Chlorinated Hydrocarbons in Eels (*Anguilla anguilla* L.) from the River Rhine

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Polychlorinated biphenyls (PCBs) and other chlorinated hydrocarbons were detected in the environment only long after the onset of their production. Due to their high persistence and widespread distribution, PCBs, DDT, and their metabolites can be detected in different environmental compartments even after production has ceased [1]. Through bioaccumulation and bioconcentration residues are found in body lipids and organs of fish [2–4], and animals at high trophic levels (e.g., fish-eating mammals such as otters) are thought to be negatively affected [5].

In this paper we report on the concentrations of selected chlorinated hydrocarbons in eels from the High Rhine. In earlier quantitative analyses, either only the total PCB concentration was determined without reporting on individual congeners [6, 7], or only little data have been reported on particular sites [8]. As the congeners show different physical, chemical, and toxicological characteristics depending on

their degree of chlorination and structure congener-specific data are needed. Here, concentrations of some selected PCB congeners are given and compared with data from 1984 [8] to detect trends. The results indicate a still considerable degree of contamination.

Nineteen eels were caught near the hydroelectric power plant Rheinsfelden-Eglisau, Switzerland (Fig. 1). Ten eels were caught along the right bank of the river, and nine along the left bank, below the mouth of the River Glatt. This river, flowing through the urban agglomeration of Zurich, is polluted by

contaminants of anthropogenic origin. The fish were caught by electroshocking on May 14, 1990, and transported live in an oxygenated container to Saarbrücken, FRG. A filet of about 8 cm long was cut from each fish around the base of the dorsal fin for residue analyses performed at the Zentrum für Umweltforschung (Universität des Saarlandes).

The following substances were determined: α - and β -hexachlorocyclohexane (HCH), lindane, dieldrin, hexachlorobenzene (HCB), DDT and its metabolites DDE and DDD, PCB con-

Fig. 1. The High Rhine between Lake Constance and Basel. The sampling site near Eglisau, Switzerland, just below the mouth of the River Glatt, is marked by an arrow

genera 28 (trichlorobiphenyl), 52 (tetrachlorobiphenyl), 101 (pentachlorobiphenyl), 138 and 153 (hexachlorobiphenyls), and 180 (heptachlorobiphenyl) as defined by Ballschmitter and Zell [9] and IUPAC. The analytical procedure employing capillary gas chromatography was used as described in [10].

The concentrations measured are given in Table 1 and Fig. 2 and are compared to statutory German [11] and Swiss [12] maximum allowable concentrations (MAC). Concentrations of HCH and HCB are near the detection limit in all 19 eels, and by a factor 5 to 200 below the MAC values (Fig. 2). β -HCH values always exceed those of α -HCH. Dieldrin and lindane were detected in

small quantities: 0.002 to 0.040 mg/kg for dieldrin and 0.003 to 0.040 mg/kg for lindane, both being clearly below MAC values of 1.0 and 2.0 mg/kg, respectively. Whereas residues of HCH are similar, HCB residues are lower than those reported for eels in the Upper and High Rhine during 1976–1981 [7].

Table 1 gives average concentrations of DDT and its metabolites, individual PCB congeners and total PCB content of the 19 eels that were divided into three size groups. Contents of DDT and its metabolites (Σ DDT) between individual fish range between 0.065 and 0.750 mg/kg and remain clearly below the German MAC value of 3.5 mg/kg. Eels of the size group 50.5–81.5 cm

show a significantly higher concentration (ANOVA, Fisher PLSD test, $p < 0.05$) of Σ DDT than those belonging to the size group 32–40 cm. Eel DDT residues (Σ DDT) tend to be slightly lower than 1976–1981 [7].

Of the PCB congeners congeners 52, 101, 138, 153, and 180 were quantified, whereas congener 28 could not be detected. The hexachlorobiphenyls 138 and 153 show the highest concentrations, but heptachlorobiphenyl 180 is also abundant (Table 1). The concentrations of the congeners 101 and 52 are markedly lower. The total PCB content was estimated with congeners 138, 153, and 180 using the formula given in [13]. The total PCB content between individual fish varies between 0.58 and 5.30 mg/kg wet weight. The data also indicate a tendency towards higher concentrations in larger (older) fish for congeners 52, 101, and 138, however, this cannot be proved statistically (Fig. 3). Also, no significant, positive correlation could be found between total PCB and fat content (ANOVA). The two longest and heaviest eels show high values (Σ PCB 5.3 and 4.6 mg/kg). The Swiss MAC value for Σ PCB (1.0 mg/kg for the edible part of fish) was exceeded in all but four eels. Notably, all fish that had reached the legal catching size of 50 cm exceeded the Swiss MAC value (Fig. 3). Five eels exceeded the German MAC value for PCB 138 and 153, three fish the value for congener 180. No difference was found in the PCB and pesticide contamination of eels caught on the right or left bank of the Rhine.

