



Dioxins and PCBs in solid matter from the River Elbe, its tributaries and the North Sea (longitudinal profile, 2008)

Gunther Umlauf, Burkhard Stachel, Giulio Mariani, and Rainer Götz



Photo on cover page:

Tide-Elbe at Hanskalbsand (Wedel, downstream the City of Hamburg) view towards the North Sea.

Source: Wassergütestelle Elbe, 12.05.2008.



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Summary

The most recent longitudinal sampling profile, taken in 2008 from the river Elbe and its tributaries Vltava (Moldau), Mulde, Spittelwasser, Saale, Bode the Stör and the North Sea near Helgoland, shows contaminations of solid matter with polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (dioxins, PCDD/Fs) and polychlorinated biphenyls (PCBs). While the dioxin contamination is mainly located along the German part of the catchment, PCBs are more abundant in the Czech section. In some of the 43 solid samples investigated high levels of contamination were detected. Selected orientation benchmarks for dioxins and PCBs in sediments and fish are exceeded, suggesting potential hazards for organisms in the contaminated rivers and for human consumption.

Elevated dioxin concentrations in the Spittelwasser-Mulde system and the Saale catchment, together with consistent dioxin congener patterns Elbe downstream of the confluence, indicate that the region of Bitterfeld-Wolfen is the predominant source of the dioxin pollution, which can be traced until far off shore in the sediments of the North Sea near Helgoland. This hypothesis, suggested by the spatial distribution of dioxins, was confirmed through statistical analysis (neuronal networks), showing that the historic dioxins sources were in the region Bitterfeld-Wolfen in the Mulde catchment as well as in the Saale catchment. Thermal metal, presumably Magnesium production via fused salt electrolysis during the 2nd world war is the most probable primary, historic source of the dioxin contamination.

In particular the German Mulde tributary *Spittelwasser* exhibited a maximum dioxin concentration of 1260 pg WHO₂₀₀₅-TEQ/g. The river Bode, a tributary of the river Saale, showed a value of 102 pg WHO₂₀₀₅-TEQ/g. In the longitudinal profile of the River Elbe, a significant increase in the concentrations was registered after the Mulde confluence near Magdeburg. Concentrations increased from 12 pg WHO₂₀₀₅-TEQ/g (Domnitzsch, km 173, upstream Mulde) to 68 pg WHO₂₀₀₅-TEQ/g (Magdeburg, km 318, downstream Mulde). Further downstream of Magdeburg the concentrations then decreased until the Elbe estuary.

The spatial distribution of dioxins as seen in 2008 matched well with earlier campaigns in 2002, both for aquatic solids and alluvial soils, suggesting minor change of the situation since then.

The main factors contributing currently to the dioxin pollution of the Elbe arise from the sinks of the historic primary releases, which are under hydraulic redistribution since then. In particular the remobilisation of contaminated sediments from the Mulde and Saale catchments and from the slack water zones of the Elbe, as well as soil erosion from contaminated floodplains in the course of high water events, are continuing to introduce dioxins into the river. This can be seen from the comparison of time series of dioxins in suspended solid matter from the Elbe and the tributaries concerned, demonstrating contaminated suspended solid matter from Mulde and Saale being still introduced into the Elbe.

Also the samples from the North Sea revealed elevated levels of dioxins of up to 16 WHO₂₀₀₅-TEQ/g (KS11) that display the congener pattern from the Bitterfeld-Wolfen Region. The

observations suggest that suspended solids originating from Bitterfeld-Wolfen have been transported into the North Sea South of Helgoland.

The spatial information obtained on the occurrence of PCDD/Fs, as well as the fingerprint based source apportionments suggest the need to inhibit further remobilization from the Spittelwasser catchment and the adjacent historic production sites and, in second line, from contaminated alluvial soils and slack water zones downstream of the Spittelwasser.

In contrast to the PCDD/Fs, PCBs are mainly present in the in the Upper Elbe in the Czech Republic. After the German border PCBs display an overall decrease.

Dioxin-like PCBs (DL-PCBs) in the Elbe had a maximum value of 20 pg WHO₂₀₀₅-TEQ/g at Pardubice-Semtin (CZ, km -237). The overall maximum of 37 pg WHO₂₀₀₅-TEQ/g was detected in the *Spittelwasser*, the latter not impacting the catchment significantly due to its low discharge.

The maximum concentration of the 7 indicator PCBs in the river Elbe was 180 ng/g at Decin (CZ, km -14). Downstream of Decin and along the whole German stretch a decline in the PCB concentrations was registered.

Higher values for the 7 indicator PCBs found in the former sewage sludge dumping zones in the North Sea were 4.5 ng/g (average KS8) and 8.2 ng/g (average KS11) respectively. In comparison, the indicator PCBs from the sampling site 69 and the reference area (site 90) yielded about 3 ng/g, which could be indicative of the influence of the dumping.

Other than PCDD/Fs, PCB emissions into the Elbe cannot be attributed to a dominant source or region. Indicator PCBs did rise more or less constantly in concentration until the German border, suggesting a variety of cumulative emission sources along the whole Czech stretch.

Thus, no specific recommendation on how to decrease the PCB pressure on the River Elbe can be given on the basis of the data acquired in this study. Detailed regional scale monitoring in the Czech stretch, together with the evaluation of production statistics regarding potential PCB sources are needed here. After all the PCB toxicity in eel is exceeding that of PCDD/F up to an order of magnitude (investigations of eels taken after the flood event in August 2002).

As an amendment to the chemical analyses, two Ah-receptor based bioassays (DR CALUX^R and EROD), which display the dioxin-like activity of all pollutants present, were performed on a subset of the samples (blind study). For The DR CALUX^R the comparison revealed a good agreement between the HRGC/HRMS results on dioxins and dioxin-like PCBs along the German stretch and the bioassay. However, along the Czech section of the Elbe the DR CALUX^R displayed a 10 times higher dioxin-like activity than the chemical analyses. This suggests that the solid material in the Czech section contains additional persistent dioxin-like acting pollutants. In comparison to the DR CALUX^R test, the EROD assay displayed even higher dioxin-like activities, less than 1 % of the observed signal could be explained by the PCDD/Fs and dioxin like PCBs quantified via chemical analyses. The differences can be explained by the fact that the clean up procedure for the DR CALUX^R eliminated the less

persistent organic pollutants in the extract, while the EROD procedure remained sensitive to those.

More research is needed to identify the compounds behind the so far unexplained signal of the bioassays and to localize their emission sources.

Regarding the risk for the aquatic food chain and the human diet, the reduction of PCBs in the River Elbe ecosystem appears crucial as indicated by the dominance of the PCB over the PCDD/Fs in toxicity equivalents detected in eel samples.

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1 Introduction

The Elbe is one of the most important of the Central European Rivers. A large proportion of its catchment area remained in a near-natural state, and it includes extensive conservation areas. In particular the floodplains contain a variety of endangered plant and animal species. The fall of the Iron Curtain led to the closure of production plants in the former German Democratic Republic, the construction of municipal and industrial waste water treatment plants and thus to a noticeable improvement in the quality of the aquatic environment. The reduction of pollutant loads into the Elbe resulted in an increase in the number of fish species from 79, as registered between 1991 and 1993, to 104 in 2005. Even salmon (*Salmon salar*), absent in the Elbe for decades, reappeared in the small tributaries of the Upper Elbe for spawning (Füllner et al. 2003).

