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Dioxins and dioxin-like PCBs in different fish from the river Elbe and its tributaries, Germany

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Abstract

In a long-term program polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) as well as dioxin-like polychlorinated biphenyls (DL-PCBs) were analyzed in the muscle tissue of eels (*Anguilla anguilla*), bream (*Abramis brama*), European chub (*Leuciscus cephalus*) and ide (*Leuciscus idus*) from the river Elbe and its tributaries Mulde and Saale. The variation of the PCDD/F and DL-PCB concentrations in all fish samples is very large, whereby the DL-PCBs predominate in comparison to the PCDD/Fs. In the eels, the concentrations (pg WHO-TEQ/g ww) for the PCDD/Fs lie in the range of 0.48–22 and for the DL-PCBs between 8.5 and 59. In the whitefish, the concentration range is 0.48–12 for the PCDD/Fs and 1.2–14 for the DL-PCBs. Statistical analysis using relative congener patterns for PCDD/Fs allow spatial correlations to be examined for sub-populations of eels and whitefish. The results are compared to the maximum levels laid down in the European Commission Regulation (EC) No. 466/2001 and the action levels of the European Commission Recommendation 2006/88/EC. Eels caught directly after the major flood in August 2002 as well as eels near Hamburg (years 1996 and 1998) show high concentration peaks. Compared to the eels whitefish is less contaminated with PCDD/Fs and DL-PCBs.

Keywords: Dioxins; Dioxin-like PCBs; Fish; Elbe

1. Introduction

With a length of 1091 km and a catchment area of 148268 km^2, the river Elbe is one of the largest rivers in Central Europe. Its source lies in the Riesengebirge mountain range of the Czech Republic, from where it flows to the North Sea, enter-

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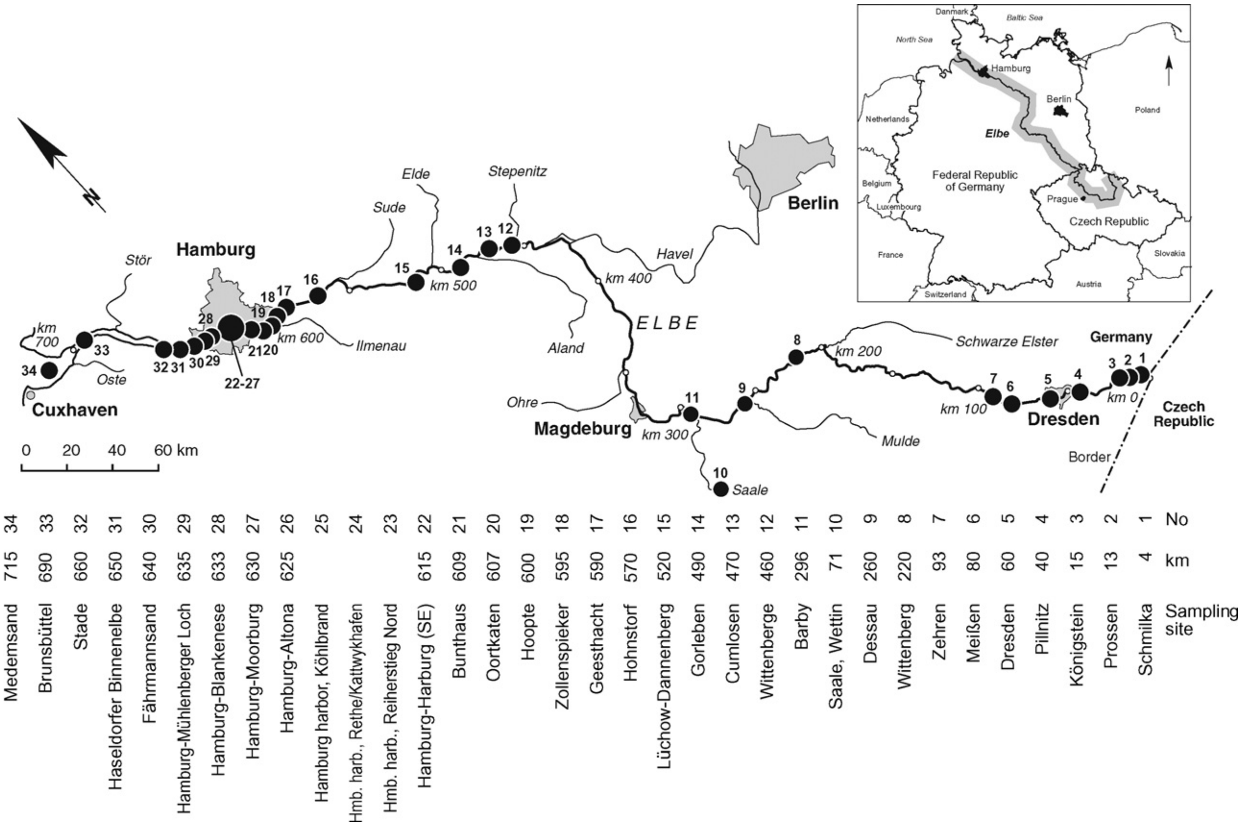

Fig. 1. Locations and stream-km, where eels, bream, ide and European chub were caught in the Elbe, Mulde and Saale.

ing it at Cuxhaven in the Federal Republic of Germany. About one-third of the length is in the Czech Republic and two-thirds in Germany (Fig. 1). After the political reunification of East and West Germany many large chemical plants in the former German Democratic Republic (GDR) were shut down, mainly for economic reasons, and numerous sewage treatment works (STW) were built or significantly improved. Funds from the European Community and the Federal Republic of Germany were invested in construction and improvement schemes. As a result of this the water quality has recovered considerably and the number of fish species found in the river has increased from 79 counted in the years 1991–1993 to 104 recorded in 2005. Even salmon (*Salmon solar*), which had not been seen in the Elbe for decades, spawning in the small tributaries of the upper part of the river again [1]. Commercial fishing has recommenced in the Elbe on a small scale, whereby marketing restrictions still have to be enforced on account of food quality regulations, particularly in respect of certain organic contaminants.

