DIOXIN-LIKE PCB, INDICATOR-PCB AND PCDD/PCDF IN DIFFERENT FISH SPECIES FROM STREAMS AND RIVERS IN BAVARIA, SOUTHERN GERMANY

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Introduction

Persistent organic chemicals enter streams, rivers and lakes via treated and untreated sewage as well as by surface runoff. Another route of entrance is direct atmospheric deposition of such pollutants, which are semivolatile and thus prone to atmospheric long-range transport. Among these contaminants, dioxin-like and non-dioxin-like polychlorinated biphenyls (PCB) and polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) are of special relevance due to their strong biomagnification within aquatic food chains and to high toxicity of a number of congeners. Thus, fish are suitable bioindicators for the environmental contamination with these ubiquitous pollutants. In recent years, several studies were published regarding levels of dioxin-like PCB and PCDD/PCDF in marine fish but less is known about the contamination of fresh water fish with these substances. In the state of Bavaria in southern Germany, different wild freshwater fish species have been used as bioindicators for many years. They have been analyzed annually for heavy metals and persistent organic pollutants such as hexachlorobenzene and non dioxin-like indicator PCB. The main purpose of this long-term monitoring program of the Bavarian Environment Agency is the evaluation of spatial distribution, time trends and species dependency of the pollution of freshwater ecosystems with persistent contaminants. Within this framework, the monitoring program was extended to dioxin-like PCB and PCDD/PCDF in 2002 and 2003. Predominantly barbel *(Barbus barbus)* as a benthic and location-faithful fish species with medium fat content was investigated. Where barbel was not caught, common bream *(Abramis brama)* or other species were subject for analysis. Another focus was on eel *(Anguilla anguilla)* because this species strongly accumulates lipophilic contaminants due to its high body fat content. Eel samples were analyzed from all five sites of the river Main in northern Bavaria and from all other rivers where eel was caught.

Materials and Methods

Wild freshwater fish was caught in Oct. 2002 and 2003 in Bavarian streams, rivers and lakes of different size. The sites were either background sites or close to outlets of municipal or industrial wastewater treatment plants. Each year, a subset of 45 samples from 35 of 49 monitoring sites from all seven Bavarian districts was analyzed. Skinless fillets of one body side of either single or composites of several individuals were homogenized and stored below –20 °C.

Samples were freeze-dried and extracted by accelerated solvent extraction with toluene at 175 °C and 14 MPa. After addition of all 17 2,3,7,8-substituted PCDD and PCDF as well as 12 dioxin-like PCB according to WHO and six indicator PCB (congeners 28, 52, 101, 138, 153, 180) as $^{13}C_{12}$-labelled standards the fat mass was determined. Clean-up, separation of PCDD/PCDF from PCB and fractionation of PCB was performed as described elsewhere[1]. Laboratory blank samples were analyzed in parallel for quality control. PCDD/PCDF and PCB fractions were analyzed by high resolution capillary gas chromatography coupled with high resolution mass spectrometry (HRGC/HRMS). Gaschromatographic separation was performed on a 60 m DB-XLB capillary column. Toxicity equivalent concentrations (TEQ) were calculated using the WHO-TEFs[2]. For congeners with a concentration below the limit of quantification (signal to noise value of 10:1 of the mass used for quantification), TEQ values were calculated with half of the limit of detection (signal to noise value of 3:1 of the quantification mass).

Table 1: Median, minimum and maximum concentrations based on fresh weight (fw) of indicator PCB (sum of congeners 28, 52, 101, 138, 153, 180), dioxin-like PCB and PCDD/F in eel and other fish species from Bavarian streams and rivers.

