ANALYTICAL EXPERIENCES WITHIN THE GERMAN ENVIRONMENTAL SPECIMEN BANK: TIME TRENDS OF PCDD/F AND DL-PCB IN BREAM (ABRAMIS BRAMA) CAUGHT IN GERMAN RIVERS

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Introduction

The German environmental specimen bank (ESB), one of the largest specimen collection programmes worldwide, is sampling and storing specially targeted matrices throughout the whole biosphere and ecosphere[1]. This collection is able to deliver the basis for retrospective evaluations of baseline contaminations and time trends for important pollutants as in this study the persistent and highly toxic polychlorinated dibenzo-p-dioxins and -furans (PCDD/F) and dioxin-like PCB (dl-PCB). In the last few decades, there has been a notable decrease of this type of pollution but monitoring is nevertheless extremely important given the fact that e.g. still very high amounts of PCB are deposited or enclosed in the environment. For the German aquatic systems, monitoring of fish from the main rivers delivers a sound data base and also allows for a discussion of the overall state of environmental protection within the tributary system of these rivers. The bream (common bream, *abramis brama*) is an especially suitable fish species for this purpose. It is a common and wide-spread species at a fairly high trophic level, being easily sampled and allowing both for links to the surrounding environment as to food[2]. This paper gives an evaluation of PCDD/F and dl-PCB data for bream samples collected in the time period of 2003 to 2008. It shows that there is still a notable contamination of PCDD/F and dl-PCB in fish samples in the main rivers of Germany. The current levels are – if compared to food – partially above the limits given by EU legislation, especially for the sampling points being downstream of the big rivers Rhine and Elbe.

Materials and methods

Sampling and treatment of bream prior to archiving were performed according to ESB standard operating procedures[2]. In short, bream are caught annually after spawning between mid-July and early October. 20 fish aged between 8 and 12 years are taken usually at each sampling site. The muscles are pooled, grinded and stored as homogenized powder in sub-samples of approx. 10 g at temperatures below -150°C in an inert atmosphere resulting from evaporating liquid nitrogen. Sampling sites (fig.1) cover the rivers Rhine, Saar, Danube, and Elbe with the tributaries Mulde and Saale, as well as the lake Belauer See which represents a low polluted reference area. All samples have been analysed for the 17 2,3,7,8-substituted PCDD/F and the 12 dioxin-like PCB (dl-PCB, "WHO-PCB"; IUPAC# 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189). All analytical data are reported in pg/g wet weight (ww). TEQ values are given as maximum TEQ using WHO-TEF1998. The analyses have been performed at the Eurofins GfA GmbH Dioxin/POP competence centre, Hamburg. The analytical procedure consisted of an extraction (Soxhlet/toluene), multiple column chromatography and a state-of-the-art GC/HRMS determination method on Waters Autospec mass spectrometers.

