 i.d., 0.25 μm film thickness, Folsom, CA, USA) was temperature programmed as follows: 180°C isothermal for 2 min, 15°C per min to 205°C, increase 2°C per min to 300°C. The ion source was kept at 250°C and operated under electron ionization (EI) conditions, and the MS was tuned in the SIR mode and the two most abundant ions in the chlorine cluster of the molecular ion were monitored. Isotopically labelled PCBs nos. 80 (internal standard) and 101 (recovery standard) were used for compensation of possible losses during the enrichment procedure.

Results and Discussion

Pentachlorobiphenyls (33-46%) and hexachlorobiphenyls (36-46 %), dependent on the species of fish examined, were dominating PCB homologue groups detected, while tri- (0-0.9 %), tetra- (5.5-11 %), hepta- (7.4-13 %), octa- (0.23-0.53 %) and nonachlorobiphenyls (0-0.05 %) were a minor constituents. Also decachlorobiphenyl was quantified in fish and its relative concentration ranged from <0.01 to 0.01 %.

An order of magnitude differences of the total PCB concentration when based on a lipid weight were found between fish investigated (Table 1). Cod (*Gadus morhua*), sand eel (*Heperoplus lanceolatus*) and lamprey (*Lampetra fluviatilis*) showed much lower concentration (from 1400 to 1700 ng PCBs/g lipid weight) then perch (*Perca fluviatilis*), round goby (*Neogobius melanostomus*), flounder (*Platychthis flesus*), pikeperch (*Stizostedion lucioperca*) and eelpout (*Zoarces viviparus*) (from 6400 to 11000 ng/g lipid weight). Since the variations in the lipids content between fish were relatively small (from 3.02 to 6.26 %), other factors then the lipids content itself are responsible for the differences observed.

There is no earlier congener-specific data on chlorobiphenyls in fish inhabiting the Gulf of Gdańsk. Eelpout caught in the western part of the Gulf of Gdańsk in 1986 contained in their muscle tissue total PCBs in concentration 110 ng/g wet weight (5200 ng/g lipid weight), and flounder caught in 1990 contained 210 ng/g wet weight (4400 ng/g lipid weight) [9].

Table 1

PCB concentrations in fish from the Gulf of Gdańsk (ng/g on a lipid weight basis)

PCB congener	Flounder 1(3)*	Eelpout 1(3)	Round goby 1(6)	Perch 1(8)	Pike-perch 1(3)	Sand eel 1(20)	Lamprey 1(3)	Cod 1(3)
PCB#19	ND	ND	ND	ND	ND	ND	ND	ND
PCB#15,18	ND	ND	ND	ND	ND	ND	ND	ND
PCB#17	ND	ND	ND	ND	ND	ND	ND	ND
PCB#27	ND	ND	ND	ND	ND	ND	ND	ND
PCB#16,32	ND	ND	ND	ND	ND	ND	ND	ND
PCB#26	ND	ND	ND	ND	ND	ND	ND	ND
PCB#25	ND	ND	ND	ND	ND	ND	ND	ND
PCB#28,31	21	ND	33	16	ND	15	7.1	0.87
PCB#33	ND	ND	ND	ND	ND	ND	ND	ND
PCB#22	ND	ND	ND	ND	ND	ND	ND	ND
PCB#53	1.7	ND	1.3	ND	1.2	1.1	ND	ND
PCB#51	0.73	ND	ND	0.21	0.37	0.20	ND	ND
PCB#45	0.89	0.69	0.60	0.41	0.77	0.51	ND	0.32
PCB#52	83	68	68	96	130	23	19	10
PCB#49	30	37	30	36	52	7.7	2.2	4.5
PCB#47,48	31	41	17	18	24	4.4	5.6	3.7
PCB#44	19	8.9	13	30	38	9.5	3.2	4.0
PCB#42	ND	5.6	ND	6.5	11	2.2	1.2	2.2
PCB#41,64,71,72	43	27	27	34	51	12	7.8	5.7
PCB#74	160	190	87	82	62	21	17	12
PCB#70,76	120	14	120	110	120	57	11	13
PCB#66	220	250	120	130	160	34	22	21
PCB#56,60	62	49	31	40	57	19	6.0	7.7
PCB#88,95	310	19	140	230	270	52	21	15
PCB#91	62	10	31	48	65	8.1	4.1	3.2
PCB#84,89,92	57	11	54	65	93	14	11	9.1
PCB#101	400	220	400	390	720	100	5.6	58
PCB#99,113	590	900	360	350	560	67	85	52
PCB#97	78	24	7.2	100	200	30	6.8	10
PCB#85	260	280	120	130	200	26	24	14
PCB#110	520	140	460	430	970	140	89	62
PCB#123	100	77	82	77	110	18	9.0	13
PCB#118	920	2000	630	570	1300	160	250	160
PCB#105,127	640	820	400	370	660	88	88	55
PCB#136,148	39	3.4	31	30	45	10	3.2	2.2
PCB#151	93	14	85	74	86	16	10	16
PCB#135,144	64	14	57	57	78	15	7.1	8.3
PCB#149	450	57	330	310	500	75	69	52