On the other hand the catchment in both the Czech and German section contains many contaminated industrial areas, agriculturally used land and sewage treatment plants, resulting in a wide spectrum of contaminants and nutrients being released into the Elbe. This is exemplarily reflected in the contamination of Elbe fish with dioxins and PCBs. Samples of muscle tissue taken from eels (*Anguilla anguilla*) contained concentrations of PCDD/Fs as well as with dioxin-like PCBs (DL-PCBs), which significantly exceeded the maximum Residue Limits of the European Food Legislation (Stachel et al. 2007; Figure 1). These levels were sufficient to necessitate restrictions in the consumption of this popular food fish. In particular eels caught in Hamburg surface waters returned high levels of pollutants in muscle tissue, at least in the past (Götz 2010).

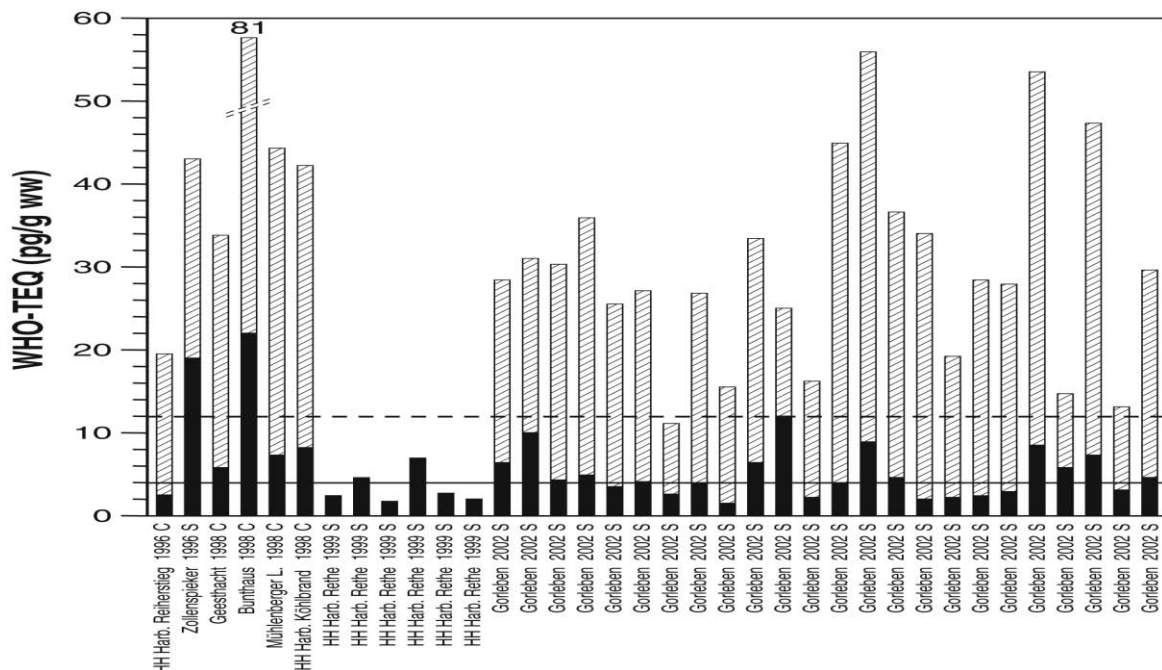


Figure 1: Contamination of muscle tissue obtained from eels (*Anguilla anguilla*) caught in the Elbe and Hamburg Harbor with dioxins (black columns) and DL-PCBs (hatched columns).

Perm. maximum for dioxins=4 pg/g ww, Perm. maximum for sum of dioxins and DL-PCBs=12 pg/g ww. S=single fish, C=composite sample, ww=wet weight (Stachel et al. 2007).

Flood events occur several times every year in the Elbe and its tributaries, each time resulting in the deposition of solid matter in the floodplains, which leads to the contamination of soils and vegetation. As a result, enhanced pollutant levels in foodstuffs from productive livestock consuming contaminated forage were observed (Umlauf et al. 2005, Stachel et al. 2006). At the same time, pollutants present historically in the floodplains can be remobilized and introduced into the rivers.

In order to obtain an updated dataset about the levels and the spatial distribution of PCDD/Fs, DL-PCBs and indicator PCBs in the River Elbe, its main tributaries and the North Sea, solid matter samples were taken in September 2008. The results obtained shall serve as a basis for taking further steps towards effectively improving the water quality of the Elbe and, both at an international level as well as within the FGG Elbe¹. The adopted measures will become part of the FGG Elbe's sediment management scheme.

2 The institutions involved and reporting obligations

The investigation presented in this paper was carried out on the initiative of the ad-hoc contaminants working group with the approval of the task force on surface waters (AG Oberflächengewässer). Technical aspects were agreed with the ad-hoc contaminants working group. The following member institutions of the FGG Elbe and the IKSE (International Commission for the Protection of the Elbe River) participated:

- Vyzkumny ustav vodohospodacky T.G. Masaryka (VUV), Prague
- Povodi Labe, Hradec Kralove
- Povodi Vltavy, Prague
- Sächsisches Landesamt for Umwelt and Geologie, Dresden
- Staatliche Betriebsgesellschaft for Umwelt and Landwirtschaft, Neusörnewitz
- Bundesanstalt for Gewässerkunde, Coblenz
- Landesbetrieb fuer Hochwasserschutz and Wasserwirtschaft, Dept. of Chemistry, and Sachbereich Wasseranalytik
- Landesumweltamt Brandenburg, Potsdam
- Niedersächsische Landesbetriebe for Wasserwirtschaft, Küsten- and Naturschutz, Lüneburg, Hannover-Hildesheim and Stade
- Behörde for Soziales, Familie, Gesundheit and Verbraucherschutz, Hamburg
- Ministry of Urban Development and Environment, Hamburg
- Flussgebietsgemeinschaft Elbe (FGG Elbe)
- Internationale Kommission zum Schutz der Elbe (IKSE)

¹ Flussgebietsgemeinschaft Elbe – the River basin Community Elbe, inaugurated by the German Federal States involved

- Hamburg Port Authority
- Landesamt für Landwirtschaft, Umwelt und ländliche Räume des Landes Schleswig-Holstein, Flintbek
- Anstalt Helgoland, Alfred-Wegener-Institut, Helgoland

The chemical analyses were carried out by the Dioxin and POPs laboratory of the European Commission's Joint Research Centre (JRC), Institute for Environment and Sustainability (IES) in Ispra (Italy).

The Biotests were conducted by BioDetection Systems b.v., Science Park 406, 1098 XH Amsterdam, The Netherlands and the Institute for Environmental Research, RWTH Aachen University, Worringerweg 1, 52074 Aachen, Germany

Neurostat Hamburg conducted a cluster analysis of the results (neuronal networks - Kohonen networks).

The chemical analysis results were sent to the FGG Elbe and the IKSE institutions listed above in June and August 2009, and then presented and discussed in the course of the 13th meeting of the ad-hoc contaminants working group in Berlin in October 2009 as well as the 38th meeting of the Coordinating Council of the FGG Elbe in February 2010 in Erfurt. The presentation of the results was summarized in a condensed report which was made available to the participants. In its 14th meeting held in March 2010, the Elbe Council gave its approval for the results to be published on the FGG Elbe website.

3 Materials and Methods

3.1 Sampling sites and sampling

Figure 2 shows the Elbe catchment area and the sampling sites used, distinguished by different colours: The sites on the Elbe are shown in yellow, those on the tributaries mauve and those in the North Sea in black. A table of the respective coordinates can be found in the Appendix I. A total of 35 solid matter samples were taken during September 2008. The appended tables II-IV provide the analytical results and details of the sampling. Samples were taken from sediments (individual samples), settling material originating from suspended matter (four-week composite samples from monitoring stations, Stachel et al. 1995) and suspended particulate matter (continuous centrifuge). Sampling devices are shown in Appendix VII. The sediment samples were obtained from the upper surface using a Van-Veen grab. The depth for the river sediments is 0-12 cm, and for the North Sea sediments 0-18 cm.