The improvements in the ecology are confirmed by findings for many different compounds like nutrients or heavy metals [2], but the situation remains problematical. The treated waste water from industrial and municipal STWs as well as pollutants from industrial sites of the former GDR (Bitterfeld-Wolfen) contains a wide range of hazardous and potentially hazardous compounds which are transported into the Elbe, polluting suspended particulate matter (SPM), sediments, soils, feeding-stuffs, foodstuffs and the aquatic fauna [3–15].

The aim of this paper is to provide an overview of the contamination situation with respect to PCDD/Fs and DL-PCBs in different fish species from the river Elbe and its tributaries Mulde and Saale. After the flood event in August 2002, public attention was focused on the release of these pollutants into the aquatic environment. The question arose as to the extent to which contaminants accumulated in fish on account of the increased contaminant levels caused by the flood. In this study, the results of PCDD/Fs and DL-PCBs in the muscle tissue from eels (*Anguilla anguilla*) and the three whitefish species bream (*Abramis brama*), European chub (*Leuciscus cephalus*) and ide (*Leuciscus idus*) are presented and discussed. The fish data were subjected to statistical analysis and the results are discussed here. Further, the results are evaluated in the light of the European Commission Regulation (EC) No. 199/2006 [16] and the European Commission Recommendation 466/2001/EC [17].

2. Materials and methods

The use of selected indicator fish species constitutes a means of obtaining information to assess general environmental levels and trends, the health of the ecosystem, the quality of fish on the market and the possible exposure of humans to contaminants, and health risks. In recognition of this, the investigation of different fish species from the Elbe began in 1984 [18] and has continued to 2005.

In a long-term program in the Elbe and its tributaries Mulde and Saale four different fish species were investigated. The choice of the species depended on their natural behavior in the different ecosystems and their differing propensities for accumulating lipophile contaminants in their muscle tissue. Eels (*A. anguilla*) do not spawn during their residence in European waters, and exhibit behavior which differs from that of other fish species. Further, eels accumulate PCDD/Fs and DL-PCBs in their muscle tissue very readily because it contains a high proportion of fat. For this reason they are well suited for use in monitoring programs. Moreover, the eel is a popular foodstuff and therefore represents a potential health hazard to consumers.

The three species bream (*A. brama*), European chub (*L. cephalus*) and ide (*L. idus*) were chosen as representatives of whitefish species for the purposes of the study. Their behavior is quite different from that of the eels: they exhibit differing degrees of mobility and their habitats differ from an ecological point of view. Whereas the ide and the European chub are considered to be nomadic and rheophile, i.e. preferring flowing waters, the bream is a carp-like still water fish known for its tendency to remain in one place. Lühmann and Mann [19] obtained that the bream's mobility is normally limited to a range of up to 20 km. In view of its relatively small radius of action the bream is suitable for passive monitoring purposes and can be assumed, on the whole, to reflect a local contamination situation quite faithfully. The carp-like mouth enables the bream to select sedimentary benthic organisms from the substrate. All three species are omnivorous.

For the program composite samples and individual fish were analyzed. The composite samples describe the mean concentrations of a batch and are used for monitoring when comparing the results for many years. Concentration peaks from single fish are suppressed in the mixed samples, but these items of data are of importance for an evaluation with reference to existing maximum levels or action levels. The monitoring program is designed to address both questions.

2.1. Sampling

Eels were caught in creels or in static nets. The use of a static net is an efficient method catching eels in deep and wide rivers like the Elbe, whilst the European chub, bream and ide were obtained using static nets or by means of electrofishing. The sampling periods differed for the various fish species: eels were caught from April to June. Choosing spring time greatly reduces the likelihood of catching silver eels, which are not representative for the monitoring. The whitefish species were caught after spawning in August and September. Fig. 1 shows the locations on the Elbe and its tributaries Mulde and Saale where the fish were caught. Until they were analyzed the samples were either preserved using liquid N_2 at −196 °C [20] or frozen at −22 °C. Both individuals and composite samples of muscle tissue were analyzed.

2.2. Analyzed compounds and analytical methods

2.2.1. Compounds

PCDD/Fs and PCBs are organic compounds that exhibit potential risks for human health. The most toxic dioxin, 2,3,7,8-TCDD, is one of the most extensively investigated chemicals of this type and it is used as a reference of all other related chemicals. Most of its effects are caused by the fact that it binds to the so-called dioxin receptor (aryl hydrocarbon (Ah) receptor), which is a cytosolic ligand-activated transcription factor [21]. It is believed that other PCDD/F congeners have similar effects, but they are less potent than 2,3,7,8-TCDD. Some of the effects of PCB compounds are also assumed to occur on account of their binding to the Ah receptor, especially planar non-*ortho* PCBs; although the less potent PCBs may have other effects as well [22]. The complex nature of PCDD/Fs and PCB mixtures complicates the risk evaluation for humans, fish and wildlife. For this purpose, the concept of toxic equivalent factors (TEFs) has been developed to facilitate risk assessment and regulatory control of exposure to these mixtures [23]. TEF values in combination with chemical residue data, can be used to calculate toxic equivalent (TEQ) concentrations in various environmental samples, including animal tissues, soil, sediment, and water. In order to obtain the total toxicity, expressed in 2,3,7,8-TCDD equivalent, the congener-specific TEFs are multiplied with the concentration analyzed for the 17 WHO-PCDD/Fs and also for the 12 WHO-PCBs.

In muscle tissue of all fish samples the 17 WHO-PCDD/Fs and either 3 or 12 WHO-PCBs were analyzed:

PCDDs: 2,3,7,8-TCDD; 1,2,3,7,8-PeCDD; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; 1,2,3,4,6,7,8-HpCDD and OCDD. PCDFs: 2,3,7,8-TCDF; 1,2,3,7,8-PeCDF; 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF and OCDF. DL-PCBs: non-*ortho* substituted PCBs: TeCB-77; TeCB-81, PeCB-126 and HxCB-169. Mono-*ortho* substituted PCBs: PeCB-105; PeCB-114; PeCB-118; PeCB-123; HxCB-156; HxCB-157; HxCB-167 and HpCB-189.

In eels from the years 1996 and 1998 the non-*ortho* substituted PCBs TeCB-77, PeCB-126 and HxCB-169 were analyzed, and in eels from the years 1999, 2003 and 2005 as well as in bream from 1989, 1990 and 1994 only PCDD/Fs were analyzed. In these cases, the aim of the investigations was limited to the determination of PCDD/Fs or the method for analyzing DL-PCBs was not established in the laboratory.

