LEVELS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN LIVERS OF BREAMS (*ABRAMIS BRAMA*) FROM THREE RIVERS OF GERMANY

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Introduction

To monitor contamination of limnic and marine ecosystems with persistent organic contaminants such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F), fish can be used as a biological indicator. Its potential for that purpose was demonstrated by several monitoring studies[1]. Within the scope of the German Environmental Specimen Bank breams (*Abramis brama*) were caught from different sampling sites along the german parts of the rivers Elbe, Rhine and Saar. This species has a minimal migration radius compared to other freshwater fish and is present along the whole rivers. Adult breams are carnivorous feeding on benthic invertebrates, mostly mussels and oligochaetes. Because of that, they are in permanent direct contact with the sediments.

Livers of breams from the year 1997 were analysed for PCDD/F with special attention to the pattern of the 2,3,7,8-substituted congeners and their changes along the rivers. Also the TEQ values were calculated, applying the common used I-TEF (NATO/CCMS) and the new groups of TEF released by the WHO in 1998[2].

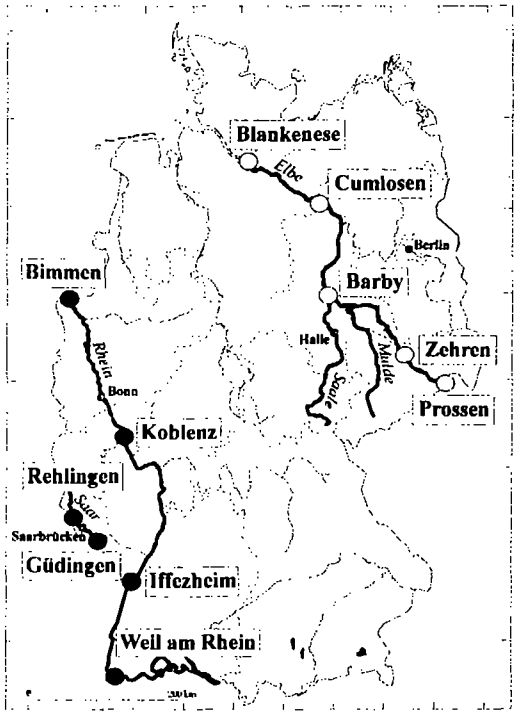

Fig. 1: Sampling locations at the rivers Elbe, Rhine and Saar

Methods and Materials

The fish were collected, prepared and stored according to the standard operation procedures of the German Environmental Specimen Bank[3]. The samples were taken between July and October 1997 from the german rivers Elbe, Rhine and Saar. The sampling locations are shown in figure 1. The age of the fish are from 8 to 12 years. Samples were analysed as homogenated pools (n=15-55). For PCDD/F analysis the thawed homogenisates were ground with sea sand and anhydrous sodium sulphate and filled in a glass column. Prior to extraction they were spiked with ^{13}C-labeled

standards.The clean-up procedure shown in figure 2 was applied to the extracts. The instrumental analysis was performed with a high resolution mass spectrometer

(Finnigan MAT 95S) coupled with an HP GC 6890. Chromatographic separation was achieved by splitless injection (cold on column injector KAS4, Gerstel, Germany) of 1 µl on a Restek Rtx-2330 column (60 m, ID 0.25 mm, ft 0.1 µm). The GC oven was programmed as follows: 90°C initial hold for 1.5 min, increase at a rate of 25°C/min to 180°C followed by an increase of 2°C/min to 260°C, final hold at 260°C for 15 min. The MS was operated in SIM mode at a resolution of 10000 and the two most intense ions of the molecular ion cluster were monitored for the unlabeled and labeled isomers.

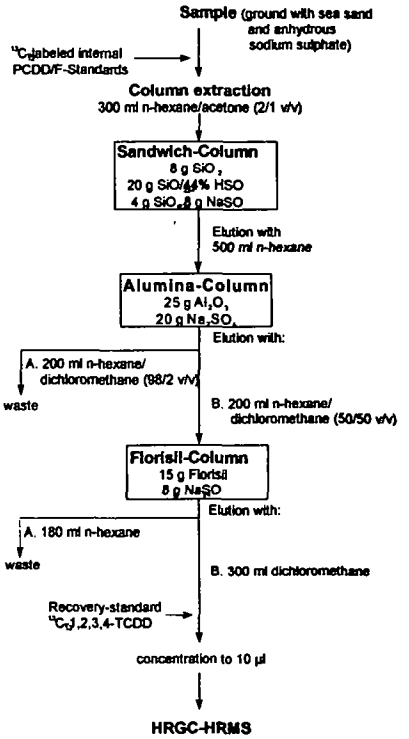

Fig. 2: Clean-up procedure for the bream livers

Results and discussion

In table 1 the analysed TEQ values are listed. They are calculated for the wet material and, for a better comparison, on the base of the extracted fat.