The North Sea sampling sites KS8 and KS11 are situated within the area previously used for dumping digested sewage sludge from Hamburg. In 2008 samples were obtained there at depths of 16 m (KS8) and 21 m (KS11). Additional samples were taken from these locations for confirmation in September 2009.

In a pilot project the Hamburg Port Authority dumps sediments of the Hamburg delegation stretch at ton E3 in the North Sea. This project is accompanied by a comprehensive monitoring programme (Hamburg Port Authority, Report 2009). Three sampling sites of the monitoring programme are part of our study: site 21 at a distance of 2 km from E3, site 69 at a distance of 12 km from E3, and site 90 which is located in a reference region at a distance of 10 km from E3.

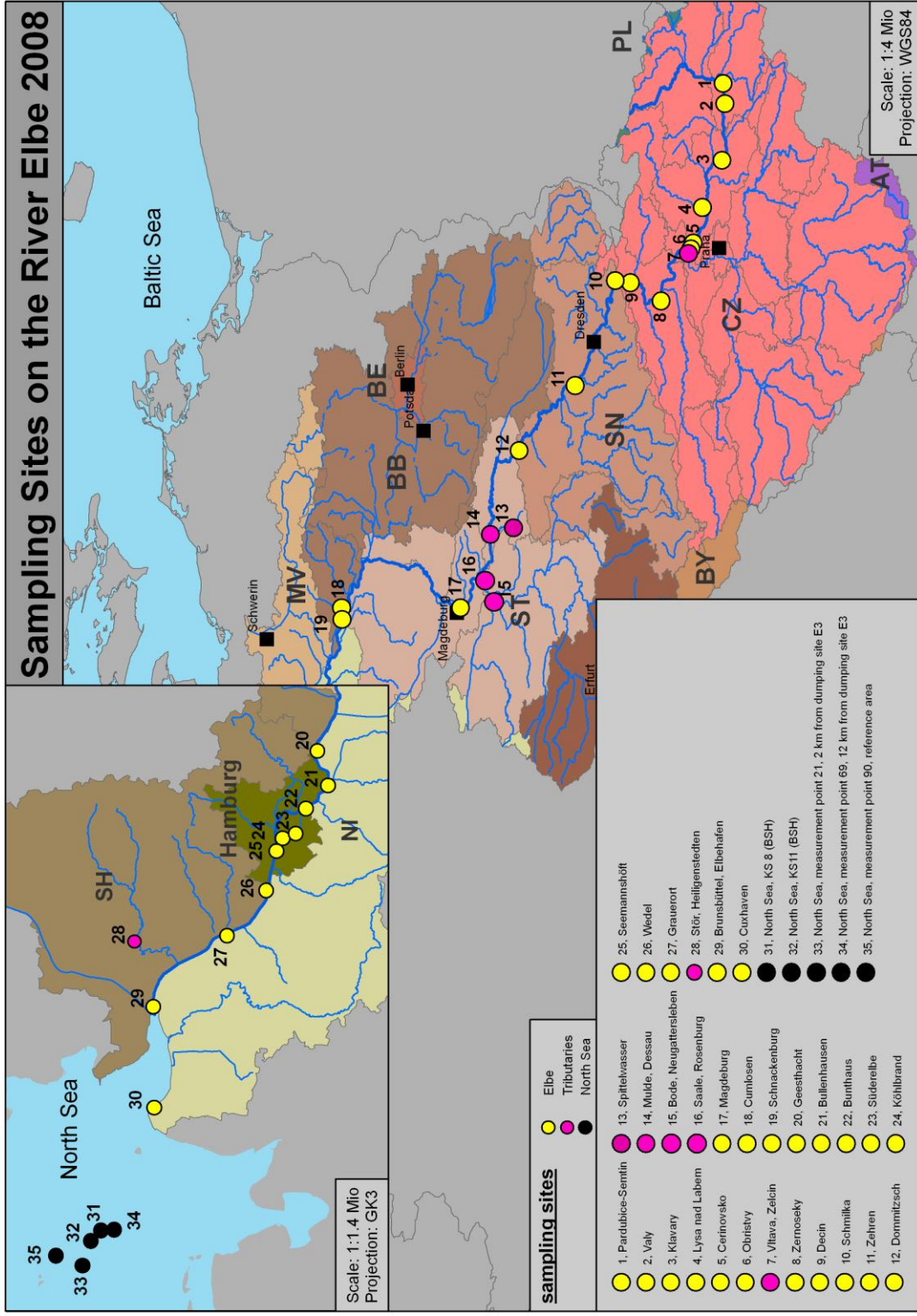


Figure 2: Catchment of the Elbe with sampling sites from 2008. In 2009 additional samples were taken at the sites KS1.1 (32) and KS8 (31)

3.2 Investigated compounds

Dioxins and PCBs include a large number of structurally similar compounds with comparable effect profiles, which pose a hazard to human health and the aquatic ecosystem. The PCB substance group includes coplanar (non-ortho and mono-ortho) congeners whose structure can display a planar, dioxin like geometry. The generic term used for them is ‘dioxin-like PCBs’ (DL-PCBs). Their physical and biological properties are comparable with those of the 2,3,7,8 substituted PCDDs and PCDFs.

As the individual dioxin and furan congeners display differing degrees of toxicity, the ‘toxicity equivalent system’ (TEQ) was introduced as a simplified method for estimating the overall hazard potential of dioxin and PCB mixtures. According to the ability of combining with the aryl-hydrocarbon receptor (Ah-receptor), the individually determined substance concentrations for the 17 2,3,7,8-substituted PCDD/Fs and 12 DL-PCBs are weighed for their relative toxicity and the sum of all individual toxicities is condensed to a single value reflecting the total toxicity of the mixture.

As a reference, the toxicity of 2,3,7,8-tetrachloro dibenzo-p-dioxin (TCDD, the most toxic compound in the group of polychlorinated dibenzo-p-dioxins) is set to 1. In relation to this, toxicity equivalence factors (TEFs) are assigned to the other PCDD/Fs and PCBs ranging from 0.0001 to 1. Thus a dioxin/furan with a toxicity equivalent of 0.5 is considered to be half as toxic as 2,3,7,8-TCDD (Van den Berg et al. 2006).

The total TEQ-value of a dioxin or PCB mixture is obtained by multiplying the individual PCDD/F and DL-PCB concentrations with the corresponding TEFs, and summing them up. The toxicity equivalence system is only used for the chlorinated dioxins and furans as well as the DL-PCBs with their stereoisomerism similarity to 2,3,7,8-TCDD.

Another group of PCBs, the so called “indicator PCBs” is often reported as an indicator for describing the whole technical mixture of PCBs. The total content of unaltered, technical PCB mixtures can be described by summing up the concentrations of the individual indicators and multiplying them by a factor of 5. However, in the environment, where the PCB composition is often altered due to the different transport and decomposition properties of the individual PCBs, the concept of the total PCB estimate is very limited. In such cases, only the sum of the “seven indicator PCBs” is reported.

The solid samples were analysed for the 17 2,3,7,8-substituted PCDD/Fs, the homologue sums, the 12 DL-PCBs and the 7 indicator PCBs.

PCDD/Fs

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; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-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

Indicator PCBs:

TriCB-28; TeCB-52; PeCB-101; PeCB-118; HxCB-138; HxCB-153 and HpCB-180

Currently the samples are reprocessed at the JRC for the analysis of additional persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs).