2.2.2. Analytical methods

The analytical procedure is based on the US EPA method 1613 [24] and the European Directive 2002/69/EC [25] for the PCDD/Fs and the US EPA 1668A [26] method for the DL-PCBs. Freeze dried and disaggregated samples of the muscle tissue were soxhlet extracted with toluene. Prior to extraction $^{13}C_{12}$-labeled analogs were added to the sample for identification and quantification. The measurement was performed with the use of high-resolution gas chromatography/high resolution mass spectrometry. For quality control a blank and samples from stored composite samples (internal reference material) were run with each batch of ten samples. The relative standard deviation (R.S.D.) was (%) 12 (PCDDs), 10 (PCDFs), 18 (non-*ortho* PCBs) and 11 (mono-*ortho* PCBs). A further quality control measure was performed using certified fish oil. The relative

R.S.D. were (%) 9.0 (PCDDs), 8.1 (PCDFs), 14 (non-*ortho* PCBs) and 9.5 (mono-*ortho* PCBs). The upper-bound method was used: upper-bound concentrations are calculated assuming that all the values of the different congeners less than the limit of quantification are equal to the limit of quantification.

The age of the bream was mainly determined by counting the microscopic otholithes in the fish ears. In those bream where this counting method was not applied the age was calculated by means of a mathematic function, involving its length [M. Bergemann, personal communication]. The age of the eels, European chub and ide were not determined.

2.3. Statistical analyses

The data basis for the statistical analyses is provided by the congener profiles of the PCDD/Fs found in fish which were caught in the years 1989, 1990, 1994, 1995, 1998, 1999, 2002 and 2003 in the river Elbe. In the sum, 118 PCDD/F datasets of eels and whitefish were used for the statistical analysis, composite samples as well as individual fish (Tables 1 and 2).

The statistical model calculates relative congener patterns with the maximum likelihood approach [27]. This technique was applied to the analysis results for the fish samples from the Elbe. On the one hand, it can be used to estimate concentrations for individual congeners, and on the other hand it provides the basis for the likelihood ratio test, which enables sub-populations to be assigned to different river sections.

It is assumed that the concentration matrix c_{ij} for the analyses $i = 1, \ldots, n$ and for congeners $j = 1, \ldots, m$ are log-normally distributed. The following linear model is used for the logarithms of the concentrations, $Y_{ij} = \ln c_{ij}$

$$Y_{ij} = \mu_i + \alpha_j + \varepsilon_{ij}$$

where

$$\sum_i \mu_i = 0$$

The parameters μ_i and α_j are fixed, unknown quantities, whereas ε_{ij} is a normally distributed quantity with variance σ_{ij}^2, determined by the expected value of Y_{ij} and the congener j:

$$\ln \sigma_{ij} = \ln(\sigma_0 \gamma_j) + (\lambda - 1)(\mu_i + \alpha_j)$$

or equivalently

$$\sigma_{ij} = \sigma_0 \gamma_j \exp[(\lambda - 1)(\mu_i + \alpha_j)]$$

The multiplicative factor σ_0 and its relative variance σ_0^2 are assumed to be unknown.

The data basis for the calculation of the parameters λ and γ_j in the uncertainty function described above are the analysis results from an intercalibration study in which PCDD/Fs in salmon (*S. salar*, muscle tissue) were determined [27].

The model formulated using these parameters can be estimated using the maximum likelihood principle. The likelihood function provides the basis not only for estimating individual congeners, but also for the likelihood ratio test used to segregate sub-populations.

2.3.1. Analytical uncertainty

The extended Horwitz function provides a tool which enables the analytical uncertainty to be taken into account and thus detect significant peaks or, as the case may be, to test whether samples differ from each other. The data basis for computing these uncertainty values was provided by analysis results from an intercalibration study on PCDD/Fs in salmon [27].

3. Results

Results for PCDD/Fs and DL-PCBs in muscle tissue (composite samples and individual fish) from eels, European chub and ide caught in the Elbe and its tributaries Mulde and Saale are presented in Fig. 2a and b (eels) and Fig. 3a and b (whitefish). The locations where the fish were caught are shown in Fig. 1. Tables 1 and 2 summarize the basic data for the investigated eels (Table 1) and the whitefish (Table 2) as well. Both tables include the WHO-PCDD/F-TEQ, WHO-PCB-TEQ (concentrations, range and median values), sampling locations, stream km and sampling times (year and month). The *biometric data* are (mean values ± R.S.D.): eels length = 54 ± 8.5 cm,

Table 1
Concentrations of PCDD/Fs and DL-PCBs in muscle tissue of eels (*Anguilla anguilla*) from the river Elbe and Hamburg harbor (pg WHO-TEQ/g ww)

Sample	WHO-PCDD/F-TEQ	WHO-PCB-TEQ	Sampling site, month, year
SF, $n = 1$	2.5	17[a]	Reiherstieg Nord, Hamburg Harbor; April 1996
SF, $n = 1$	19	24[a]	Elbe, Zollenspieker to Geesthacht, km 590–600; May 1996
CS, $n = 10$	5.8	28[a]	Elbe, Geesthacht, km 590; May to June 1998
CS, $n = 20$	22	59[a]	Elbe, Bunthaus, km 609; May to June 1998
CS, $n = 10$	7.3	37[a]	Elbe, Mühlenberger Loch, km 635; May to June 1998
CS, $n = 10$	8.2	34[a]	Köhlbrand, Hamburg Harbor; May 1998
SF, $n = 6$	1.7–6.9 (2.6)	n. a.	Rethe/Kattwykhafen, Hamburg Harbor; June 1999
SF, $n = 24$	1.5–12 (4.2)	8.5–47 (24)[b]	Elbe, Gorleben, km 490; September 2002
SF, $n = 25$	1.5–6.9 (1.5)	n. a.	Elbe, sampling sites: Lüchow-Dannenberg, km 520, Hamburg-Harburg, km 615, Stade, km 660, Medemsand (Cuxhaven), km 715; June 2003
SF, $n = 4$ CS, $n = 5$	0.48–10 (3.5)	n. a.	Elbe, sampling sites: Gorleben, km 490, Hohnstorf, km 570, Hoopte, km 600; Brunsbüttel, km 690, Medemsand (Cuxhaven), km 715; July to August 2005

[a] Sum of PCB Nos. 77, 126 and 169.
[b] Sum of 12 WHO-PCBs. SF, single fish; CS, composite sample; n, number of individuals; (), median value; n.a., not analyzed; km, stream-km.