Comparison of the present PCB data with those of previous studies on fish from the River Rhine [6, 7] is hindered because different sample treatment and analytical methods were employed. However, they can be compared with those given in [8] and those of Krüger and Kruse [14] who used the same analytical procedures. Eels from the River Rhine and its tributaries were reported in 1984 to contain PCB residues (individual congeners and total PCB) only slightly higher than those determined here [8]. Table 2 shows that the DDE and DDD contamination in eels from the High Rhine is higher than in other rivers except for eels from the Elbe at Lauenburg which were more contaminated [14]. Also, average contents of PCB congeners 138, 153, and 180 in

Table 1. Concentrations of selected PCBs and chlorinated hydrocarbons (in mg/kg wet weight), biometric data, and maximum allowable concentration (MAC) values [11, 12] for three size groups of eels

Length [cm]	32.0–40.0		40.5–50.0		50.5–81.5		MAC-value
Substance	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	CH
DDE	0.101	0.071	0.117	0.06	0.215	0.124	
DDD	0.016	0.004	0.036	0.029	0.093	0.064	
DDT	0.039	0.028	0.063	0.053	0.093	0.049	
Σ DDT	0.156	0.097	0.217	0.131	0.407	0.241	3.5
PCB 52	0.007	0.004	0.014	0.012	0.030	0.019	0.2
PCB 101	0.022	0.013	0.043	0.027	0.051	0.031	0.2
PCB 138	0.163	0.1	0.179	0.088	0.325	0.183	0.3
PCB 153	0.169	0.095	0.183	0.089	0.294	0.172	0.3
PCB 180	0.088	0.079	0.084	0.05	0.148	0.095	0.2
Σ PCB	1.59	1.05	1.68	0.83	2.85	1.65	1.0
	4.20	2.11	6.86	3.82	14.07	8.46	
	70.3	18.2	154.1	18.8	509.3	293.4	
	36.6	2.6	46.4	1.5	63.5	10.6	
	7		6		6

Fig. 2. Average concentrations $\pm$ SD ($n = 19$) of hexachlorocyclohexane (HCH, sum of α - and β -HCH), hexachlorobenzene (HCB), dieldrin, and lindane. Measured concentrations are partly near the detection limit (0.005 mg/kg wet weight)

Fig. 3. Correlation between total PCB content and fish length. Eels of similar length show considerable differences in contamination. Regression: $y = 0.063x - 1.014$, $r^2 = 0.356$

Table 2. Comparison with data from [14], using the same analytical methods. Concentration in mg/kg wet weight (n.d. = not detected)

	High Rhine (present study)	Elbe (Lauenburg)	Ems (Meppen)	Hase (Meppen)	Aller (Gifhorn)	Lutter (Südheide)	Dümmer Lake
<i>n</i>	19	11	11	15	6	9	19
Length [cm]	48.2	49.9	32.8	32.8	47.5	48.2	45.8
Weight [g]	235.4	259.0	60.9	63.4	215.0	218.0	166.0
Fat [%]	8.2	9.9	12.2	15.1	14.1	9.1	8.2
α-HCH	0.004	0.047	0.005	0.007	0.003	0.003	0.002
HCB	0.004	0.344	0.037	0.011	0.007	0.009	0.003
Lindane	0.016	0.066	0.109	0.032	0.013	0.006	0.005
DDE	0.142	0.155	0.091	0.040	0.061	0.035	0.013
DDD	0.048	0.202	0.036	0.017	0.030	0.022	0.009
PCB 28	n.d.	n.d.	0.025	0.011	0.004	0.003	n.d.
PCB 52	0.016	0.020	0.060	0.018	0.070	0.006	0.002
PCB 101	0.038	0.030	0.037	0.017	0.094	0.006	0.004
PCB 138	0.219	0.061	0.160	0.095	0.152	0.031	0.021
PCB 153	0.213	0.065	0.156	0.099	0.186	0.042	0.026
PCB 180	0.106	0.029	0.062	0.042	0.061	0.020	0.013

eels from the High Rhine were reached by no other group.

This study shows that higher residue concentrations occur for higher chlorinated PCB congeners (in particular congeners 138 and 153) than for less chlorinated congeners, similar to data reported for eels in 1984 [8]. Congener 28 could not be detected at all. A similar distribution of congeners was found in salmonids of Lake Ontario (Canada). There, congener 153 occurred in highest concentrations, and

the penta- and hexachlorobiphenyls showed higher values than the heptachlorobiphenyls [3]. Oliver and Niimi [4] showed in the food chain of Lake Ontario that the chlorine content of PCBs increased with trophic level, and that less chlorinated congeners dominated in water. Other studies revealed that congeners 101, 138, 153, and 180 (as detected in our study) together with congeners 95, 110, 118, 149, and 187, were prevalent in animals such as bivalves, fish, penguins, and whales from

several sites in the USA, Canada, Europe, and the Antarctic [15]. In the blood of fish consumers from Wisconsin (USA), the congeners 118, 138, 153, and 180 were most frequent [16], and in human adipose tissue the congeners 99, 138, 153, 170, and 180 dominated [17]. Coplanar PCBs (congeners 77, 126, 169) are generally the most toxic congeners, followed by the mono-ortho analogs and the di-ortho analogs of the coplanar PCBs [18]. Breams (*Abramis brama* L.) from the River Saar near Völklingen, FRG, showed a different distribution in that less chlorinated PCBs dominated [14]. This was probably caused by the application of PCBs with a low boiling temperature in the mining industry. However, other PCB sources account for the fish residues at the sampling site in the River High Rhine.

The present study shows that the PCB contamination of eels in the River Rhine can still be significant (highest measured value 5.3 mg total PCB/kg wet weight). Further studies using larger sample sizes and standard analytical methods are needed to further substantiate concentrations and distribution of the different PCB congeners in other fish species. In particular, emphasis should be placed on the quantification of the highly toxic coplanar congeners, rather than only estimating total PCB levels.

We thank K. E. Krüger (Universität des Saarlandes) for help with the analysis, and W. Giger (EAWAG) for reading the manuscript.

Received November 18, 1991 and March 9, 1992

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