PCDDs, PCDFs, and Dioxin-like PCBs in Breams (Abramis brama) from German Rivers: Results from the German Environmental Specimen Bank

Christa Schröter-Kermani[1], Thomas Herrmann[2], Olaf Päpke[2], Burkhard Stachel[3]

[1]Federal Environmental Agency, Berlin
[2]ERGO Forschungsgesellschaft mbH, Hamburg
[3]Wassergütestelle Elbe der Arbeitsgemeinschaft für die Reinhaltung der Elbe, Hamburg

Introduction

In July 2002 a new regulation of the European Commission came into force setting maximum permitted values for PCDD/Fs in food[1]. Until the end of 2004 these limit values have to be verified with current monitoring data, especially in regard to the integration of dioxin-like PCBs in this regulation. It is well known that fish accumulate lypophilic substances to a high degree from their aquatic surroundings so that fish and fish products are an important source of human intake of dioxins.

Several studies have been published recently regarding the contamination of marine fish species with PCDD/Fs and dioxin-like PCBs[2,3], but less is known about the contamination of fresh water fish with these substances. To bridge this gap, the German environmental specimen bank (ESB)[4] analyzed archived bream muscle samples for PCDD/Fs and dioxin-like PCBs.

Breams are widely distributed in Europe and often used as a monitoring organism for fresh water and sediment contamination because of their small migration radius[5]. As adult breams feed mainly on benthic invertebrates they are permanently in direct contact with the sediments.

Although bream is less consumed at least in Germany the here presented results might facilitate general statements regarding the contamination of other fresh water fish species with PCDD/Fs and dioxin-like PCBs.

Methods and Materials

Samples. Breams (*Abramis brama*) are caught annually after spawning in August/September. At least 20 fish with an age between 8 to 12 years are taken at each sampling site and their muscles are pooled. Collection and processing is performed under well defined and reproducible conditions according to standard operating procedures[6]**.** The material is stored as a fresh homogenized and grinded powder in sub-samples of approx. 10 g in the vapor phase above liquid nitrogen. Sampling areas are the rivers Rhine, Saar, Danube, the river Elbe with the tributaries Mulde and Saale, and Lake Belau as a nonpolluted reference area[7]. The sampling sites are shown in Fig.1.

Analysis. Sample aliquots ranging between 10 g and 30 g fresh weight material (representing approx. 0.5 g of lipids) were homogenized with sodium sulphate and a column extraction by means of cyclohexane/dichloromethane (v:v, 1:1) was done. Before extraction, a mixture of ^{13}C-labelled internal standards (17 2.3.7.8 substituted PCDDs/PCDFs, 4 non-ortho PCBs and 8 mono-ortho PCBs) was added to the sample. All ^{13}C-labelled internal standards were delivered by Cambridge Isotopes Laboratories (USA) or Wellington Laboratories (Canada). After solvent evaporation gravimetric lipid determination was performed. A multicolumn clean-up including silica gel, differently treated silica gel (H_2SO_4-SiO_2, CsOH-SiO_2), activated carbon and alumina oxide followed. $^{13}C_{12}$-1.2.3.4-TCDD and $^{13}C_6$-1.2.3.4.6.7.8- Hepta-CDF were added to the final extract as recovery standards.

The measurement was performed by HRGC/HRMS on a HP 5890 II GC coupled with a Micromass AutoSpec mass spectrometer (ionisation mode: Electron impact (EI), resolution: 10,000). A DB 5 column (60 m) was used for gas chromatographic separation. Quantification was done by means of isotope dilution method using a five-point calibration.

TEQ data were calculated by using WHO-TEFs and by taking into account the whole detection limit for non-detected compounds (upperbound procedure).

Quality control. For quality control a blank and an ESB-pool of bream muscles was run with each batch of ten samples. Relative standard deviation for TEQ-data of 14 ESB-pool samples (analyzed from day-to-day) was found to be 12% for PCDDs, 10% for PCDFs, 18% for non-ortho PCBs and 11% for mono-ortho PCBs. As further quality control measure certified standards were analyzed.

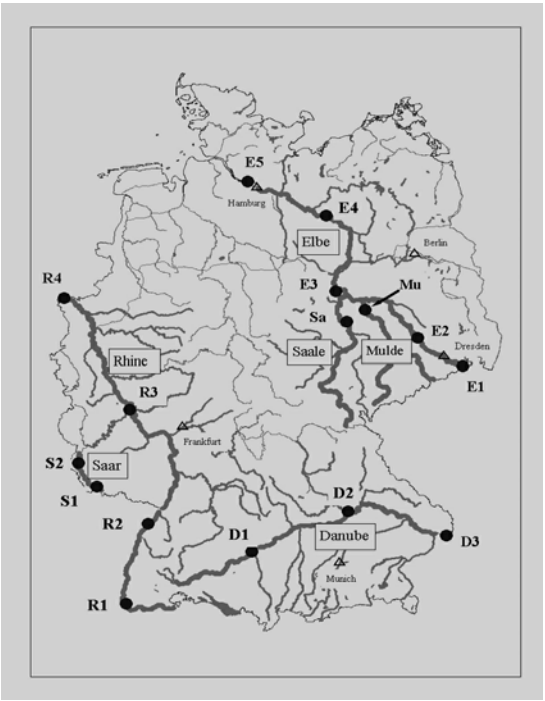

Fig.1: Sampling sites of breams.
River Elbe: E1 - Prossen (km 13), E2 - Zehren (km 93), E3 - Barby (km 296), E4 - Cumlosen (km 470), E5 – Blankenese (km 632); River Mulde: Mu – Dessau (mouth); River Saale: Sa – Wettin; River Rhine: R1 – Weil (km 174), R2 – Iffezheim (km 334), R3 – Koblenz (km 590), R4 – Bimmen (km 865); River Saar: S1 – Güdingen, S2 – Rehlingen; River Danube: D1 – Ulm (km 2.593), D2 – Kelheim (km 2.404), D3 – Jochenstein (km 2.210).