Table 2
Concentrations of PCDD/Fs and DL-PCBs in muscle tissue of bream (*Abramis brama*), European chub (*Leuciscus cephalus*) and ide (*Leuciscus idus*) caught in the river Elbe and its tributaries Mulde and Saale (pg WHO-TEQ/g ww)

Sample	WHO-PCDD/F	WHO-PCB	Sampling site
1989			
CS, $n = 2$	5.2	n.a.	Elbe, Oortkaten, km 610
CS, $n = 3$	3.1	n.a.	Elbe, Oortkaten, km 610
SF, $n = 2$	4.7; 6.0	n.a.	Elbe, Altona, km 625
CS, $n = 3$	4.7	n.a.	Elbe, Altona, km 625
SF, $n = 3$	1.9–12 (2.7)	n.a.	Elbe, Mühlenberger Loch, km 635
SF, $n = 4$	4.0–10 (6.3)	n.a.	Elbe, Fährmannsand, km 640
1990, September–November			
SF, $n = 1$	3.3	n.a.	Elbe, Königstein, km 15
CS, $n = 2$	18	n.a.	Elbe, Pillnitz, km 40
SF, $n = 1$	14	n.a.	Elbe, Dresden, km 60
CS, $n = 5$	5.0	n.a.	Elbe, Wittenberge, km 460
CS, $n = 4$	2.8	n.a.	Elbe, Gorleben, km 490
1993, August–September			
CS, $n = 40$	6.0	14	Elbe, Prossen, km 13
CS, $n = 20$	4.4	7.3	Elbe, Barby, km 296
CS, $n = 40$	5.5	10	Elbe, Blankenese, km 633
1994, April–May			
SF, $n = 1$	0.88	n.a.	Elbe, Meißen, km 80
CS, $n = 15$	4.3	n.a.	Elbe, Meißen, km 80
CS, $n = 5$	2.0	n.a.	Elbe, upstream of Wittenberg, km 205–210
CS, $n = 15$	1.9	n.a.	Elbe, downstream of Wittenberg, km 220
SF, $n = 2$	0.72; 14	n.a.	Elbe, Gorleben, km 490
CS, $n = 17$	2.9	n.a.	Elbe, Gorleben, km 490
SF, $n = 2$	0.48; 2.0	n.a.	Elbe, Moorburg, km 630
CS, $n = 13$	4.4	n.a.	Elbe, Moorburg, km 630
SF, $n = 1$	1.9	n.a.	Elbe, Fährmannsand, km 640
CS, $n = 16$	2.2	n.a.	Elbe, Fähmannsand, km 640
CS, $n = 13$	2.4	n.a.	Elbe, Mühlenberger Loch, km 635
CS, $n = 15$	1.9	n.a.	Elbe, Haseldorfer Binnenelbe, km 650
1995, August–September			
CS, $n = 20$	2.0	9.9	Elbe, Prossen, km 13
CS, $n = 22$	1.8	11	Elbe, Zehren, km 93
CS, $n = 32$	2.4	6.0	Elbe, Barby, km 296
CS, $n = 40$	1.9	4.5	Elbe, Cumlosen, km 470
CS, $n = 40$	5.4	9.2	Elbe, Blankenese, km 633
CS, $n = 15$	1.0	4.7	Saale, Wettin, km 71
CS, $n = 18$	1.8	3.5	Mulde, Dessau, km 260
1996, April–May			
CS, $n = ?$	2.2	3.0[a]	Elbe, Zollenspieker to Geesthacht, km 590–600
CS, $n = ?$	3.8	9.1[a]	Reiherstieg Nord (Hamburg Harbor)
1998, August–September			
CS, $n = 21$	1.7	6.4	Elbe, Prossen, km 13
CS, $n = 20$	2.0	6.5	Elbe, Barby, km 296
CS, $n = 20$	6.3	8.9	Elbe, Blankenese, km 633
CS, $n = 20$	0.86	4.0	Saale, Wettin, km 71
CS, $n = 22$	1.4	3.2	Mulde, Dessau, km 260
2000, August–September			
CS, $n = 22$	1.3	5.9	Elbe, Prossen, km 13
CS, $n = 21$	1.3	5.4	Elbe, Zehren, km 93
CS, $n = 20$	1.2	3.4	Elbe, Barby, km 296
CS, $n = 20$	2.7	5.5	Elbe, Cumlosen, km 470
CS, $n = 20$	4.4	7.2	Elbe, Blankenese, km 633
CS, $n = 20$	0.98	4.9	Saale, Wettin, km 71
CS, $n = 28$	1.1	1.6	Mulde, Dessau, km 260
2001, August–September			
CS, $n = 23$	1.9	10	Elbe, Prossen, km 13
CS, $n = 20$	1.1	2.4	Elbe, Barby, km 296

Table 2 (*Continued*)

Sample	WHO-PCDD/F	WHO-PCB	Sampling site
CS, $n=20$	6.3	8.3	Elbe, Blankenese, km 633
CS, $n=20$	0.74	3.7	Saale, Wettin, km 71
CS, $n=21$	1.1	1.8	Mulde, Dessau, km 260
2002, August–September			
CS, $n=22$	1.2	5.3	Elbe, Prossen, km 13
CS, $n=21$	0.55	1.2	Elbe, Barby, km 296
CS, $n=20$	3.8	3.7	Elbe, Blankenese, km 633
CS, $n=20$	1.4	7.0	Saale, Wettin, km 71
CS, $n=20$	1.3	1.8	Mulde, Dessau, km 260
2003, August–September			
CS, $n=20$	1.6	5.3	Elbe, Prossen, km 13
CS, $n=22$	1.7	6.8	Elbe, Zehren, km 93
CS, $n=20$	2.6	5.1	Elbe, Barby, km 296
CS, $n=16$	1.7	2.7	Elbe, Cumlosen, km 470
CS, $n=20$	4.1	4.2	Elbe, Blankenese, km 633
CS, $n=20$	0.94	5.7	Saale, Wettin, km 71
CS, $n=20$	1.9	2.3	Mulde, Dessau, km 260
2002, October			
SF, $n=2$ (E. Chub)	0.48; 0.88	3.9; 4.4	Elbe, Meißen, km 80
SF, $n=2$ (Ide)	0.37; 1.2	1.8; 5.5	Elbe, Meißen, km 80
SF, $n=3$ (Ide)	0.57–1.5 (0.88)	2.2–5.7 (3.4)	Elbe, Schmilka, km 4

