Levels of coplanar and non-coplanar polychlorinated biphenyls (PCB) in eel and sediment samples from Berlin/Germany

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Introduction

Since polychlorinated biphenyls proved to be of environmental importance, great efforts have been made to determine them in nearly every compartment of the environment, especially those which could possibly influence the human nutrition.
The city of Berlin has a population of nearly 3.5 million and covers an area of 889 km^2. 58 km^2 (6,4%) consists of rivers, lakes and man-made channels. The main waterways are the rivers Spree, Dahme and Havel, which can be characterised as slow-flowing, lowland rivers with shallow lakes of a depth between 3 to 5 metres. The intense use of the water system leads to a high ecological pressure. In the past a survey programme has been executed to determine the 6 most common indicator-PCB (No. 28, 52, 101, 138, 153 and 180) in fish and sediment samples in the area of Berlin since 1983. Due to the discussion of certain PCB congeners as "dioxin-like compounds"[1], some congeners have been added to the "classic" monitoring programme in 1995 and 1996. (co-planar PCB, IUPAC-No. 77, 126, 169; mono-ortho-PCB No. 105, 114, 118, 123, 156, 157, 167; di-ortho PCB No. 170). In 1996 PCBs were measured in 58 eel and 50 sediment samples. Furthermore the compounds musk xylene, musk ketone, the polycyclic musk compounds HHCB, AHTN,ADBI, Bromocyclen and organophosphorous esters have been analysed within the programme. These results will be discussed elsewhere.[2)]
Synthetic halogenated compounds, esp. PCBs, were produced in high quantities in Germany until their ban in 1989 (75,000 tons in the former FRG; 13,000 tons in the former GDR). The substances were used in paints, printing inks, elastic building sealants, oils of transformers and hydraulic fluids.

Material and Methods

In 1996 58 eel samples (Anguilla anguilla) and 50 sediment samples from Berlin waters have been analysed for the PCB-congeners given above. The sampling and preparation of the fish has been performed by the Berlin fishing authority (Fischereiamt) according to German guidelines.

Preparation and clean-up of the fish samples

The fresh eel samples were filleted, skinned and stored frozen at -20°C until analysis.
10g of the homogenised fish sample has been ground with glowed sea sand and 10g of water free Na_2SO_4 to form a free floating powder. It has been extracted by Soxhlet-extraction using Cyclohexane/Ethylacetate. The extracts have been evaporated to a defined volume and an aliquot used for a further clean-up step by means of a gel permeation column (Biobeads SX3) and a silica column. The cleaned extracts were used for analysis.
The lipid content was determined gravimetrically in an aliquot of the extract.

Preparation and clean-up of the sediment samples

The sediments have been freeze-dried according to German sewage sludge ordinance (Klärschlammverordnung) and extracted by Soxhlet extraction, using Toluene. The extracts have been evaporated and cleaned/fractionated using silica and alumina columns in order to separate interferences. The cleaned extracts were used for analysis.

Analysis for Polychlorinated Biphenyls (PCB)

The analysis took place using a mixture of ^{13}C-labelled internal standards which have been added prior to extraction. The PCBs have been separated by HRGC (Fisons 8000) with a DB-XLB column (60m, 0.32 mm iD, 0.25 µm dF) using splitless injection mode. Determination has been performed by HRGC/HRMS with a Micromass Autospec Ultima MS in EI SIM mode with a resolution ≥ 10,000 in order to gain detection limits of about 0.01 µg/kg especially for the coplanar congeners.

PCB in	eel samples [µg/kg fw]					sediment samples [µg/kg dw]				
#	mean	SD	min.	max.	TEQ	mean	SD	min.	max.	TEQ
PCB 77	0,084	0,075	0,005	0,316	0,042	1,45	1,77	0,015	7,21	0,726
PCB 126	0,354	0,301	0,021	1,6	35,4	0,130	0,114	0,005	0,443	13,0
PCB 169	0,387	0,383	0,011	2,09	3,87	0,087	0,083	0,005	0,272	0,867
PCB 105	43,4	40,9	1,4	187	4,34	3,84	3,87	0,062	17,1	0,384
PCB 114	5,39	4,95	0,18	22	2,70	0,392	0,367	0,005	1,49	0,196
PCB 118	201,4	191,6	6,3	851	20,1	15,1	13,8	0,256	56,2	1,51
PCB 123	7,08	6,31	0,3	28,3	0,708	1,39	1,35	0,02	5,12	0,139
PCB 156	34,3	31,4	1,1	159	17,2	3,84	3,31	0,043	10,8	1,92
PCB 157	4,80	4,38	0,18	21,7	2,40	0,584	0,496	0,005	1,82	0,292
PCB 167	25,8	22,9	0,74	101	0,258	2,31	2,01	0,028	6,3	0,023
PCB 170	63,1	40,2	2,6	190	6,31	9,64	8,11	0,062	31,6	0,964
PCB 28	25,3	23,0	1,5	100	n.c.	6,83	8,69	1	35	n.c.
PCB 52	49,3	43,5	2,5	170	n.c.	5,19	5,25	1,5	18	n.c.
PCB 101	65,2	47,1	3	190	n.c.	11,1	10,5	1	38	n.c.
PCB 138	227,3	147,1	12	630	n.c.	30,7	26,9	1	101	n.c.
PCB 153	202,9	124,9	13	560	n.c.	31,3	26,1	1	92,9	n.c.
PCB 180	91,1	61,4	5	250	0,911	19,6	17,0	1	66,5	0,196
Total [Σ]	1049		51,3	2493	94,192	143		7.5	370	20,245
					Coplanar PCB: percentage 41,7%					Coplanar PCB: percentage 72,2%
					Mono-ortho PCB: percentage 50,6%					Mono-ortho PCB: percentage 22,1%
					di-ortho PCB: percentage 7,7%					di-ortho PCB: percentage 5,7%