At the river Elbe a little increase for the TEQ levels from Prossen, near the border to the Czech Republic, to Barby, located downstream the inflow of the river Saale, can be observed. Whereas the sampling site Prossen reflects the contamination coming from the czech part of the Elbe, Zehren the influence of the conurbation of Dresden and Barby the loadings of the rivers Saale and Mulde, which are running along the industrial areas of Leipzig, Halle and Bitterfeld. At Cumlosen, near the border to the former German Democratic Republic and downstream of the river Havel, the highest TEQ value at the river Elbe is found. Blankenese is located directly downstream the Hamburg harbour, where the lowest contamination was measured.

Tab. 1: TEQ levels of the bream livers and their fat contents

	TEQ (NATO/CCMS		TEQ (WHO Humans)		TEQ (WHO Fish)		TEQ (WHO Birds)		
	pg/g w.w.	pg/g fat	pg/g w.w.	pg/g fat	pg/g w.w.	pg/g fat	pg/g w.w.	pg/g fat	% fat
Prossen	4.8	57.3	5.2	62.0	4.7	55.6	16.5	196.6	8.4
Zehren	4.1	69.0	4.3	71.0	3.8	63.5	14.8	246.8	6.0
Barby	4.0	72.2	4.2	76.4	3.8	68.9	13.4	243.3	5.5
Cumlosen	7.9	162.0	8.4	171.2	7.6	155.9	26.0	530.1	4.9
Blankenese	3.1	63.9	3.3	67.4	3.0	62.0	9.9	202.8	4.9
Weil am Rhein	40.8	261.5	58.0	372.1	57.1	366.1	81.1	519.7	15.6
Iffezheim	9.2	95.4	11.4	118.7	10.9	113.7	24.5	254.7	9.6
Koblenz	6.8	85.6	7.8	98.7	7.2	91.5	20.1	254.5	7.9
Bimmen	14.5	160.7	15.6	172.9	14.7	162.8	36.0	399.9	9.0
Güdingen	2.4	35.8	2.6	39.2	2.3	34.9	9.1	135.6	6.7
Rehlingen	3.3	41.1	3.6	44.0	3.1	37.7	14.5	178.7	8.1

Looking at the pattern of the 2,3,7,8-substituted PCDD/F in the liver of the breams from the river Elbe (Fig. 3) a continous change from Prossen to Cumlosen can be observed, especially for the dibenzofurans. Relative to the 2,3,7,8-TCDF the amounts of 1,2,3,7,8-PeCDF, 1,2,3,4,6,8- and 1,2,3,6,7,8-HxCDD are increasing. At Blankenese the pattern is nearly the same as for Cumlosen, but the concentrations in all are lower.

At the river Rhine, the contamination of the breams are relatively high after it crossed the border between Switzerland and Germany near Weil am Rhein, not far away from the industrial area of Basel. The TEQ levels at Iffezheim, representing the upper course of the Rhine, and Koblenz, after the inflows of the rivers Main and Mosel, are much lower. At Bimmen, downstream of the industrial area of the Ruhr and at the border to the Netherlands, the TEQ values are nearly doubled again. Weil am Rhein is the only sampling site where the amount of the 2,3,7,8-TCDF is not the highest of all 2,3,7,8-substituted congeners. Here the PCDD congeners are more dominating, especially the 1,2,3,7,8-PeCDD. At Iffezheim a touch of this PCDD pattern could still be seen, but the concentrations are much lower. The difference between Koblenz and Bimmen is the higher amount of 2,3,7,8-TCDD, which is mainly responsible for the higher TEQ value at Bimmen. Between the sampling sites Güdingen and Rehlingen the conurbation of Saarbrücken is located. It seems to have an influence on the PCDD/F levels downstream, but the observed increase is not very significant.