[a] Sum of PCB Nos. 77, 126, 169. SF, single fish; CS, composite sample; *n*, number of individuals; (), median value; ?, number of individuals not known; n.a., not analyzed; km, stream-km.

weight = 345 ± 183 g, fat = 28 ± 8.7% (years 2002 and 2005). Bream: length = 44 ± 4.5 cm, weight = 922 ± 303 g, fat = 3.2 ± 2.5% (years 1989 and 1994), age = 8.7 ± 2.5 years. Two individuals of the European chub: length = 41 cm, weight = 1025 g, fat = 2%. Ide: length = 36 ± 1.6 cm, weight = 812 ± 129 g, fat = 3.2 ± 2.5%. The results of the correlation analysis (Kendall, 0.01 significance level and a two side calculation) for the bream and eel datasets show minor or middle coherences within the parameters PCDD/F-TEQ, DL-PCB-TEQ, fat and age.

3.1. Eels

Fig. 2a and b show that the results reflect large variations in the course of time. Further, the DL-PCB-concentrations are much higher than those of the PCDD/Fs (Fig. 2a). For comparison, the permitted maximum levels of the European Commission Regulation (EC) No. 466/2001/EC [16] are drawn parallel to the abscissa. The WHO-PCDD/F-TEQ values lie in the range of 0.48 pg/g wet weight (ww) (Brunsbüttel, stream-km 690) to 22 pg/g ww (Bunthaus, stream-km 609) and for the WHO-PCB-TEQ between 8.5 pg/g ww (Gorleben, stream-km 490) and 59 pg/g ww (Bunthaus, stream-km 609). The highest concentration of 81 pg WHO-TEQ/g ww for the sum of PCDD/Fs + DL-PCBs was found in the composite sample from the sampling site Bunthaus in the year 1998. One probable explanation for the wide divergence in the results is to be found in the eels' nomadic tendencies, which brings them into contact with a wide range of inhomogeneously polluted river sections of the river Elbe and its tributaries. This in turn exposes them to differing degrees of contamination, most of which they incorporate and accumulate with their food.

One dataset was obtained from 24 single eels caught in September 2002, directly after the flood event in August of the same year (Fig. 2a). The sampling site was at (Gorleben, stream-km 490) in Lower Saxony (Fig. 1). The range for the PCDD/Fs is between 1.5 and 12 pg WHO-TEQ/g ww with a median value of 4.2 pg WHO-TEQ/g ww. The DL-PCB concentrations (12 WHO-PCB) range from 8.5 to 47 pg WHO-TEQ/g ww with a median value of 24 pg WHO-TEQ/g ww. Comparing the median values, this indicates that the DL-PCB-TEQ concentrations are around five times higher than those of the PCDD/F-TEQ. The four non-*ortho* PCB-TEQ are about 54% of the total WHO-TEQ, 31% for the eight mono-*ortho* PCB-TEQ and only 15% for the PCDD/F-TEQ.

3.2. Whitefish

The whitefish were caught at different locations in the Elbe from the Czech-German border at Schmilka (stream-km 4) downstream to the city of Hamburg (Haseldorfer Binnenelbe, stream-km 650) as well as the tributaries Mulde (Dessau, stream-km 260) and Saale (Wettin, stream-km 71) (sampling sites see Fig. 1). Fig. 3a and b show the results of the whitefish samples. The WHO-PCDD/F-TEQ values show a considerable degree of variation, as is the case for the eels, ranging from 0.48 pg/g ww (Moorburg, stream-km 630) to 18 pg/g ww (Pillnitz, stream-km 40). Again, the permitted maximum levels of the EC are drawn parallel to the abscissa. In most samples the DL-PCB concentrations are significantly higher than those of the PCDD/Fs; their concentrations lie in the range of 1.2 pg/g ww (Barby, stream-km 296) to 14 pg/g ww (Prossen, stream-km 13). There appears to be a tendency for the PCDD/F concentrations to be higher in the years 1989 and 1990 than in the following years. In contrast to