3.3 Analytical methods

The samples were analysed after being freeze dried, disaggregated and sieved (<2 mm). The samples were homogenized and spiked with ¹³C-labelled standards and extracted in a Soxhlet extractor for 24 h using n-hexane/acetone (220/30, v/v). An automated clean-up system was used for purification, consisting of a multi-layer silica column (acid/neutral) together with a combination of basic aluminium oxide and activated charcoal. The instrumental analysis was based on the isotope dilution procedure and the quantification was carried out according to US EPA Method 1613 and Method 1668 using HRGC-HRMS. Details are given in the Appendix VI.

In parallel, a sediment from the 13th Round International Inter calibration 2008 was analysed as intra-laboratory reference material (see Appendix V).

Together with the samples, four analyses of the intra-laboratory reference material were carried out. For selected congeners and homologue sums the criteria average (AV, in ng/g) and the relative standard deviations (RSTD, in %) were as follows. For 2,3,7,8-TCDD: AV=0.0071, RSTD=14; 1,2,3,4,6,7,8-HpCDF: AV=0.1959, RSTD=29.1. For the homologue sums TCDD: AV=0.0918, RSTD=12.6; HpCDF: AV=0.3083, RSTD=23.6. More results obtained from the analyses of the reference material are shown in the Appendix V.

3.4 Bioassay-tests

As a complementation to the analysis of individual substances, bioassay-tests can be used to register the combined effects of pollutants on a test system. These tests are action specific; for instance, they describe interactions which take place with cell components such as the Ah-receptor. The Ah-receptor is a protein in the cytosol and in the cell nucleus of vertebrates. It participates as a transcription factor for the regulation in the gen activity. For

example dioxins, DL-PCBs and components of tobacco smoke activate the Ah-receptor. The originated receptor-ligand-complex links in the cell nucleus to the DNA and activates the enzyme production of the cytochrome P450 family which is mostly localized in the liver cells and is responsible for the metabolism of xenobiotics in the liver. Research results of the recent years show that the Ah-receptor is part of the carcinogenesis and is responsible for the toxic effect of dioxins and DL-PCBs. An indication that pollutants and Ah-receptors mutually affect each other can provide evidence for toxicological damage to vertebrates.

In vitro bioassays such as ethoxyresorufin-O-deethylase (EROD) or chemical-activated luciferase expression (DR-CALUX^R) allow an insight into Ah receptor-mediated toxic effects.

In this project, the DR CALUX^R test was executed by BioDetection Systems² on a representative set of 25 solid samples. This testing system is specifically designed for the detection of dioxin-like chemicals. The following procedure was used: The dried solid matter samples were extracted using toluene/acetone and the ASE technique. An aliquot of about 5 g was pre-cleaned through a multilayer silica gel column. Finally, the extract obtained was restricted using a stream of N₂ and assimilated with dimethyl sulphoxide. Details can be found in Besselink et al. 2004. The samples were coded to BDS.

In addition a subset of sediment samples was analysed with the EROD test at the RWTH Aachen University³. Freeze-dried sediments were extracted with n-hexane/acetone (1:1, v/v) by means of pressurized liquid extraction (PLE). The Neutral red assay on cytotoxicity and the EROD (7-ethoxy-resorufin-o-deethylase) assay on dioxin-like activity were then applied with the resulting extracts using the RTL-W1 permanent cell line.

3.5 Mathematical clustering (classification) procedure

3.5.1 Preparation of the dioxin data for the mathematical evaluation methods

For the purposes of applying the cluster procedure it was necessary to transform the dioxin raw data – i.e. the measured concentrations for the 17 highly toxic (2,3,7,8-substituted) dioxin and furan congeners – in a suitable way. In accordance with Hagenmaier et al. (1994), the concentrations of the individual congeners were divided by the corresponding homologue sums. For instance, the concentration value obtained for 2,3,7,8-tetrachlordibenzo-p-dioxin (2,3,7,8-TCDD) was divided by the value for the sum of the 22 tetrachlorinated dibenzodioxins (sum of TCDD). The concentrations of the OCDD and OCDF were divided by the sums of the PCDDs or PCDFs respectively. As an 18th variable, the quotient obtained

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by dividing the sum of the dioxins by the sum of the dioxins and furans was incorporated as well. The following passage describes the algorithm for the transformation of the 18 dioxin variables:

$rD48 = \frac{2,3,7,8\text{-TCDD}}{\text{sum TCDD}}$; $rD54 = \frac{1,2,3,7,8\text{-PeCDD}}{\text{sum PeCDD}}$; $rD66 = \frac{1,2,3,4,7,8\text{-HxCDD}}{\text{sum HxCDD}}$; $rD67 = \frac{1,2,3,6,7,8\text{-HxCDD}}{\text{sum HxCDD}}$; $rD70 = \frac{1,2,3,7,8,9\text{-HxCDD}}{\text{sum HxCDD}}$; $rD73 = \frac{1,2,3,4,6,7,8\text{-HpCDD}}{\text{sum HpCDD}}$; $rD75 = \frac{\text{OCDD}}{\text{sum PCDD}}$; $rF83 = \frac{2,3,7,8\text{-TCDF}}{\text{sum TCDF}}$; $rF94 = \frac{1,2,3,7,8\text{-PeCDF}}{\text{sum PeCDF}}$; $rF114 = \frac{2,3,4,7,8\text{-PeCDF}}{\text{sum PeCDF}}$; $rF118 = \frac{1,2,3,4,7,8\text{-HxCDF}}{\text{sum HxCDF}}$; $rF121 = \frac{1,2,3,6,7,8\text{-HxCDF}}{\text{sum HxCDF}}$; $rF124 = \frac{1,2,3,7,8,9\text{-HxCDF}}{\text{sum HxCDF}}$; $rF130 = \frac{2,3,4,6,7,8\text{-HxCDF}}{\text{sum HxCDF}}$; $rF131 = \frac{1,2,3,4,6,7,8\text{-HpCDF}}{\text{sum HpCDF}}$; $rF134 = \frac{1,2,3,4,7,8,9\text{-HpCDF}}{\text{sum HpCDF}}$; $rF135 = \frac{\text{OCDF}}{\text{sum PCDF}}$; $rD = \frac{\text{sum PCDD}}{\text{sum (PCDD+PCDF)}}$; (T=tetra; Pe=penta; Hx=Hexa; Hp=Hepta; O=Octa; CDD=chlorinated dibenzo-p-dioxin; CDF=chlorinated dibenzofuran).

This transformation is based on two assumptions: Firstly, that the differences in the physico-chemical characteristics of the PCDD/F congeners within a given homologue group (with the same degree of chlorination) are smaller than those of congeners belonging to different homologue groups (having differing degrees of chlorination). Secondly, that the behaviour of the PCDD/Fs within a given environmental compartment (such as migration, biotic and abiotic degradation) and their distribution amongst the compartments is determined largely by their physico-chemical properties. According to these two assumptions, changes in concentration levels occur in a similar manner within a homologue group. For example, if dioxins belonging to two different homologue groups are transported from a contamination source elsewhere, the following situation could arise: For one homologue group 50% degradation takes place during the transport, whilst for the other one the degree of degradation is zero. As a result, in respect of the absolute congener concentrations the dioxin pattern after the transport will be different compared with the original pattern. However, when the Hagenmaier transformation is applied to the congener concentrations the dioxin pattern reverts to the original, because the transformation has the effect of compensating the differences in the two dioxin individual patterns which arise as a result of the degradation. In other words, the pattern of the relative dioxin concentrations remains practically unchanged in the course of the transport. For this data transformation the pattern recognition is independent of the absolute amounts of the dioxin concentrations. The pattern remains detectable even for extremely small absolute concentrations, so that it becomes possible to trace dioxin transport paths over very long distances.