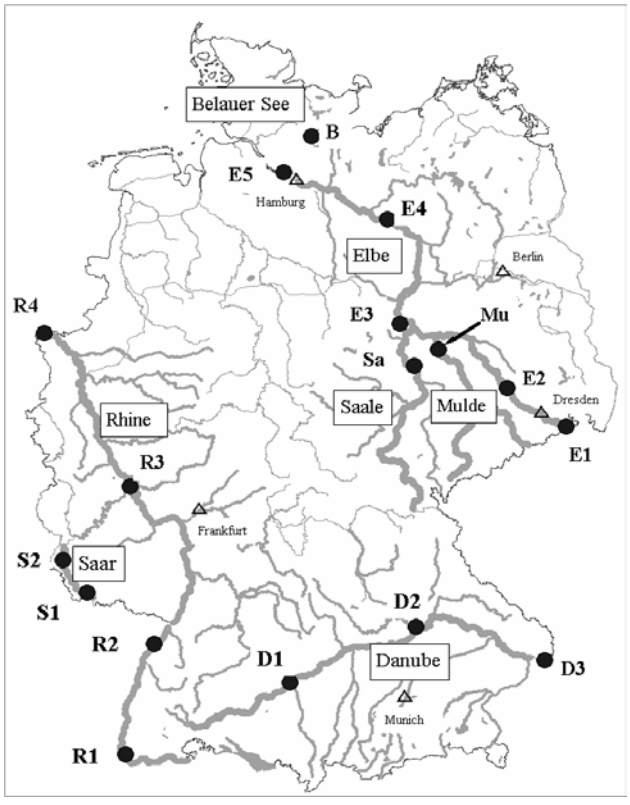
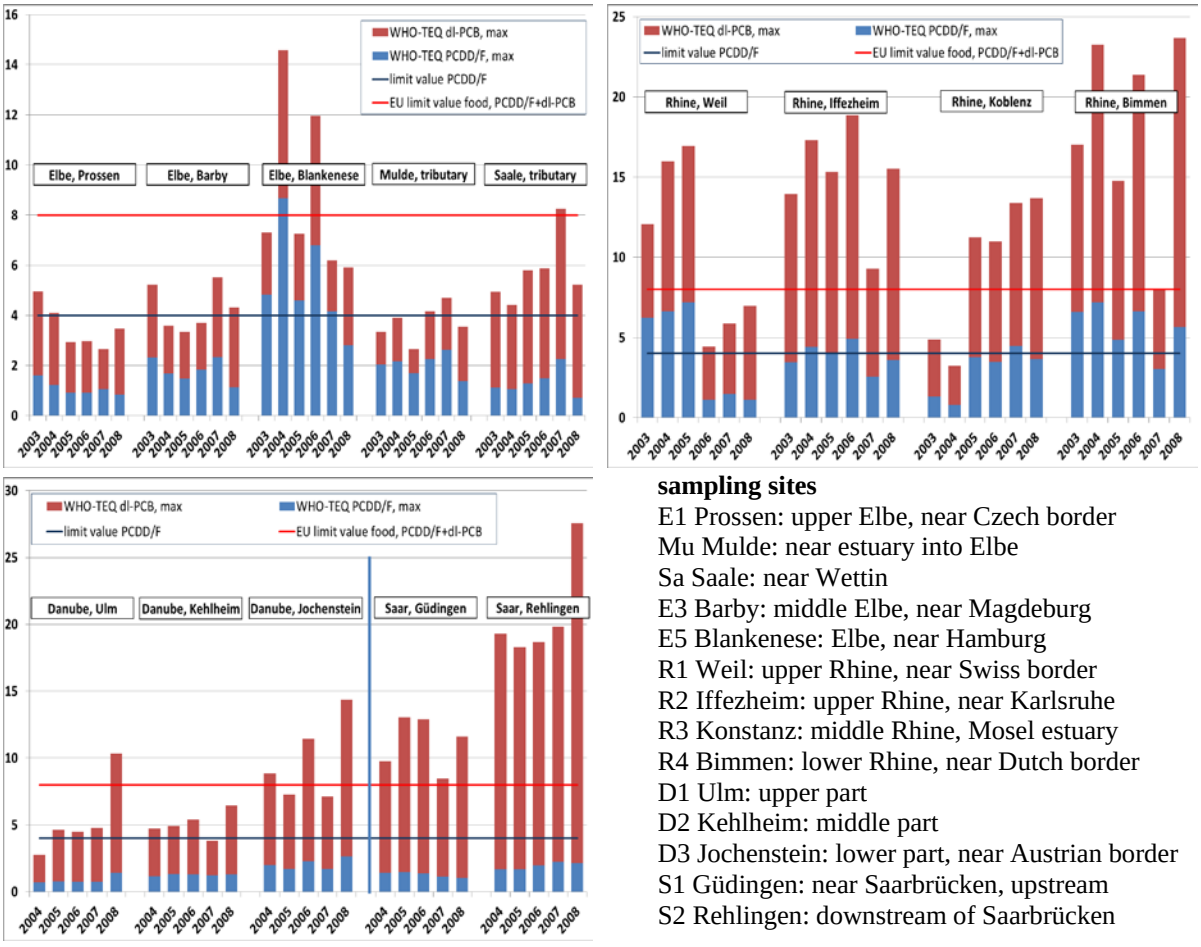