	2002						2003					
	Eel (n = 20)			other species (n = 25)			Eel (n = 17)			other species (n = 28)		
	median	minimum	maximum	median	minimum	maximum	median	minimum	maximum	median	minimum	maximum
Sum 6 indicator PCB [µg/kg fw]	**160**	**25.8**	**824**	**28.6**	**1.86**	**425**	**264**	**28.1**	**575**	**12.4**	**1.88**	**116**
PCB 105 [µg/kg fw]	6.54	0.720	26.1	0.744	0.021	9.25	9.39	0.92	21.8	0.278	0.030	2.33
PCB 114 [µg/kg fw]	0.322	0.022	1.45	0.039	0.005	0.464	0.411	0.054	1.10	0.017	0.002	0.128
PCB 118 [µg/kg fw]	19.9	2.75	90.9	2.37	0.196	27.3	28.8	2.83	64.8	0.844	0.109	8.34
PCB 123 [µg/kg fw]	1.20	0.203	4.96	0.254	0.006	2.74	1.58	0.251	3.95	0.093	0.014	0.924
PCB 156[µg/kg fw]	4.64	0.728	22.1	0.704	0.043	12.1	5.56	0.531	13.1	0.238	0.013	3.87
PCB 157 [µg/kg fw]	0.742	0.146	3.41	0.116	0.004	1.79	0.925	0.075	2.25	0.043	0.002	0.384
PCB 167 [µg/kg fw]	2.63	0.416	14.9	0.484	0.021	7.50	3.92	0.472	8.78	0.194	0.012	1.38
PCB 189 [µg/kg fw]	0.515	0.091	2.46	0.114	0.003	1.80	0.766	0.070	1.60	0.045	0.004	0.603
Sum mono-ortho PCB [µg/kg fw]	**36.1**	**5.08**	**159**	**4.95**	**0.341**	**63.0**	**50.5**	**5.21**	**114**	**1.73**	**0.208**	**15.9**
PCB 77 [µg/kg fw]	0.023	0.005	0.414	0.047	0.006	0.877	0.023	0.008	0.093	0.025	0.001	0.286
PCB 81 [µg/kg fw]	0.002	0.001	0.024	0.002	0.0003	0.050	0.001	0.0005	0.007	0.001	0.0002	0.011
PCB 126 [µg/kg fw]	0.137	0.027	0.494	0.015	0.001	0.161	0.152	0.032	0.274	0.004	0.0002	0.046
PCB 169 [µg/kg fw]	0.024	0.003	0.061	0.002	0.0003	0.020	0.021	0.004	0.036	0.0004	0.0001	0.003
Sum non-ortho PCB [µg/kg fw]	**0.208**	**0.038**	**0.591**	**0.067**	**0.007**	**0.968**	**0.193**	**0.044**	**0.409**	**0.031**	**0.002**	**0.345**
PCB-TEQ (1/2 NG) [ng/kg fw]	**20.7**	**3.61**	**75.0**	**2.20**	**0.15**	**27.7**	**24.2**	**3.95**	**42.8**	**0.79**	**0.07**	**7.13**
% PCB 126 of PCB-TEQ	**66.9**	**52.1**	**84.7**	**68.6**	**45.1**	**93.5**	**67.4**	**46.4**	**80.2**	**62.0**	**13.5**	**75.9**
PCDD/F-TEQ [ng/kg fw]	**1.13**	**0.35**	**2.72**	**0.28**	**0.04**	**1.72**	**1.32**	**0.38**	**3.48**	**0.18**	**0.06**	**0.87**
Total-TEQ [ng/kg fw]	**23.3**	**4.60**	**77.7**	**3.33**	**0.182**	**28.7**	**26.3**	**4.58**	**46.3**	**1.51**	**0.13**	**8.00**
% PCB-TEQ of total TEQ	**94.5**	**87.8**	**96.5**	**88.4**	**60.8**	**97.7**	**92.7**	**86.4**	**98.8**	**81.2**	**22.4**	**95.0**

Results and Discussion

Median, minimum and maximum concentrations of the sum of six indicator PCB, of four non-ortho and eight mono-ortho substituted dioxin-like PCB and PCB TEQ as well as PCDD/F TEQ measured in eel and other fish species from 2002 and 2003 are shown in table 1. PCB and PCDD/F levels in eel were similar in samples from both years. PCB and PCDD/F levels in other fish species were lower in samples from 2003 but sample numbers analyzed for each species were not identical in both years. PCB and PCDD/F concentrations based on fresh weight (fw) were generally much higher in eel than in all other species due to the high fat content of eel.