3.5.2 Multivariate statistical cluster methods

A cluster analysis serves to categorize the dioxin patterns of the samples into clusters (agglomeration) in such a way that the patterns within a cluster are as similar as possible and the differences from cluster to cluster as large as possible.

Hierarchical cluster analysis

The hierarchical agglomeration takes place in several steps. The input consists of a 338 x 18 data matrix: 338 dioxin samples and 18 transformed dioxin variables.

Initially, each individual dioxin sample is considered to constitute an autonomous cluster (338 clusters). In the first processing stage, the two clusters which display the highest degree of similarity are put together to form a common cluster. In this case it is sufficient simply to calculate the degrees of similarity for all possible pairs of the 338 dioxin samples and select the pair which returns the highest value. This reduces the number of clusters by one to 337. The measure of similarity is calculated using the cosine as follows:

similarity is calculated using the cosine as follows:

$$\text{cosine: } \frac{\sum (X_i * Y_i)}{\sqrt{\sum X_i^2 * \sum Y_i^2}}$$

X_i : value of the dioxin sample X in the i th dioxin variable

Y_i : value of the dioxin sample Y in the i th dioxin variable

Now the process is repeated for the 337 clusters, of which one contains two dioxin samples, in order to obtain new similarity values for all the pairs of clusters. Again, the two clusters which return the highest degree of similarity are combined to form one. The procedure is repeated until all the 338 dioxin samples have been collected together into a single cluster.

In order to calculate the similarity values for clusters containing more than one dioxin sample, the 'linkage between the groups' clustering method was implemented. This method involves selecting all pairs of dioxin samples present in both clusters which each contain a single dioxin variable from each of the two clusters. The degree of similarity is then calculated for each of these pairs as described above. The arithmetic mean of the similarities is then taken as the measure of similarity between the two clusters.

In an earlier study carried out by Götz and Lauer (2003) the best measure for similarity and the clustering method to be used for dioxin data collectives from the Elbe with this composition and structure was established. The procedure does not automatically generate a 'correct' number of clusters. Clustering solutions involving 5 to 15 clusters were computed. It transpired that the 7 cluster solution was the most plausible.

The implementation of the cluster-centres analysis (previously known as k-means analysis) did not yield any plausible results. A useful introduction to multivariate-statistical cluster methods can be found in Brosius (2006).

The hierarchical cluster analysis and the cluster-centres analysis were performed using the SPSS program package SPSS 15 for Windows, Chicago

3.5.3 Cluster analysis with the Kohonen network of the neuronal networks

1st stage: In this case the initial vector for the Kohonen network consists of the 18 transformed dioxin concentrations (18 number components) of a dioxin sample. The data input is the same as that used for the hierarchical cluster analysis: a 338 x 18 data matrix made up of 338 dioxin samples and 18 transformed dioxin variables.

The basic framework of the Kohonen network is a one-dimensional or two-dimensional array consisting of neurons with feedback being generated over short distances between neighbouring neurons. In our case, each neuron is also associated with a weighting vector which also consists of 18 number components. When an initial vector (signal) consisting of a dioxin environmental sample is 'sent' through the Kohonen network, all the neurons (weighting vectors) compete with each to obtain 'possession' of it. The neuron (weighting vector) which can claim to have the greatest degree of 'similarity' with the initial vector is the 'winner' ('the winner takes all') and is allowed to transmit its initial activity to the neighbouring neurons. In this way, not only the weighting of the winning neuron, but also that of its nearest neighbours is adjusted. The initial vectors of all the dioxin environmental samples are sent through the Kohonen network. This procedure is repeated until the weighting factors for the neurons no longer change significantly.

A Kohonen network consisting of 49 neurons (7 x 7 neurons) was used, resulting in two sets of output data. The first one contains the code of the winning neuron. Each neuron in the Kohonen network has a number assigned to it, ranging in this case from 1 to 49. The other set contains the codebook vector for each neuron. These are the 18 weightings (numbers) of the winning neuron. Thus the entire second output set consists of a 49 x 18 matrix, i.e. 49 winning neurons and 18 weighting variables. The 338 dioxin samples are distributed over the 49 neurons. The calculation determines which dioxin sample is assigned to which neuron.

2nd stage: The output of the Kohonen network, the 49 x 18 matrix, is used as input for the hierarchical cluster analysis in order to generate cluster solutions. The implementation of a two-stage procedure is based on a recommendation made by Giller (1997). A description can be found in Samarasinghe (2007).

The computations for the Kohonen network were carried out using the SPSS program package SPSS Neural Connection 2.1 for Windows, Chicago in combination with SPSS 10 for Windows, Chicago.

4 Results and discussion

Through the participation of and support received from the institutions listed in chapter 1.1 it became possible, for the first time, to generate a longitudinal profile for the whole River Elbe for the analysis of solid material. The area covered by this study ranged from Pardubice-Semtin (km -237) in the Czech Republic to the North Sea south of Helgioland and included the main tributaries Vltava, Mulde, Saale and Stör as well as the secondary tributaries Spittelwasser and Bode (for sampling sites see Figure 2). The results obtained for the Spittelwasser and the Bode exemplify how these hazardous substances are introduced into primary tributaries, which then contribute to the contaminant load of the Elbe.

4.1 Longitudinal profile

4.1.1 TOC and fine-grain fraction

In order to obtain an overview of the sample characteristics, the total organic carbon (TOC) content and the fine-grain fraction <20 µm were determined for each sample (see Appendix I). Both parameters display a broad range depending on the sampling site and the type of sample. The samples taken from the tidal Elbe and the North Sea tend to be of fine sand, whereas those taken from the upper and middle stretches and the tributaries contain large proportions of fine-grained material (silt, clay). In general, finely grained material with a large organic fraction readily adsorbs hydrophobic compounds such as PCDD/Fs and PCBs.

The evaluation of the results yields the following distribution: In the Upper Elbe, the TOC levels lie between 3 and 31 % by weight (dry mass); in the Middle Elbe the levels (in % by weight, dry mass) are between 5.6 and 7.9; the range for the Lower Elbe is from 1.7 to 3.9, and in the North Sea the levels remained below <1 to 2. For the fine-grain fraction <20 µm, the values were as follows (in % by weight, dry mass): Upper Elbe: 3 to 7; Middle Elbe: 46 to 69; Lower Elbe 26 to 70; North Sea: 33 to 41.

The Appendix I provides an overview of these results. Together with the TOC content, a standardization of the PCDD/F analysis results was carried out in order to determine whether a relationship can be established between them. It transpires that no such connection could be established for this study series (results not shown).

4.1.2 PCDD/Fs and PCBs

The PCDD/F and DL-PCB results are presented graphically as WHO-TEQ (Figure 3, Figure 4); Figure 5 shows the summed concentrations of 7 PCB congeners, the indicator PCBs. The tables in Appendix II-IV contain details of the individual substance concentrations (on a dry weight basis), the WHO-TEQ values and the summed homologue values for the PCDD/Fs.

PCDD/Fs

The PCDD/F longitudinal profile in the Elbe River displays relatively low concentrations in samples obtained in the CZ stretch and also in GER upstream of the confluence of the tributary Mulde. Considerably higher values appeared downstream the Mulde and Saale confluence (68 pg WHO₂₀₀₅-TEQ/g near Magdeburg compared to 12 pg WHO₂₀₀₅-TEQ/g at Domnitzsch upstream of the Mulde). Further downstream, the concentrations decrease until North of the City of Hamburg. It is evident, that the River Mulde and Saale catchments have an important impact on the PCDD/Fs present in Elbe solids sampled after their confluence. The values obtained for the North Sea sediments at the sampling sites KS8 and KS11 lie in the same range as those obtained in the course of the last 100 kilometres before the Elbe enters the North Sea (Figure 3).