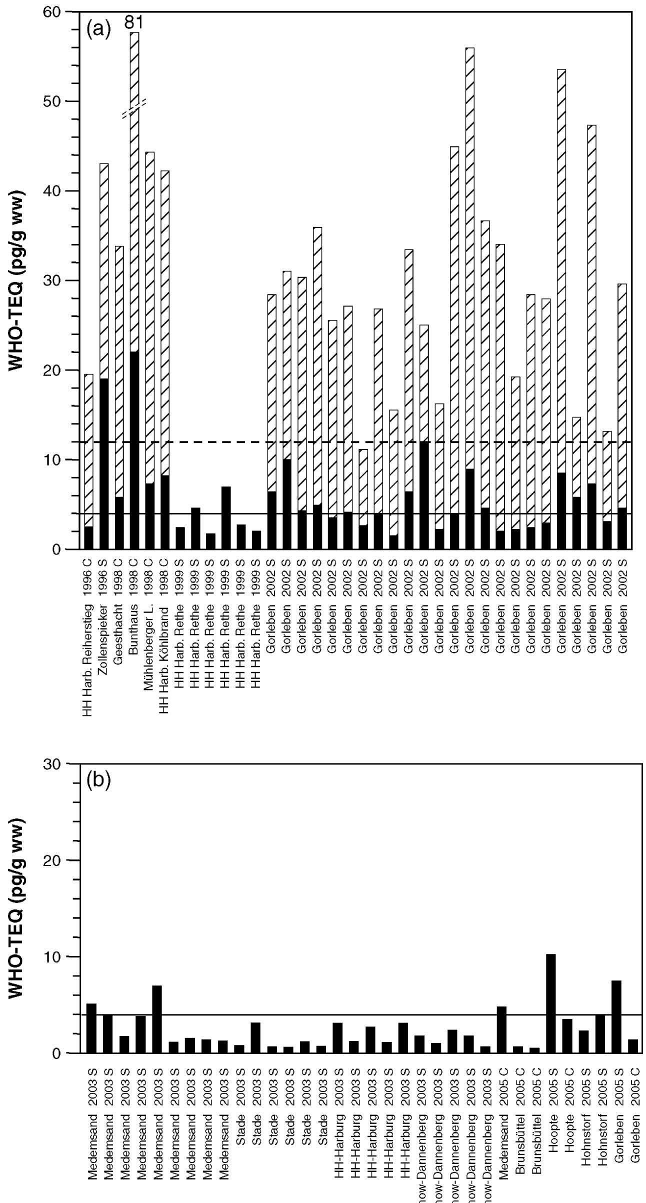

Fig. 2. (a and b) Concentrations of (▬) WHO-PCDD/F-TEQ and (▨) WHO-PCB-TEQ in eels (muscle tissue) from the river Elbe and Hamburg harbor. (—) maximum level PCDD/F = 4 pg/g ww, (- -) maximum level PCDD/F + DL-PCB = 12 pg/g ww; (S) single fish, (C) composite sample.

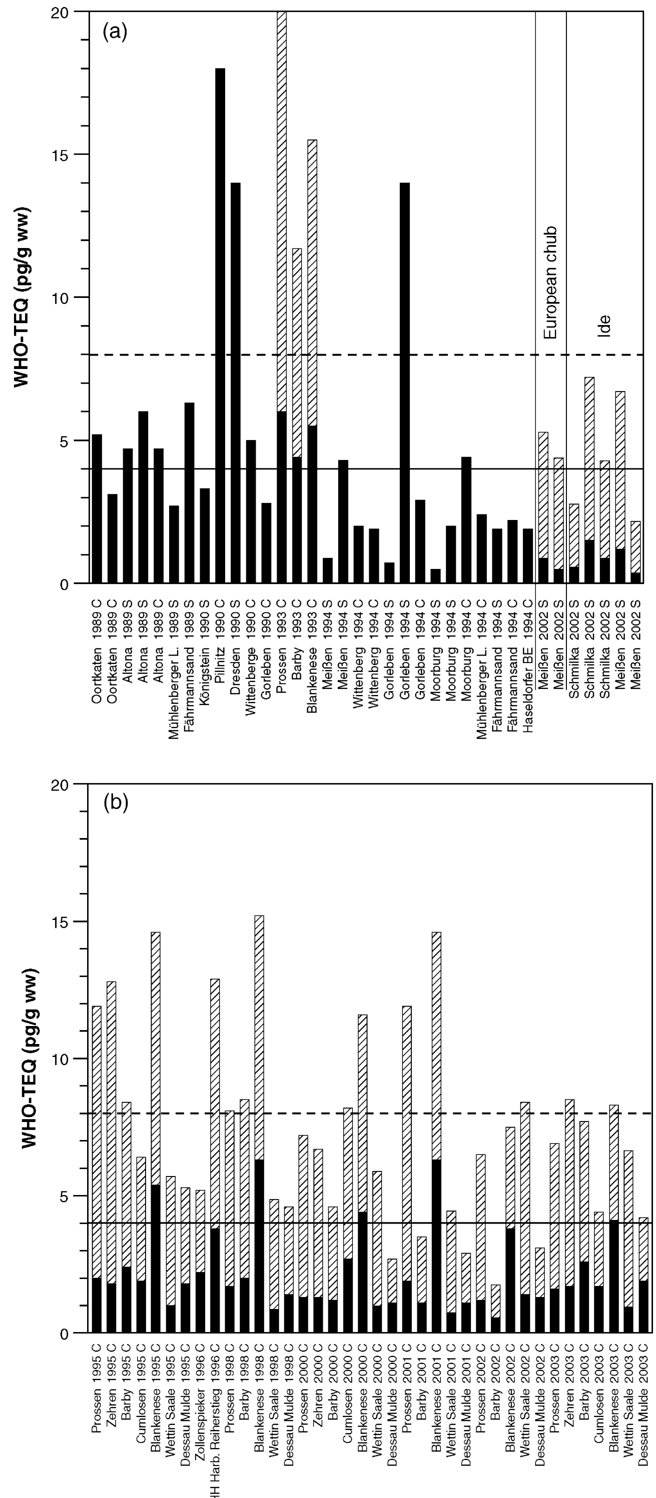

Fig. 3. (a and b) Concentrations of (▬) WHO-PCDD/F-TEQ and (▨) WHO-PCB-TEQ in bream, European chub and ide (muscle tissue) from the river Elbe, Mulde, Saale and Hamburg harbor. (—) maximum level PCDD/F = 4 pg/g ww, (- -) maximum level PCDD/F + DL-PCB = 8 pg/g ww; (S) single fish, (C) composite sample.

the high PCDD/F concentrations in sediments from the Mulde [12] the accumulation of these pollutants in bream from Dessau (Mulde) is comparable to those from other sampling sites. These results lead to the question that bream probably is not an efficient monitoring fish to reflect a contamination situation at every sampling location.

The European chub and ide (Fig. 3a) were caught in October 2002 at Schmilka (stream-km 4) and Meißen (harbor, stream-km 83). Taking both species into account, the WHO-PCB-TEQ levels range between 3 and 6 times as high as those of the WHO-PCDD/F-TEQ, which represents a proportional distribution comparable to that established for the bream. Similarly, the proportion of the four non-*ortho* PCBs is higher than that of mono-*ortho* PCBs (not shown in Fig. 3a).

4. Discussion

The accumulation and metabolic characteristics of PCDD/Fs and DL-PCBs from eels are different from those in the three whitefish species. Due to the larger proportion of fatty tissue in eels, PCDD/Fs and DL-PCBs accumulate more readily in this species than in the whitefish species. In all species, the absolute concentration levels for the DL-PCBs are considerably higher than those for the PCDD/Fs. Amongst the absolute concentrations of the DL-PCBs the non-*ortho* PCBs predominate over the mono-*ortho* PCB.