Figure 1: Germany: river system and sampling sites

Quantification is based on isotope dilution using a set of 13C-labelled standards added to the sample before extraction. All analytes are covered by a 13C-labelled standard, only exception being 123789-HxCDD. The methods are based on the EC requirements for reference analyses[3], using HRMS at mass resolution r ≥ 10.000. Analytical quality has been maintained e.g. by monitoring recovery rates against a set of 8 13C-labelled standards added before GC injection. Recovery rates were well within an acceptable range of 50-130%. Alongside with the samples, routine QA/QC-measures have been taken, e.g. batch blank preparation over the whole procedure as well as reference samples. Blank values have been below the quantification limits given.

Results and discussion:

The results for all the PCDD/F- and dl-PCB-TEQ-values are given as timelines in figure 2, sorted by river systems and, within the systems, by sampling site. The time lines show the stacked data for PCDD/F and dl-PCB. Not shown is a reference bream sample from the uncontaminated northern German lake Belauer See with upperbound values for PCDD/F of 0.14 pg TEQ / g ww and dl-PCB of 0.50 pg TEQ / g ww.



sampling sites

E1 Prossen: upper Elbe, near Czech border
Mu Mulde: near estuary into Elbe
Sa Saale: near Wettin
E3 Barby: middle Elbe, near Magdeburg
E5 Blankenese: Elbe, near Hamburg
R1 Weil: upper Rhine, near Swiss border
R2 Iffezheim: upper Rhine, near Karlsruhe
R3 Konstanz: middle Rhine, Mosel estuary
R4 Bimmen: lower Rhine, near Dutch border
D1 Ulm: upper part
D2 Kehlheim: middle part
D3 Jochenstein: lower part, near Austrian border
S1 Güdingen: near Saarbrücken, upstream
S2 Rehlingen: downstream of Saarbrücken

Figure 2: PCDD/F- and dl-PCB-TEQ (WHO98, pg/g wet weight)

The results are generally in accordance with earlier findings of the same programme and others[4,5]. If we consider bream as food – which is possible and locally true – this gives a link towards EU food legislation. The concentrations of PCDD/F and dl-PCB exceed the EU limit values[6] in several cases. 20% of the samples are above the respective limit value of 4pg WHO-TEQ98/g ww for PCDD/F and 43.8% of the samples exceed the limit of 8pg WHO-TEQ98/g ww for PCB. These exceedances occur mainly in bream from the rivers Rhine, Saar and Elbe, where especially the Saar region is strongly influenced by border crossing industrial and mining

activities and thus related to use and release of technical PCBs. Sudden changes within single time lines might have specific explanations as e.g. for Weil (Rhine) having a drop in average age of the caught bream from 2006 and Koblenz (Rhine) bream with a higher average fat content since 2005. This will have to be examined more