The PCDD/F concentrations in the Elbe lie between 1.9 pg WHO₂₀₀₅-TEQ/g (Klavary) and 68 pg WHO₂₀₀₅-TEQ/g (Magdeburg). In the tributaries, the concentrations ranged from 3.9 pg WHO₂₀₀₅-TEQ/g (Vltava, Zelcin) to 1260 pg WHO₂₀₀₅-TEQ/g (Spittelwasser, Mulde tributary). The North Sea sediments display PCDD/F values between 2.5 pg WHO₂₀₀₅-TEQ/g (sampling site 69) and 22 pg WHO₂₀₀₅-TEQ/g (KS11) (Figure 3 and Appendix II). The sampling sites KS8 and KS11 were sampled again in September 2009, resulting in concentration ranges of 2.3 to 3.9 pg WHO₂₀₀₅-TEQ/g (KS8) and 7.7 to 18 pg WHO₂₀₀₅-TEQ/g (KS11) (see Appendix II). The mean values were 5.2 pg WHO₂₀₀₅-TEQ/g (KS8) and 16 pg WHO₂₀₀₅-TEQ/g (KS11).

The corresponding values for the samples taken downstream of Hamburg Harbour in the direction of the North Sea are again lower, between 2.1 and 3.1. These findings can be explained by the fact that downstream of the harbour the contaminated terrestrial sediments are mixed with the relatively unpolluted marine sediments which are transported upstream by the tide (tidal pumping). In addition to this, we may assume that marine and fluvial sediments are contaminated also through atmospheric input. Generally, atmospheric samples display values for the quotient (summed PCDF)/summed PCDD) which are less than 1; i.e. in such cases the congener pattern is dominated by the PCDDs.

PCBs

The PCB longitudinal distribution differs considerably from that of the PCDD/Fs, suggesting different sources and locations of PCB emissions into the catchment. The PCBs concentrations in the upper stretches of the Czech section of the River Elbe are highest, and they decrease along the German stretch (Figure 4 and Figure 5).

Dioxin-like PCBs

Figure 4 shows the DL-PCB results. In the Elbe, the concentrations range is 0.8 pg WHO₂₀₀₅-TEQ/g (Köhlbrand) to 20 pg/g (Pardubice-Semtin). The tributaries lie between 1.5 pg WHO₂₀₀₅-TEQ/g (Stör, Heiligenstedten) and 35 pg WHO₂₀₀₅-TEQ/g in the Mulde tributary

Spittelwasser. The North Sea sediments from the sites 21 and 69 (2 km and 12 km from dumping area E3) display a range from 0.4 pg/g to 0.3 pg WHO₂₀₀₅-TEQ/g. Including the samples from 2009, KS8 yields a mean value of 0.63 pg WHO₂₀₀₅-TEQ/g, and KS11 a mean value of 0.85 pg WHO₂₀₀₅-TEQ/g (see Appendix III).

DL-PCB TEQ concentrations present in the solids are relatively low compared to those of the PCDD/Fs. However, due to their lipophilic properties, combined with a higher mobility, PCBs accumulate more readily in the fatty tissue of fish and therefore in the food chain. Indeed, looking into the data of German Eels (Figure 1) it appears the DL-PCBs carry the majority of the combined dioxin and PCB toxicity. Obviously the bioavailability of the DL-PCBs is higher. This may be a result of source specific differences, and differences in the way in which PCBs and PCDD/Fs are emitted into the river. Certainly PCBs will display a higher share in the dissolved phase, which increases the share of a more bio-available fraction when compared to dioxins, which have a higher tendency to associate with solids.

Indicator PCBs

The downstream concentration profile for the indicator PCBs is shown in Figure 5. It is similar to that of the DL-PCBs, except of the sites Pardubice-Semtin and the Spittelwasser, where the indicator PCBs do not peak. In the Elbe they range from 12 to 15 ng/g (Cuxhaven, Köhlbrand) to a maximum of 180 ng/g (Decin). The corresponding values for the tributaries lie between 15 ng/g (Stör, Heiligenstedten) and 103 ng/g (Vltava, Zelcin).

Since the Elbe freight being mixed with less contaminated solids, the concentrations in the North Sea sediments are the lowest of all. At a distance of 2 km from the dumping area E3, the sum of the indicator PCBs amounts to 2.5 ng/g (sampling site 21), and at 12 km distance to 3.3 ng/g (sampling site 21); the sample from the reference area (sampling site 90, 10 km distance) returned a similar, low value of 3.1 ng/g. Taking account also the data obtained in 2009, the site KS8 yielded a mean value of 4.5 ng/g and for KS11 a mean value of 8.2 ng/g (see Appendix IV). As is the case for the PCDD/Fs and DL-PCBs, the concentration of the indicator PCBs is higher at KS11 than at KS8. The ‘Zernoseky’ sample could not be evaluated.

