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Chlorobiphenyls in Baltic Plankton

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Abstract

A congener-specific analysis of polychlorinated biphenyls in a mixed phyto- and zooplankton collected from four spatially distant sites in the southern part of the Baltic Sea (Gdańsk Depth, southern part of the Gotland Basin, Bornholm Basin and the Pomeranian Bay), revealed on higher concentration and a somewhat different pattern of those chemicals in two samples from the coast orientated sites when compared to those from the open sea. Because of the very similar fingerprint of PCBs in two an open sea plankton samples (Gotland Basin and Bornholm Basin) apart to the atmosphere also contaminated river water can be an important route of transportation and source, and especially of lower chlorinated chlorobiphenyl congeners in a specific areas (such as the Gdańsk Basin) in the southern part of the Baltic Sea.

Key words: Plankton, PCBs, chlorobiphenyls, pollution, Baltic Sea

Introduction

Polychlorinated biphenyls (PCBs) become widespread environmental pollutants, which bioaccumulate and biomagnify in trophic web. Due to relatively high vapour pressure PCBs like many other persistent organochlorines undergo a long-range atmospheric transportation and deposition on a global scale. A large number of chlorobiphenyl congeners of different physicochemical properties and persistency suggest differences in behaviour and environmental fate of those substances when released into the atmosphere. We studied whether there are differences in the concentrations and pattern of PCB residues in plankton collected from four spatially distant sites in the southern part of the Baltic Sea.

Experimental Methods

The samples of mixed phyto- and zooplankton were collected at four spatially distant sites in the southern part of the Baltic Sea during a research cruise of the R/V Oceania in September 1992. The details of the composition of mixed plankton samples collected are given elsewhere [1].

The method used for the determination of chlorobiphenyls is a part of a multiresidue procedure performed in parallel analysis of many organochlorines [2].The samples (77-219 g wet weight) 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). 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) [3]. 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 carrier 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

The HRGC/LRMS analysis revealed many congeners of congeners of chlorobiphenyl (Table 1). The lipid weight normalised concentration of the total PCBs in plankton ranged between 94 to 210 ng/g, and two samples collected from the open sea indicated lower concentrations (94-110 ng/g) then those collected at the coastal site (54°20′N; 14°40′E) in the Pomeranian Bay and also from the Gdańsk Depth (54°49′N; 14°20′E), which contained from 170 to 210 ng/g.

The two open sea plankton samples showed very similar pattern of PCB homologue groups, while plankton from the Pomeranian Bay and Gdańsk Depth contained in relatively high proportion tetrachlorobiphenyls and were free from the octachlorobiphenyls (Figure 1).
The phytoplankton communities indicate some species-specific differences in their bioconcentration potential of chlorobiphenyl congeners, and there is less variability for less

Table 1

PCB concentrations in mixed phyto- and zooplankton samples
from the southern part of the Baltic Sea (ng/g on a lipid weight basis)