As a part of the monitoring program the German Environmental Specimen Bank investigated bream from the rivers Rhine, Saar and Danube as well. The results show that bream from the river Rhine have higher WHO-PCDD/F-TEQ concentrations than specimens from the rivers Elbe, Mulde and Saale as well as those from the rivers Danube and Saar. Comparable to the results of bream from the Elbe the WHO-PCB-TEQ concentrations in all samples are significantly higher than the WHO-PCDD/F-TEQ [28].

Eels from different sampling sites of the rivers Havel and Oder in Brandenburg (Germany) showed higher concentrations of PCDD/Fs and DL-PCBs (Nos. 77, 126 and 169) in regions which are influenced by urban areas or industrialized sites as well as in regions with municipal and industrial landfills. The concentrations of the three PCB congeners were about one order of magnitude higher than those of the PCDD/Fs [29]. The accumulation of the contaminants is comparable with that of eels from the Elbe.

Eels caught within Hamburg in 1995 (from the Alster and channels of the Alster, i.e. from sites uninfluenced by the Elbe) returned summed PCDD/F + DL-PCB-TEQ values in the range of 16–46 pg TEQ/g ww [30]. The higher levels exceeded the maximum level of 12 pg/g ww (EC) by a considerable margin, albeit the maximum level for PCDD/Fs of 4 pg/g ww was not exceeded.

Knutzen et al. [31] investigated PCDD/Fs and DL-PCBs in eels (muscle tissue) from the Grenland Fjords in southern Norway. The WHO-PCDD/F-TEQ values for eels from three different locations were found to be between 5 and 23 pg/g ww (mean value 16 pg/g ww). The same specimens returned values between 0.92 and 2.9 pg/g ww for the non-*ortho* PCBs Nos. 77, 126 (dominant) and 169; for the mono-*ortho* PCBs Nos. 105, 118 and 156 the values ranged from 0.43 to 1.8 pg/g ww. In contrast to this Norwegian study, the eels from the Elbe returned the same concentration range for the WHO-PCDD/F-TEQ, but significantly higher WHO-PCB-TEQ values (Fig. 2a). These variations could be due to differing contamination sources or to characteristic differences in the accumulation processes and metabolisms between freshwater eels and those from coastal regions.

Studies on sediments, SPM and alluvial soils revealed a distinctly different accumulation behavior for PCDD/Fs and DL-PCBs compared with the fish samples [12,32–34]. Whereas the solid samples returned much higher concentration values for PCDD/Fs than for DL-PCBs, the results for the fish samples are exactly reversed. The accumulation of PCBs and PCDD/Fs in fish takes place during a number of different trophic stages within the food chain; as a result the accumulation capacity for the PCBs proves to be much higher than for the PCDD/Fs [35].

As a consequence of the flood event in August 2002 industrial sites of the region at Bitterfeld-Wolfen were flooded and pollutants like chlorinated hydrocarbons reached the Mulde and the Elbe. Further, during the phase of higher hydraulic activity large amounts of contaminated sediments were remobilized and transported downstream. In view of the flood event, eel specimens were caught in September of the same year at the location Gorleben (stream-km 490) and the analysis results were compared to those recorded for eels caught in 1999. In 1999, the chlorinated hydrocarbons *o,p*-DDTs, their metabolites, α- and β-HCH as well as seven non-dioxin-like PCBs were analyzed in eels caught at the same location [36]. The comparison with those from September 2002 showed the latter concentrations to be significantly higher. The post-flood measurements exceeded the 1999 results as follows: *o,p*-DDTs and metabolites by the factor 3, α-HCH by the factor 4, β-HCH by the factor 6 and for seven summed PCBs by the factor 5. This indicates the probability that the extreme flooding contributed to an increased accumulation of lipophile contaminants. However, it is not possible to confirm a connection between the high WHO-TEQ values in the eels shown in Fig. 2a and the August 2002 flood, because no pre-flood data on PCDD/Fs and DL-PCBs in eels from this sampling site is available.

In June 2003, the Lower Saxony Ministry for Rural Areas, Food, Agriculture and Consumer Protection commissioned a series of studies on PCDD/Fs in Elbe eels (muscle tissue). These results indicate that, 9 months after the flood, accumulation levels for PCDD/Fs are low, at least in the Lower Saxonian river section. A further study commissioned by the same Ministry in the year 2005 showed results in the same concentration range as was recorded for the year 2003 (Fig. 2b). DL-PCBs were not analyzed in either sampling set.

Statistical analyses on the basis of the log likelihood model using relative congener patterns for PCDD/Fs allow spatial correlations to be examined for sub-populations of eels and whitefish in the Elbe. Further, on the basis of this model it was possible to demonstrate that the averaged congener patterns for eels, on the one hand, and for ide and European chub, on the other hand, show marked differences (Fig. 4). For the eels, the congeners 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF predominate, whereas in the comparatively static whitefish species only 2,3,7,8-TCDF returned higher values [27]. These differences may be due to local differences specific to the sampling sites, to different emission sources or related to different metabolic processes.

It is possible to segregate individual datasets from bream caught in the year 1994 into sub-populations on the basis of statistically significant differences in the relative congener patterns Meißen (stream-km 80). Group 1 contains the sampling sites Meißen (km 80), Wittenberg (stream-km 220), Wittenberge (stream-km 460), Gorleben (stream-km 490), Moorburg

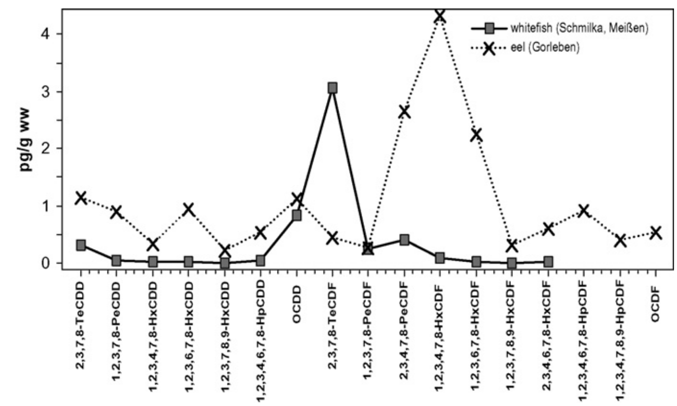

Fig. 4. PCDD/Fs in eels and whitefish (muscle tissue) from the Elbe caught in 2002 [27].