Table 1, continued

Table 1, cont'd

PCB congener	Flounder 1(3)*	Eelpout 1(3)	Round goby 1(6)	Perch 1(8)	Pike-perch 1(3)	Sand eel 1(20)	Lamprey 1(3)	Cod 1(3)
PCB#134,143	24	4.3	38	24	33	5.5	5.6	4.5
PCB#146	150	32	130	110	160	25	31	30
PCB#132,153	990	2300	730	610	1200	160	280	220
PCB#168	85	ND	100	96	170	25	12	11
PCB#141	42	26	33	53	98	11	8.7	7.7
PCB#138,160,163,164	1100	2000	790	640	1300	200	270	200
PCB#158	270	310	150	130	220	24	29	20
PCB#128	360	400	260	190	320	46	42	34
PCB#156	180	220	140	130	160	23	23	23
PCB#179	24	15	38	22	29	6.9	6.0	6.1
PCB#176	10	1.3	14	7.8	11	2.2	0.59	1.5
PCB#178	15	5.6	21	14	16	3.5	6.7	6.2
PCB#182,187	130	8.1	150	110	130	24	46	39
PCB#183	110	170	97	60	86	13	22	20
PCB#185	2.8	1.2	3.0	3.5	5.4	0.75	0.40	0.65
PCB#174	21	5.4	13	26	49	7.6	5.1	4.9
PCB#177	32	1.3	52	30	43	8.0	13	6.5
PCB#171	54	80	44	26	40	5.6	8.8	7.8
PCB#172,192	7.5	2.9	6.8	7.3	13	1.9	2.0	2.2
PCB#180	250	390	210	170	260	40	52	57
PCB#193	ND	ND	ND	ND	ND	2.5	ND	ND
PCB#191	7.9	10	7.2	4.5	9.8	1.3	1.2	1.3
PCB#170,190	120	160	79	70	130	17	19	19
PCB#202	4.2	8.9	7.1	4.8	4.8	1.0	2.5	3.0
PCB#200	2.3	1.3	4.2	2.1	2.6	0.52	0.92	1.1
PCB#197	1.3	2.8	1.5	0.84	0.96	0.19	0.46	0.56
PCB#199	0.97	2.3	1.2	1.1	1.4	0.43	ND	0.96
PCB#201	5.1	0.82	5.0	6.3	10	1.8	2.6	3.0
PCB#195	2.9	7.4	2.5	2.2	3.2	0.74	1.0	ND
PCB#194	4.8	9.6	6.4	4.4	7.5	1.5	1.7	2.3
PCB#206	0.90	1.9	0.92	0.90	1.8	0.21	0.40	0.65
PCB#209	0.16	0.33	0.16	0.14	0.29	0.02	0.14	0.13
Total PCBs	**9400**	**11000**	**6900**	**6400**	**11000**	**1700**	**1700**	**1400**
% Lipids	4.78	3.02	4.78	5.94	4.44	5.74	6.26	3.40

ND, not detected (< 0.5-15 ng/g dependent on homologue group and sample size)
*Number of samples and number of fish (in parantheses)

Fish from the Baltic proper usually contain total PCBs in higher concentration then the specimens from other areas of the North Atlantic Ocean Basin [10], however, till now there is no inventory of the sources, and also a net budget of those substances in a whole area of the Baltic proper is unknown.