No fish sample exceeded the maximum permitted PCDD/F value of 4 pg WHO-TEQ/g fw set by the European Commission for the muscle meat of fish which is intended for human consumption[3]. PCDD/F levels in eel were similar to those in eel caught from Bavarian rivers and lakes between 1992 and 1995[4]. PCDD/F concentrations in other species were lower than reported values for fish caught from 1992 to 1995.

In all fish samples analyzed the TEQ values of dioxin-like PCB exceeded the PCDD/F TEQ by about a factor of ten. In all species the non-ortho congener PCB 126 contributed by about two third to the PCB TEQ. While the contribution of dioxin-like PCB to total TEQ was rather constant in eel with a range of 86 to 99 % there was some variation in the TEQ ratio in other fish species.

Total TEQ levels (PCB + PCDD/F) in eel samples were in the range of 4.6 – 78 pg TEQ/g fw in 2002 and between 4.6 and 43 pg TEQ/g fw in 2003 with median values of 23 and 26 pg TEQ/g fw, respectively. Thus, most eel samples would exceed the future PCB+PCDD/F limit value of 12 pg total TEQ/g fw set by the European Commission for the muscle meat of eel intended for human consumption that will be implemented by November 4, 2006[5]. The highest levels of dioxin-like PCB (and of PCDD/F) were found in eel samples from the river Main, a major tributary of the river Rhine. Total TEQ levels were comparable to those found in eels from the middle course of the river Elbe near Gorleben (km 493) caught in September 2002[6].

Total TEQ levels in samples from barbel, bream and other fish species were in the range of 0.18 – 29 pg TEQ/g fw in 2002 and between 0.13 and 8.0 pg TEQ/g fw in 2003 with median values of 3.3 and 1.5 pg TEQ/g fw, respectively, and thereby on average about one order of magnitude lower than levels found in eel. Two barbels from 2002 would exceed the future limit value of 8.0 pg total TEQ/g fw set by the European Commission for the muscle meat of fish except eel intended for human consumption while one barbel caught in 2003 was exactly at that limit[5]. The levels of dioxin-like PCB and PCDD/F found in muscle meat of bream (n = 7) caught in 2003 were lower than those measured by the Federal Environmental Agency in bream (pool samples) from German rivers caught in the same period[7].

The congener pattern of non-ortho substituted PCB in eels was clearly different from those found in all other fish species. Figure 1 shows that in muscle meat from eel the concentration of PCB 126 was about 6 times higher than levels of PCB 77 and PCB 169 which were similar. In contrast, PCB 77 had the highest concentration in muscle meat from the other species, often about one order of magnitude higher than the level of PCB 126 which itself was about a factor of ten higher than PCB 169.

Although fish from streams and rivers in southern Germany is not of primary importance for human nutrition, the detected concentrations of dioxin-like PCB indicate the need of further reduction of environmental levels and human exposure, at least as a precautionary measure.

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References

1. Kerst M, Waller U, Peichl L, Bittl T, Reifenhäuser W, Körner W. *Fres Environ Bull* 2003;12:511.
2. Van den Berg M, Birnbaum L, Bosveld ATC, Brunström B, Cook P et al. *Environ Health Persp* 1998;106: 775.
3. European Commission. Council Regulation (EC) No 2375/2001 amending Commission Regulation (EC) 466/2001, 2001.
4. Mayer R. *Organohalogen Comp* 2002;57:181.

5. European Commission. Council Regulation (EC) No 199/2006 amending Commission Regulation (EC) 466/2001, 2006.
6. Stachel B, Götz R, Herrmann T, Krüger F, Knoth W, Päpke O, Rauhut U, Reincke H, Schwartz R, Steeg E, Uhlig S. *Water Science & Technology* 2004;50:309.
7. Schröter-Kermani C, Herrmann T, Päpke O, Stachel B. *Organohalogen Comp* 2004;66:1779.

Figure 1: Median congener profiles of non-ortho substituted PCB in fish from Bavarian streams and rivers.