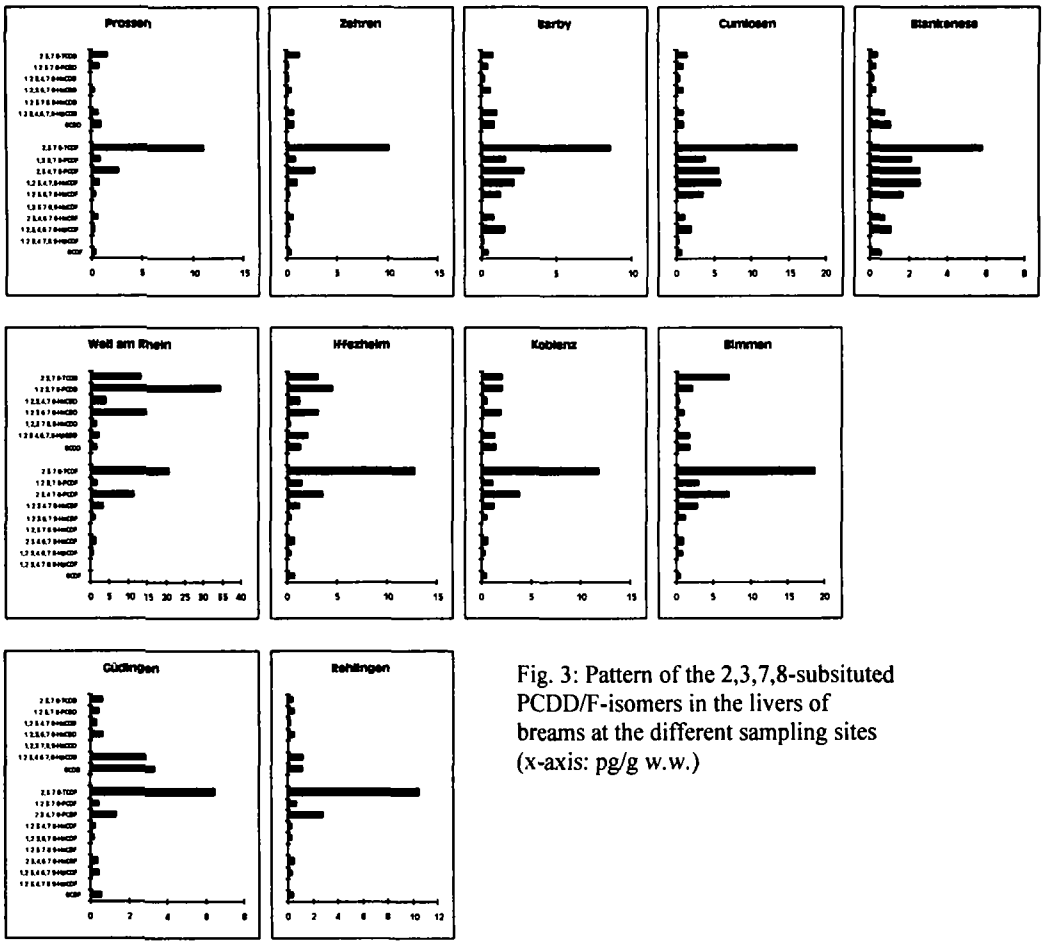

Fig. 3: Pattern of the 2,3,7,8-subsituted PCDD/F-isomers in the livers of breams at the different sampling sites (x-axis: pg/g w.w.)

In table 1 not only the common used I-TEQ (NATO/CCMS) are listed, but also the TEQ calculated with the toxic equivalents factors (TEF) released by the WHO for the different organisms. For the river Elbe and Saar the differences between the I-TEQ and the WHO-TEQ for humans (increase) and fish (decrease) are not very high. This is different to the corresponding values of the river Rhine. Here always a higher TEQ is calculated by applying the WHO-TEF, especially for the sampling site Weil am Rhein the value increases about 40%. This is caused by the TE factor for the 1,2,3,7,8-PCDD, the dominating congener in this sample, which is 1 in the WHO instead of 0.5 in the I-TEQ system.
A 2 to 3 times higher TEQ is calculated when using the WHO-TEF for birds. The reason for this is, that the factor for the 2,3,7,8-TCDF changes from 0.1 to 1. In all samples, except Weil am Rhein, the highest amounts were detected for this congener.

References

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