PCB congener	Gdańsk Depth	Gotland Basin	Bornholm Basin	Pomeranian Bay
PCB#53	ND	ND	ND	ND
PCB#51	ND	ND	ND	ND
PCB45	ND	ND	ND	ND
PCB#52	4.4	ND	ND	ND
PCB#49	1.9	ND	ND	ND
PCB#47, 48	1.1	ND	ND	ND
PCB#44	2.1	ND	ND	ND
PCB#42	1.2	ND	ND	ND
PCB#41, 64, 71, 72	3.0	ND	ND	ND
PCB#74	2.3	ND	ND	1.5
PCB#70,76	6.6	ND	ND	4.3
PCB#66	4.8	ND	ND	2.9
PCB#56,60	4.7	ND	ND	ND
PCB#88, 95	4.0	3.9	2.8	5.4
PCB#91	0.61	0.51	ND	ND
PCB#84, 89, 92	1.3	0.97	1.0	1.5
PCB#101	10	7.3	6.7	11
PCB#99, 113	5.7	2.4	2.4	3.2
PCB#97	2.3	ND	ND	1.8
PCB#85	2.1	ND	1.2	ND
PCB#110	14	9.2	7.6	11
PCB#123	1.5	ND	ND	ND
PCB#118	16	ND	ND	9.0
PCB#105, 127	7.2	ND	ND	3.1
PCB#136, 148	0.88	0.86	0.69	1.8
PCB#151	1.8	1.5	1.8	3.6
PCB#135, 144	1.6	1.3	1.4	2.8
PCB#149	9.1	5.7	6.9	13
PCB#134, 143	0.78	1.4	1.5	1.3
PCB#146	3.4	ND	ND	ND
PCB132, 153	25	20	23	36
PCB#168	3.0	1.5	2.5	4.2
PCB#141	2.0	ND	ND	ND
PCB#138, 160, 163, 164	28	14	17	28
PCB#158	1.9	ND	ND	ND
PCB#128	5.6	ND	ND	ND
PCB#156	3.3	ND	ND	ND
PCB#179	1.2	0.95	1.0	2.3

Table 1, c.d.

Table 1, cont'd

PCB congener	Gdańsk Depth	Gotland Basin	Bornholm Basin	Pomeranian Bay
PCB#176	0.44	ND	ND	0.89
PCB#178	0.93	2.8	2.5	1.5
PCB#182, 187	4.4	2.4	4.1	7.5
PCB#183	2.0	1.1	1.4	2.3
PCB#185	0.23	ND	ND	ND
PCB#174	1.9	1.1	1.9	1.4
PCB#177	1.5	0.76	1.5	2.2
PCB#171	1.0	2.7	3.0	ND
PCB#172, 192	0.42	ND	0.33	ND
PCB#180	8.8	4.3	6.4	7.8
PCB#193	ND	ND	ND	ND
PCB#191	0.23	ND	ND	ND
PCB#170, 190	3.2	1.5	2.2	ND
PCB#202	ND	2.9	2.4	ND
PCB#200	ND	ND	ND	ND
PCB#197	ND	ND	ND	ND
PCB#199	ND	ND	ND	ND
PCB#201	ND	2.5	1.8	ND
PCB#195	ND	ND	ND	ND
PCB#194	ND	ND	ND	ND
PCB#206	ND	ND	ND	ND
PCB#209	ND	ND	1.1	ND
Total PCBs	**210**	**94**	**110**	**170**
% Lipids	1.85	1.10	0.84	1.08

chlorinated/hydrophobic members [4]. Since all the plankton samples studied consisted both of phyto- (in relatively small proportion) and zooplankton, the variability of the pattern of chlorobiphenyls doesn't seem to be related to the composition of the plankton itself.

A suggestion was made that similarity in the relative concentrations and pattern of the homologue groups and the congeners of chlorobiphenyl, and also of other organochlorines in plankton from sites distant from the sources of local pollution indicate on the atmospheric deposition as a major source of PCB contamination [5-7]. A different pattern of PCBs in two "coastal" plankton samples, and especially for the Gdańsk Depth site, seem to indicate that apart to the atmosphere, the source of chlorobiphenyls can be related to the Vistula River and the Firth of Vistula River. The Gdańsk Depth is a natural area of sedimentation for the suspended matter transported by the Vistula River. The plankton collected at the Gdańsk Depth site apart to higher proportion of more water soluble tetrachlorobiphenyls (Figure 1), when compared to the samples from three other sites also contained in relatively higher proportion a less hydrophobic tetrachloronaphthalenes [8], and too greater concentration of DDTs [9], what additionally supports the hypothesis that the differences observed are related to the Vistula River and/or a military complex of Baltijsk, a base situated at the Pilawska Strait connecting the Firth of Vistula with the Gulf of Gdańsk. The Gulf of Finland was identified as a local source of PCBs in Baltic water [10].