Table 1: PCB contents in eel and sediment samples and mean TEQ-values

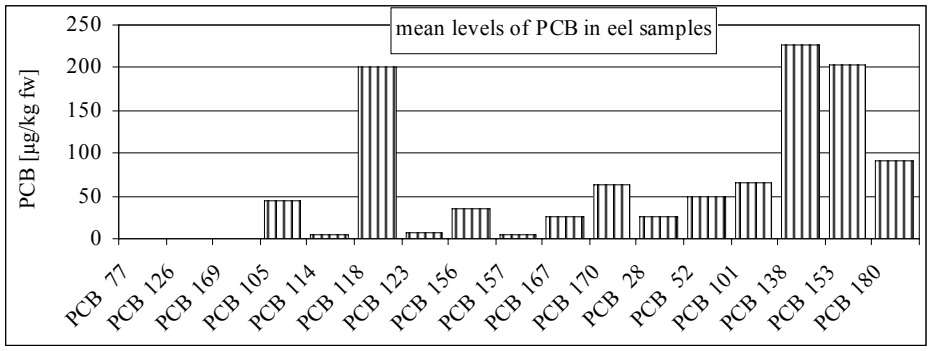

Figure 1: PCB levels in eel samples

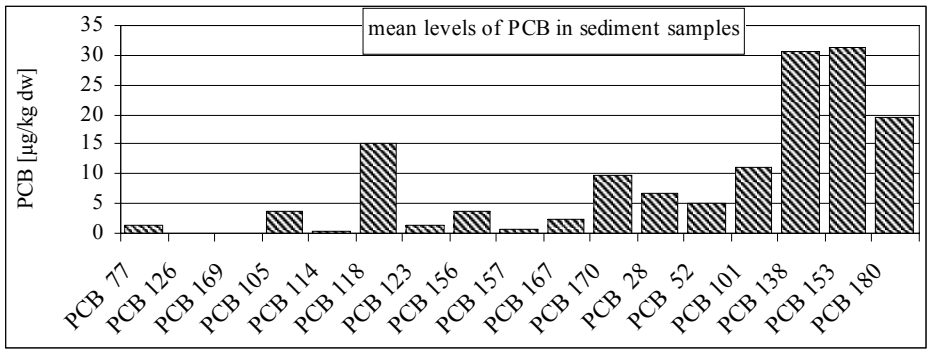

Figure 2: PCB levels in sediment samples

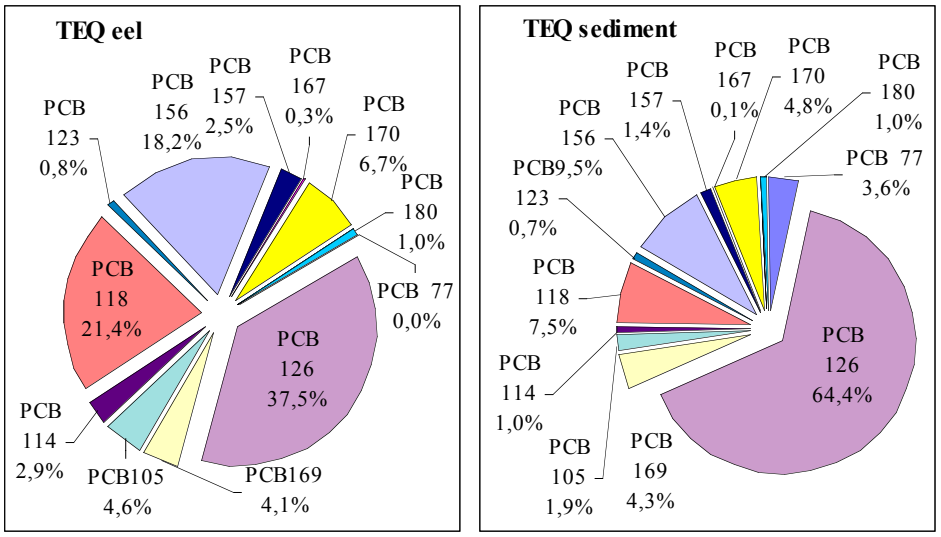

Figure 3: PCB-TEQ distribution in eel and sediment samples

Results and Discussion

In the present study the mean values of total PCBs obtained in eel samples varied from 1227µg/kg fw. or 119 pgTEQ/g in a highly polluted area (hpa) and 340 µg/kg fw. or 49 pgTEQ/g for a slight polluted area (lpa). For sediment samples the sum of total PCBs varied between 203 µg/kg dw (hpa) and 47 µg/kg dw (lpa). In table no 1 the mean levels and standard deviation (SD) of the single PCB congeners examined in eel and sediment samples are summarised together with calculated values for the toxic equivalent factors (TEQ)[3].

In the eel samples nearly 60% of the total PCB comprised of PCB 118, 138, and 153. Except for PCB 28, 153, 170 and the three non-ortho substituted compounds, a significant correlation was found between fish and sediment samples. Furthermore we obtained the same congener patterns between sediment and eel samples. Only PCB 118 shows a slight higher concentration in eel than in sediment.

The eels used for PCB analysis had a mean weight of 250 g (71.5-724 g), a mean length of 50 cm (35-69 cm) and a mean fat content of 19.1 % (1.8-40.8 %). A correlation between the fat content and the concentration of PCBs was found.

Until today only few data are published for coplanar PCBs in eel and sediment samples[4)5)6)]. The values of the presented study fit well into the frame the literature is showing, when it is remembered that the environmental conditions under which fish exist are strongly varying. Even in the same urban region the state of the water is varying from place to place, a condition which directly affects the eels.

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