(stream-km 630) and Mühlenberger Loch (stream-km 635), Fährmannsand (stream-km 640) and Haseldorf (stream-km 650). The bream from group 2 represent a separate collective; i.e. the pattern may be assumed to have been influenced by other sources of contamination which are probably to be found downstream of Hamburg. Further, the analysis shows that relatively homogeneous contamination conditions prevailed in the Elbe in this year [27].

Using the dataset from 25 eels caught in the year 2003 (Fig. 2b) the results of the cluster analysis (*k*-mean-algorithm) allow the identification of three sub-populations. Group 1 consists of longer eels from various sampling sites which show a high fat content accompanied by 'moderate' PCDD/F values. Group 2 contains mainly eels from Hamburg-Harburg and Stade with a relatively low fat content and low WHO-PCDD/F-TEQ concentrations, whereas group 3 consists mainly of representatives from Medemsand, but also from Lüchow-Dannenberg. The analysis show that eels caught in the Elbe estuary (Medemsand) in the year 2003 originated from the Middle Elbe. It is notable that the values of the relative variances from the groups 2 and 3 are low (0.156 and 0.242; Table 3). The conclusion is that the individual aberration of the relative congener concentrations is specifically lower than the analytical uncertainty. This result is of considerable importance from the point of view of consumer protection, and it underlines the nomadic nature of the eel.

The *evaluation* of the WHO-TEQ data of the fish is based on the European Commission Regulation (EC) No. 466/2001/EC [16] and the European Commission Recommendation 88/2006/EC [17]. For PCDD/Fs in muscle tissue of eels the permitted maximum level is 4 pg WHO-TEQ/g ww and for the sum of PCDD/Fs + DL-PCBs the level is 12 pg WHO-TEQ/g ww. For PCDD/Fs in the whitefish species (muscle tissue) the maximum level is the same as for eels, but for the sum of PCDD/Fs + DL-PCBs the maximum level is 8 pg WHO-TEQ/g ww.

In the Commission Recommendation 88/2006/EC [17] two action levels are named, one for the PCDD/Fs and one for the DL-PCBs. The action level for PCDD/Fs in eels is 3 pg WHO-TEQ/g ww, whilst for the DL-PCBs this level is 6 pg WHO-TEQ/g ww (muscle tissue). The action level for these contaminants in the whitefish species (muscle tissue) is 3 pg WHO-TEQ/g ww, for the PCDD/Fs and DL-PCBs, respectively.

In the eels, the maximum level for the PCDD/Fs is exceeded in 30 (43%) samples and for the sum of PCDD/F + DL-PCB in 29 (41%) samples (Fig. 2a and b). The action level for PCDD/Fs is exceeded in 36 (51%) samples and for the DL-PCBs in 30 (43%) samples.

The largest number of cases in which the action levels were exceeded was recorded for eels caught near Hamburg in 1996 and 1998 as well as from Gorleben (Lower Saxony, stream-km 490) in September 2002. It may be added that DL-PCBs were determined in only 43% of the samples, suggesting that in a more comprehensive investigation the levels may well have been exceeded more frequently. In future, we may expect to have a broader basis for assessment, for as of November 2006 both substance groups are to be determined for foodstuffs [16].

Because the eel is a popular foodstuff and therefore represents a significant potential health hazard to consumers *both* PCDD/Fs *and* DL-PCBs should be analyzed in the muscle tissue of eels, for instance, at the rate of one investigation per year. Eels from the river Mulde and Saale should be integrated into the program.

In the whitefish, the maximum level for PCDD/Fs exceeded in 19 (26%) samples, and for the sum of PCDD/F + DL-PCB this level exceeded in 18 (24%) samples (Fig. 3a and b). The action level for PCDD/F exceeded in 24 (32%), and for the DL-PCB in 39 (53%) samples. DL-PCBs were analyzed in 65% of the white fish samples. The fish caught in the years 1989, 1990, 1993, 1995 and 1996 showed the most overstepping levels.

Because of the higher PCDD/F concentration in fish the National Food Agency Finland published recommendations for its consumption. In herring and salmon caught in the Baltic Sea, particularly in the Gulf of Bothnia and the Gulf of Finland the mean values recorded for 2003/2004 exceeded the maximum level of 4 pg WHO-TEQ/g ww for PCDD/Fs. As a consequence of these investigations the National Food Agency Finland published a leaflet called "Dietary advice on fish consumption" (www.elintarvikevirasto.fi). Special recommendations have been issued to children, young people at fertile age: large herring, more than 17 cm and salmon should be eaten not more than once or twice a month.

Table 3
Results of the cluster analysis (method: *k*-mean-algorithmus) of eels (*Anguilla anguilla*) caught in the Elbe in the year 2003

Collective	Length (cm)	Fat (%)	PCDD/F-TEQ (pg/g ww)	Relative variance
Group 1 (S2, H1, LD1, LD3)	57	23	2.1	0.461
Group 2 (S1, S3–S6, H2–H5, M6, C8)	42	8.6	1.5	0.156
Group 3 (M1–M5, M7, M9, LD2, LD4, LD6)	43	17	2.8	0.242

Sampling locations (see Fig. 1). LD, Lüchow-Dannenberg; H, Hamburg-Harburg; S, Stade; M, Medemsand. Mean values: length, fat and WHO-PCDD/F-TEQ.

The Water Framework Directive 2000/60/EC [37] aim at maintaining and improving the aquatic environment in the community. One main environmental objective for surface waters is to achieve a rating of 'good' quality both for its ecological status and its chemical status. Quality objectives or quality standards represent tools for achieving satisfactory conditions in surface waters. An environmental quality standard is determined by defining a concentration level for a particular pollutant or group of pollutants in water, sediment or biota which may not be exceeded without the risk of damage to human health or the environment. Consequently, quality standards must be set to that they lead to conditions in the permitted maximum levels in fish are not exceeded (consumer health protection). For exceeding permitted maximum thresholds cannot be compatible with 'good' ecological and chemical conditions.

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