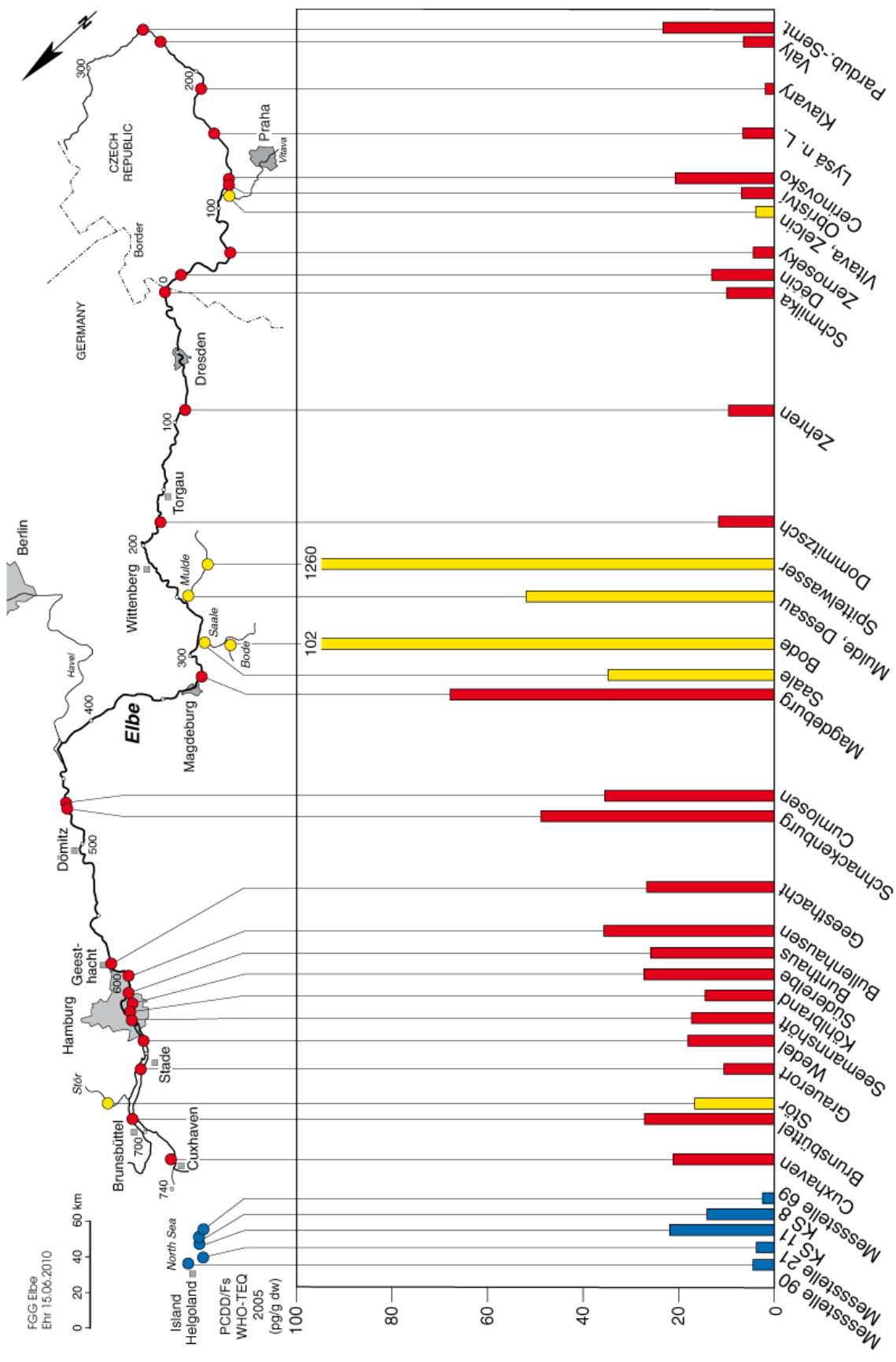


Figure 3: Dioxins in solid material samples taken from the Elbe, its tributaries and the North Sea

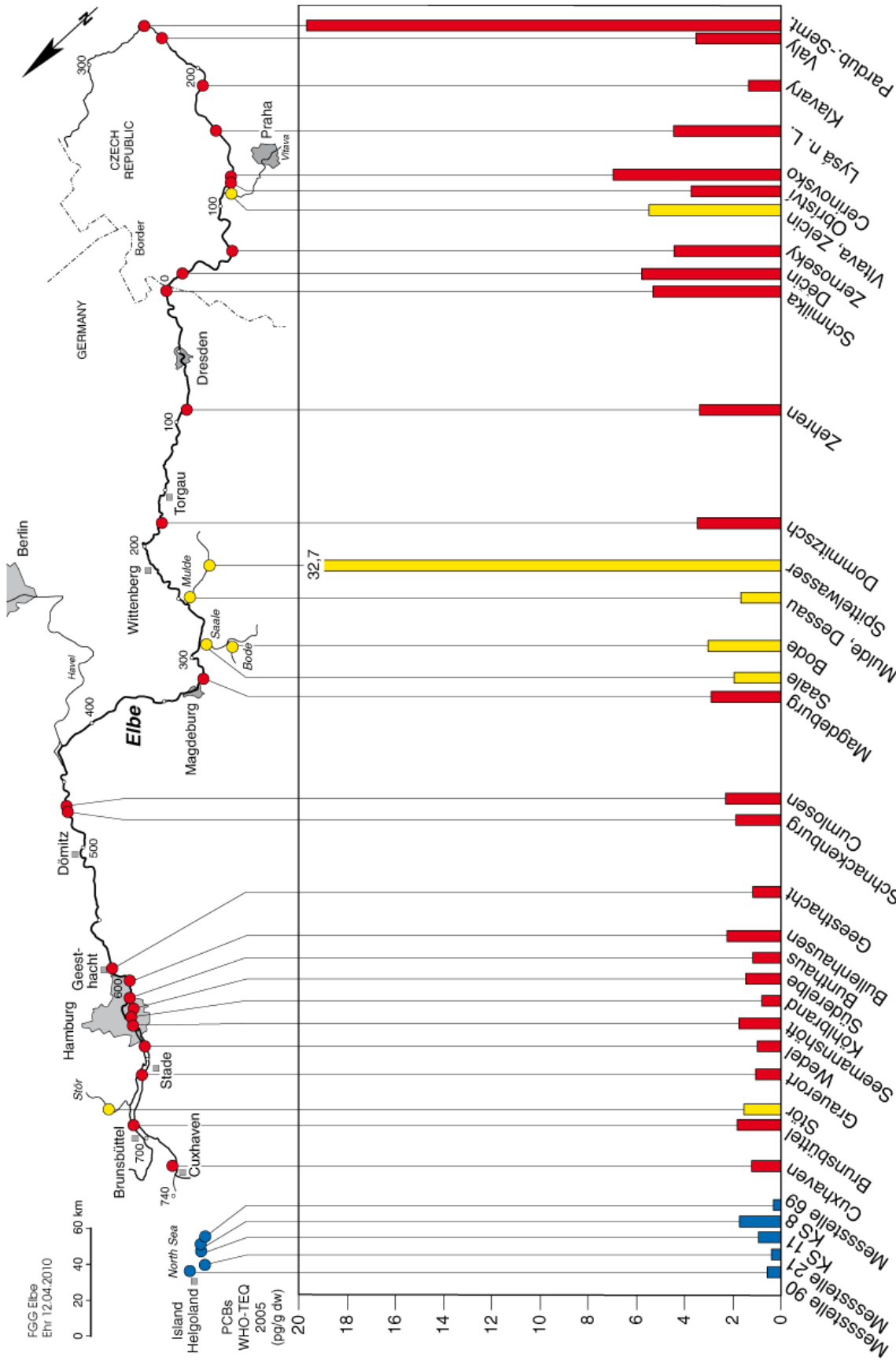


Figure 4 : Dioxin-like PCBs in solid material samples taken from the Elbe, its tributaries and the North Sea