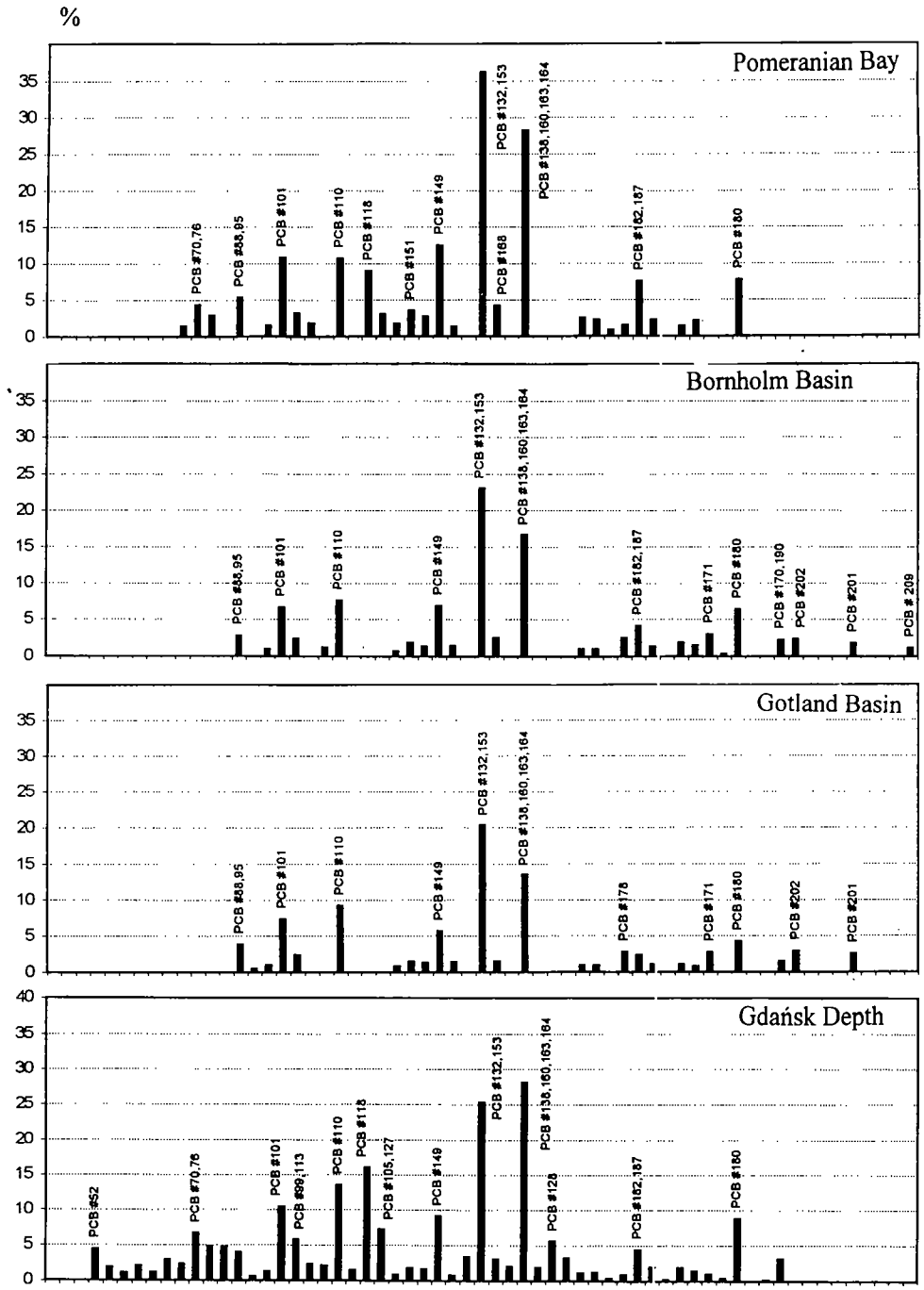

Figure 1. Pattern (%) of chlorobiphenyls in plankton from the southern part of the Baltic Sea.

Acknowledgements

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