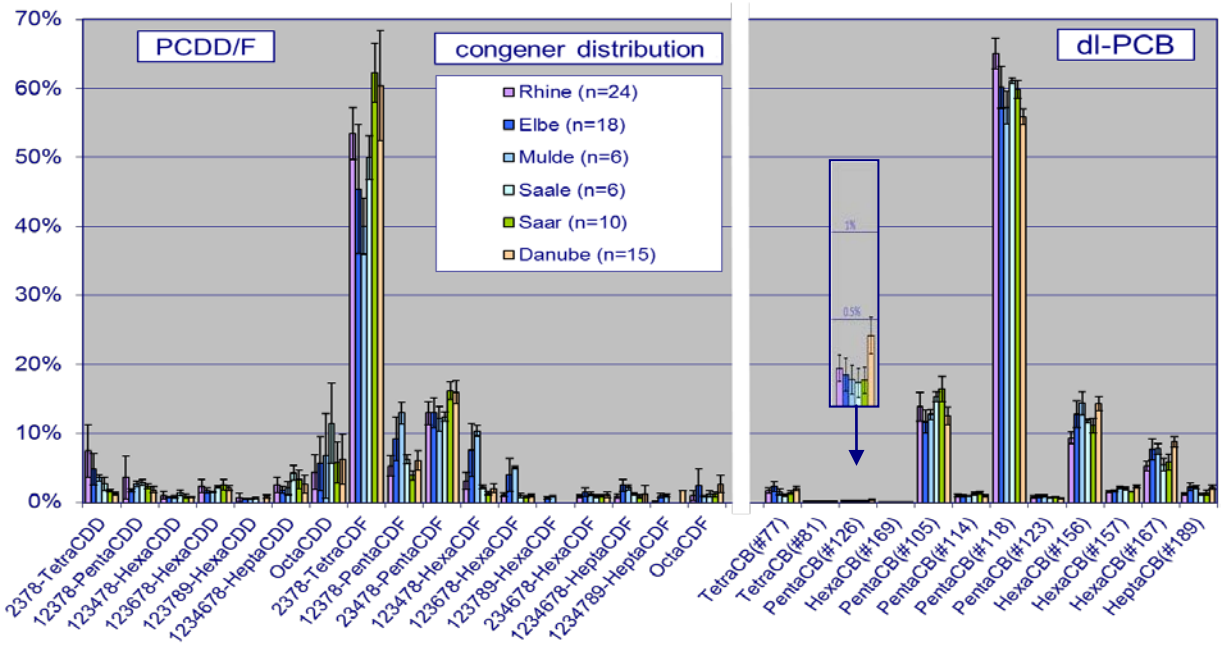


Figure 3: PCDD/F- and dl-PCB-pattern: average congener distribution per river (bars indicate SD)

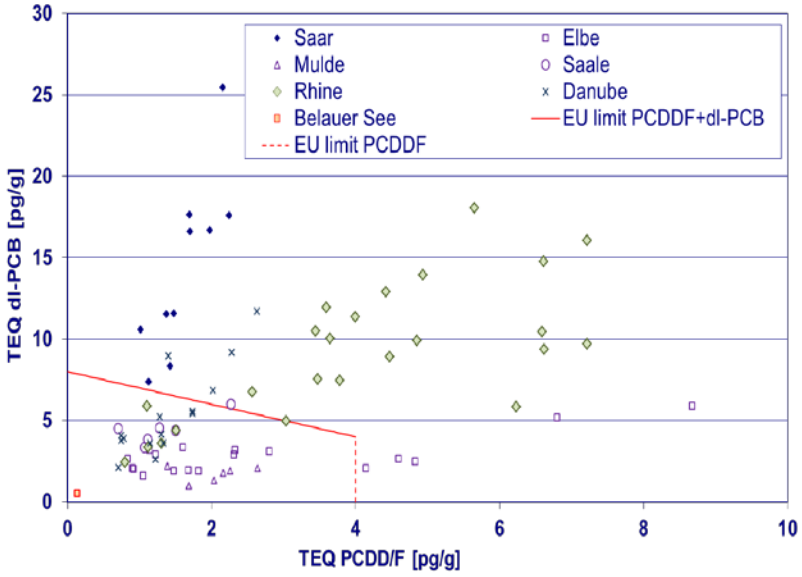


Figure 4: dl-PCB-TEQ vs. PCDD/F-TEQ (lines indicate maximum values for fish acc. to EU food legislation)