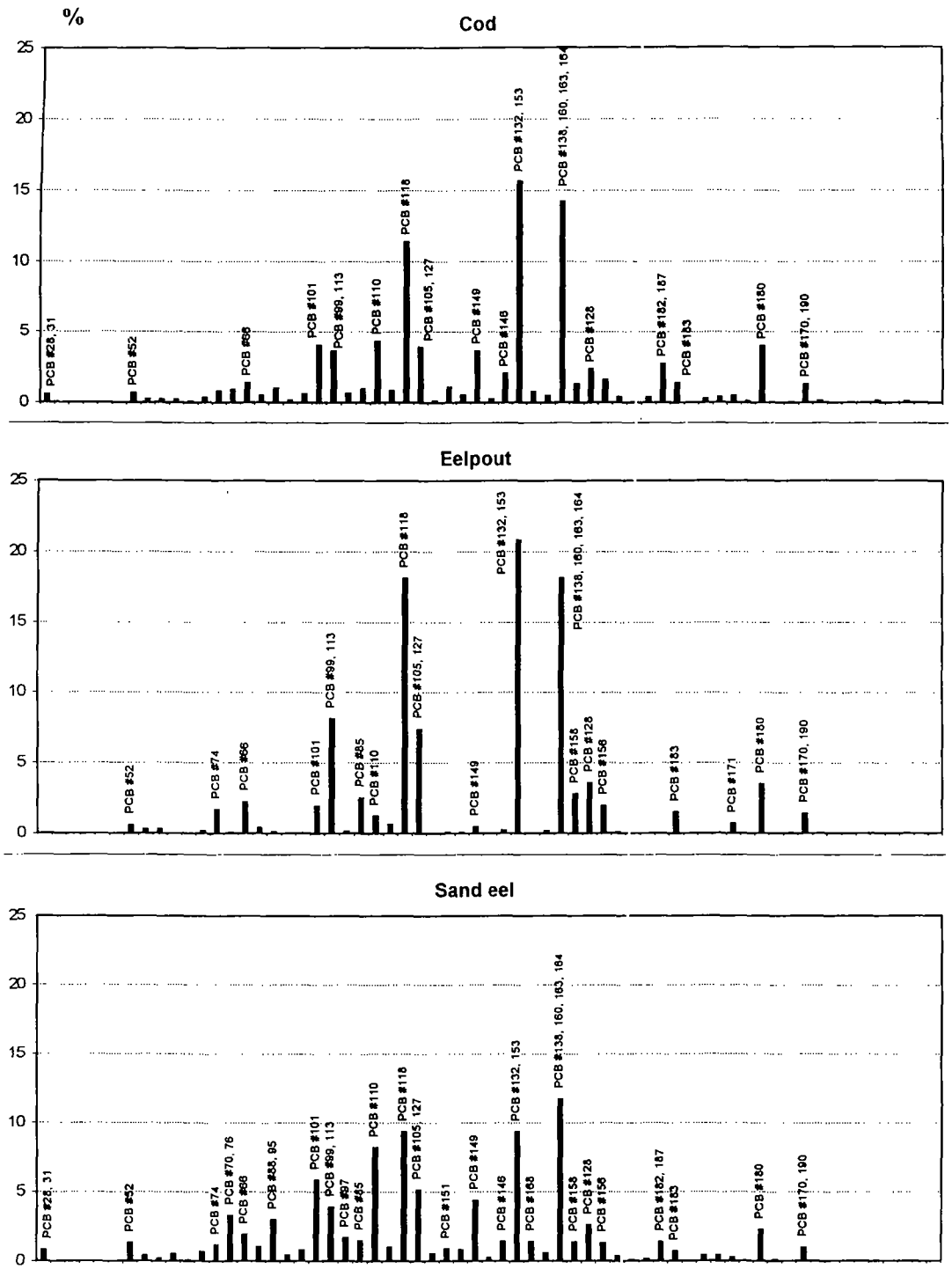

Figure 1. Pattern (%) of chlorobiphenyls in selected fish species.

Some differences could be observed in relative concentration (pattern) of the congeners of chlorobiphenyl between the fish examined (Figure 1). All fish in this study were caught at the same site using a fyke net, and only relatively young specimens were subjected for analysis. Nevertheless, some of the species examined are more or less migratory. An interspecies differences of the pattern of PCB residues found could be also related to some other factors and variabilities such as the enzymes activity, feeding behaviour, trophic niche.

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