Results and Discussion

Current PCDD/F and dioxin-like PCB concentrations, expressed as WHO-TEQs, in muscle of breams are given in Table 1. The concentrations of PCDD/Fs in breams from German rivers differ by more than one order of magnitude, ranging from 0.5 to 6.7 pg WHO-PCDD/F-TEQs /g wet weight (ww). In contrast, bream from the reference site Lake Belau is by a factor 10 less contaminated than fish from the lowest polluted river sampling site (Danube – Ulm).
Obviously no correlation between fat content of breams and PCDD/F levels can be established. However, within the river systems Elbe, Rhine, and Danube higher levels of PCDD/F-TEQs on a wet weight basis seem to be associated with higher lipid content of fish.

Table 1. WHO-TEQ levels of PCDD/Fs and dioxin-like PCBs in bream muscle. Sampling year 2003, except Danube: 2002 and Lake Belau: 2001.

Sampling sites	**Fat**	**PCDD/Fs**	**Dioxin-like PCBs**	**Total**
	%	**pg TEQ /g wet weight (lipid weight)**		
River ELBE				
E1 – Prossen, km 13	2.7	1.6 (59)	5.2 (192)	6.8 (251)
E2 – Zehren, km 93	1.6	1.7 (105)	6.8 (427)	8.5 (532)
E3 – Barby, km 296	2.5	2.6 (104)	5.1 (208)	7.7 (312)
E4 - Cumlosen, km 470	1.8	1.7 (94)	2.7 (146)	4.4 (240)
E5 – Blankenese, km 632	4.7	4.1 (88)	4.1 (88)	8.2 (176)
River SAALE				
Sa - Wettin	3.0	0.9 (31)	5.7 (189)	6.6 (220)
River MULDE				
Mu – Dessau (mouth)	2.4	1.9 (83)	2.3 (96)	4.2 (179)
River RHINE				
R1 – Weil, km 174	6.6	5.4 (82)	11 (167)	16 (249)
R2 – Iffezheim, km 334	4.8	3.0 (63)	12 (244)	15 (307)
R3 – Koblenz, km 590	2.6	1.1 (44)	4.0 (153)	5.1 (197)
R4 – Bimmen, km 865	6.7	6.7 (100)	17 (247)	23 (347)
River DANUBE				
D1 – Ulm, km 2.593	2.1	0.5 (22)	3.8 (179)	4.3 (201)
D2 – Kelheim, km 2.404	2.6	0.7 (26)	4.6 (175)	5.3 (201)
D3 – Jochenstein, km 2.210	5.3	2.0 (37)	12 (226)	14 (263)
River SAAR				
S1 - Güdingen	3.5	1.4 (42)	22 (631)	23 (673)
S2 - Rehlingen	4.6	1.7 (37)	27 (582)	29 (619)
Lake Belau	0.8	0.06 (8.2)	0.8 (99)	0.86 (107)

The concentrations of dioxin-like PCBs (ranging from 2.3 to 27 pg WHO-PCB-TEQs /g ww) exceed the PCDD/F levels in nearly all bream samples from German rivers. The ratio of PCB-TEQs to PCDD/F-TEQs runs from about 1 (Elbe – Blankenese, Mulde – Dessau) and 8 (Danube – Ulm) to 16 (Saar - Güdingen). From these results it is evident that there is no correlation between PCDD/F levels and PCB levels in fish.
Bream samples from three sampling sites (Elbe – Blankenese, Rhine – Weil and Bimmen) showed PCDD/F levels that exceed the maximum permitted value of 4 pg WHO-TEQ /g ww set by the European Commission for the muscle meat of fish which is intended for human consumption[1].
In consideration of the WHO-TEQ levels of dioxin-like PCBs all investigated bream samples from German rivers achieve or even exceed the European Commissions limit value.

Eels (*Anguilla anguilla*) from the middle course of the Elbe near Gorleben (km 493) caught in September 2002 showed WHO-PCDD/F&PCB-TEQ values in the range of 11 to 56 pg/g ww in muscle[8]. The median value of 29 pg/g ww in eels is more than a factor 3 above the concentrations of ΣWHO-TEQ measured in bream.
However, it has to bear in mind that especially eels are nomadic by nature, so that the contaminants found may have accumulated in the eels under investigation at a location different to the one where they were caught.
Analysis of white fish samples, originating from sites in the upper course of the river Elbe (km 0-83) and caught in October 2002 yielded in ΣWHO-TEQ values in the range of 2.2 to 7.2 pg/g ww. These concentrations are comparable or even lower than those found in breams from similar sampling sites.

References

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