closely. Fig.3 gives the congener patterns for PCDD/F and dl-PCB respectively. These patterns show a general tight uniformity over all samples and sampled rivers, especially for PCB where almost no pattern variation is observed and PCB#118 is the main compound amongst the dl-PCB. There are only few exceptions, e.g. a relatively higher contribution of PCB #126 for the river Danube. For PCDD/F, generally 2,3,7,8-TetraCDF is the main compound, followed by the two PentaCDF. A pattern variation for the PCDF-contributions can be seen for the river Elbe and its tributary Mulde (see below). The different ratios for dl-PCB against PCDD/F as shown in fig.4, also given as PCDD/F shares in fig.5, are an indication for the different contamination sources. The high PCB contamination of the river Saar together with a relatively low PCDD/F contribution towards total TEQ might possibly point towards a reference for the TEQ shares to be expected for presence of a pure PCB contamination. In contrary, Elbe bream reflect the long term input of PCDD/F rather than PCB by attached chemical industry regions, especially the Bitterfeld-Wolfen region at the Elbe tributary Mulde with its former magnesium production and chloralkali processes. The ratio of PCB vs. PCDD/F is clearly

shifted towards the PCDD/F, especially for the Mulde. Also the PCDF pattern variation might indicate this influence seeing the relative contributions of the HexaCDF, especially 1,2,3,4,7,8-HexaCDF, and also the relative increase for 1,2,3,7,8-PentaCDF (see fig.3) . This leads to a way of explaining the similarity of patterns. The bream metabolism for PCDD/F and PCB lead to a different accumulation of congeners in a way that only few congeners, e.g. the lower halogenated PCDD/F, can be used to trace back the pattern of origin. The information from congener patterns in bream– as for other fish – for such a purpose is to be handled carefully[5,7] As for land animals, the animal metabolism and the limited number of sufficiently different congener patterns from original contamination sources generate metabolic patterns too uniform to be easily evaluable. Additionally, the uniformity of dl-PCB pattern will result from the typical patterns for the higher chlorinated technical PCB mixtures which also reflect the mainly used technical PCBs as well as the higher environmental persistence of the higher chlorinated congeners. This is also indicated by the fact that the Saar breams show exactly the same pattern as all other samples, while having a clearly higher PCB contamination from the Saar region.

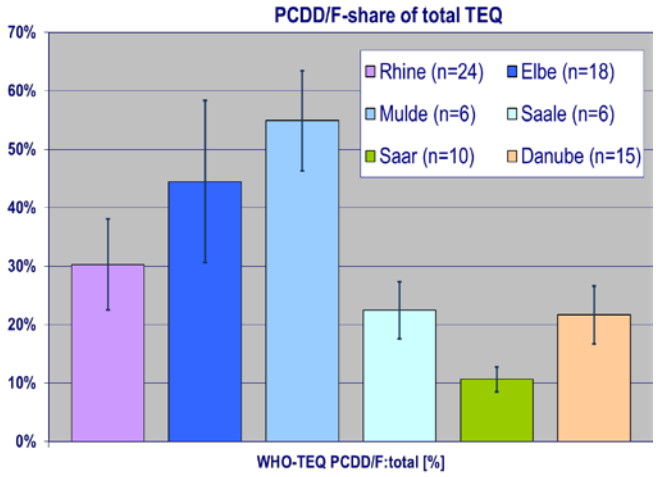


Figure 5: PCDD/F-TEQ share at total TEQ values (lines indicate single SD)

The presented data show that over the analysed period of time, there is actually no further decrease in PCDD/F and dl-PCB concentration in German breams. Even some increasing levels are found as e.g. for certain sites in 2008, pointing towards a steady state background level which is now, after some decades of decrease, giving statistical and sometimes strong variations. This might happen due to remobilisation of past pollutant depositions, e.g. by weather fluctuations (viz. annual flooding) or works influencing the sediment body. The data demonstrate the usefulness of ESBs for provision of baseline patterns for reference purposes. Since the time frame for this data collection is merely covering a decade, counting from 2003, it is still too early to draw conclusions over state and possible influences of the monitored fluvial eco systems. Further investigations, especially for corresponding sediment and water samples would give the possibility to assess influences of metabolism and deposition of sediments and solid particles. PCDD/F and dl-PCB data will be managed and provided for further assessments by the German Dioxin Database Federation/Laender http://www.pop-dioxindb.de/index-e.html.

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