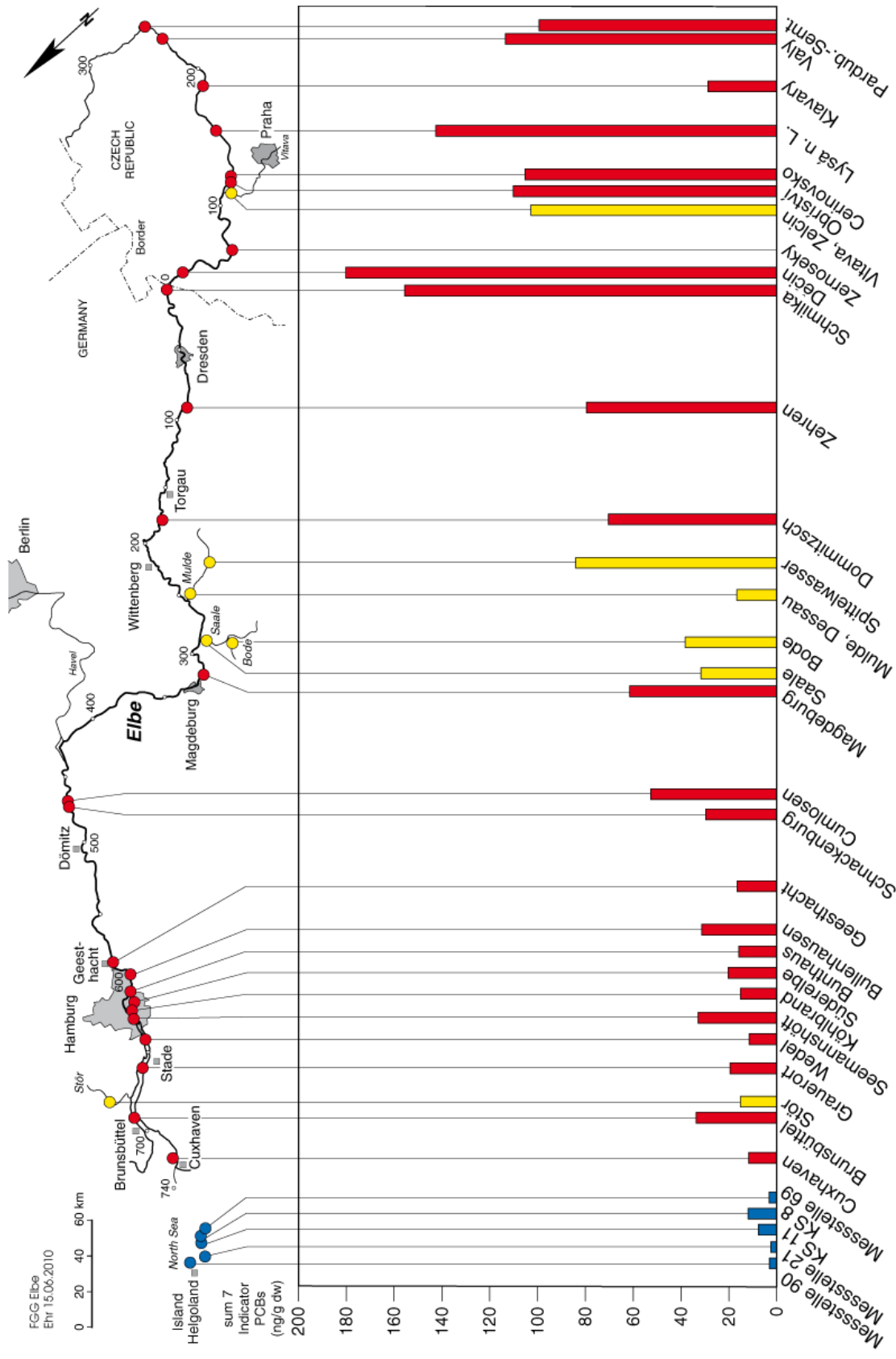


Figure 5: Sum of the 7 indicator PCBs in solid material samples taken from the Elbe, its tributaries and the North Sea

4.1.3 Homologue and isomer distribution for the PCDD/Fs and PCBs (patterns)

On basis of the data is provided in Appendix II to IV the relative composition of the congener/isomer mixtures for PCDD/Fs and the DL-PCBs is displayed in Figure 7 to Figure 10.

This relative composition is referred to as “pattern” or “fingerprint” of a compound class, since it helps identifying emission sources or environmental transformation processes altering the composition of the mixture. For compound classes of high environmental persistence, such as PCDD/Fs, these fingerprints allow conclusions on the type of possible emission sources even far from the location of their release.

This kind of evaluation shall not substitute the statistical analyses provided in chapter 4.3, but allows a quick and “easy to catch” overview on the spatial transport dynamics in relation to suspected sources.

Figure 6 identifies the individual compounds (homologue groups in the case of PCDD/Fs) as displayed in Figure 7 to Figure 10.

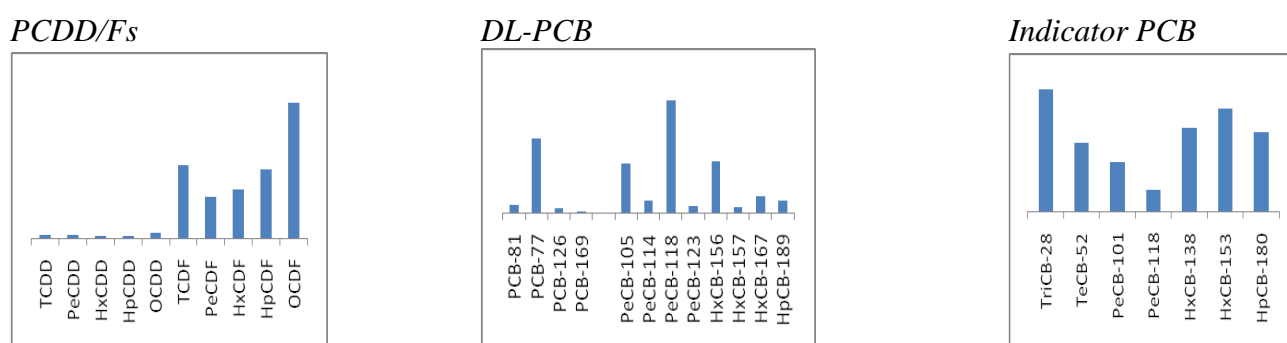


Figure 6: Exemplary fingerprints for PCDD/F homologue groups, DL-PCBs and the 7 indicator PCBs, example Pardubice-Semtin, CZ

PCDD/F patterns

Figure 7 shows the PCDD/F patterns for individual sampling sites or sections of the river Elbe and its tributaries. Figure 8 shows the PCDD/F patterns from the Elbe estuary and the North Sea in comparison to data from the Baltic Sea provided by the Landesamt für Landwirtschaft, Umwelt und ländliche Räume des Landes Schleswig-Holstein (GER).

In the upper section of the Elbe downstream from Padubice-Semtin (km -237) to Valy (km -228) the patterns are similar. The pattern is dominated by the higher boiling dioxins and the lower boiling furans.

Significant deviations in the appearance of the patterns appear in the Elbe only downstream of the Mulde confluence, an observation, which can be attributed to the influence of the Spittelwasser-Mulde system (indicated in yellow), where a similar fingerprint can be seen. The Spittelwasser-Mulde pattern is dominated by the higher boiling furans, a pattern attributed to residues from thermal production processes for refining magnesium and copper in the region of Bitterfeld-Wolfen. In particular the fused salt electrolysis applied in the

Magnesium production during World War II is known for very high PCDD/F releases. From Magdeburg (km 318) Elbe downstream there are only minor changes of this patterns that can even be observed in the North Sea sediments. This indicates no significant contribution from other PCDD/F sources along a stretch of approximately 400 km. The only exception was at Grauerort (km 661, upstream Stade), where the lower chlorinated furans were increased compared to the other sites. However, Grauerort did not display higher PCDD/F levels when compared to neighbouring sites (see Figure 5).

The pattern at Pardubice-Semtin differs from the other Czech sites (also on a TEQ base Pardubice-Semtin displayed a higher value of 23 pg/g). The pattern seems similar to those from the Spittelwasser-Mulde system, suggesting the presence of similar sources. However, the impact is only at local scale, the pattern in the next sample taken downstream 9 km at Valy had changed and the TEQ was in the range of 6.5 pg/g.

A high contribution of the PCDD/Fs in the fingerprints can also be observed in the solids from the Elbe Estuary and the North Sea, that display an overall similarity amongst each other and with those from the Spittelwasser-Mulde pattern (see also the statistical analysis in chapter 4.3). In contrast, the PCDD/F patterns in the sediments obtained from the Baltic Sea, in the vicinity of the cities of Lübeck, Kiel and Flensburg, differ from those of the North Sea samples and show an overall higher variability. This suggests that the PCDD/Fs in the Baltic Sea sediments contaminants originate from other, more local sources of different character.

Interestingly all North Sea samples are influenced by the Spittelwasser-Mulde pattern, suggesting transport of contaminated solids over more than 70 km off shore. Even the former sewage sludge dumping sites KS 8 and KS 11, highest in concentration, do not deviate from the Spittelwasser-Mulde fingerprint (sewage sludge fingerprints are commonly dominated by OCDD), suggesting negligible impact from the dumping at these sites.

An explanation for the higher values there cannot be given to date. Presumably the Wadden Sea's hydromorphology (in particular the tidal water courses and their sedimentation sinks) promotes enhanced transport and deposition of suspended Elbe solids into the area around KS8 and KS11.

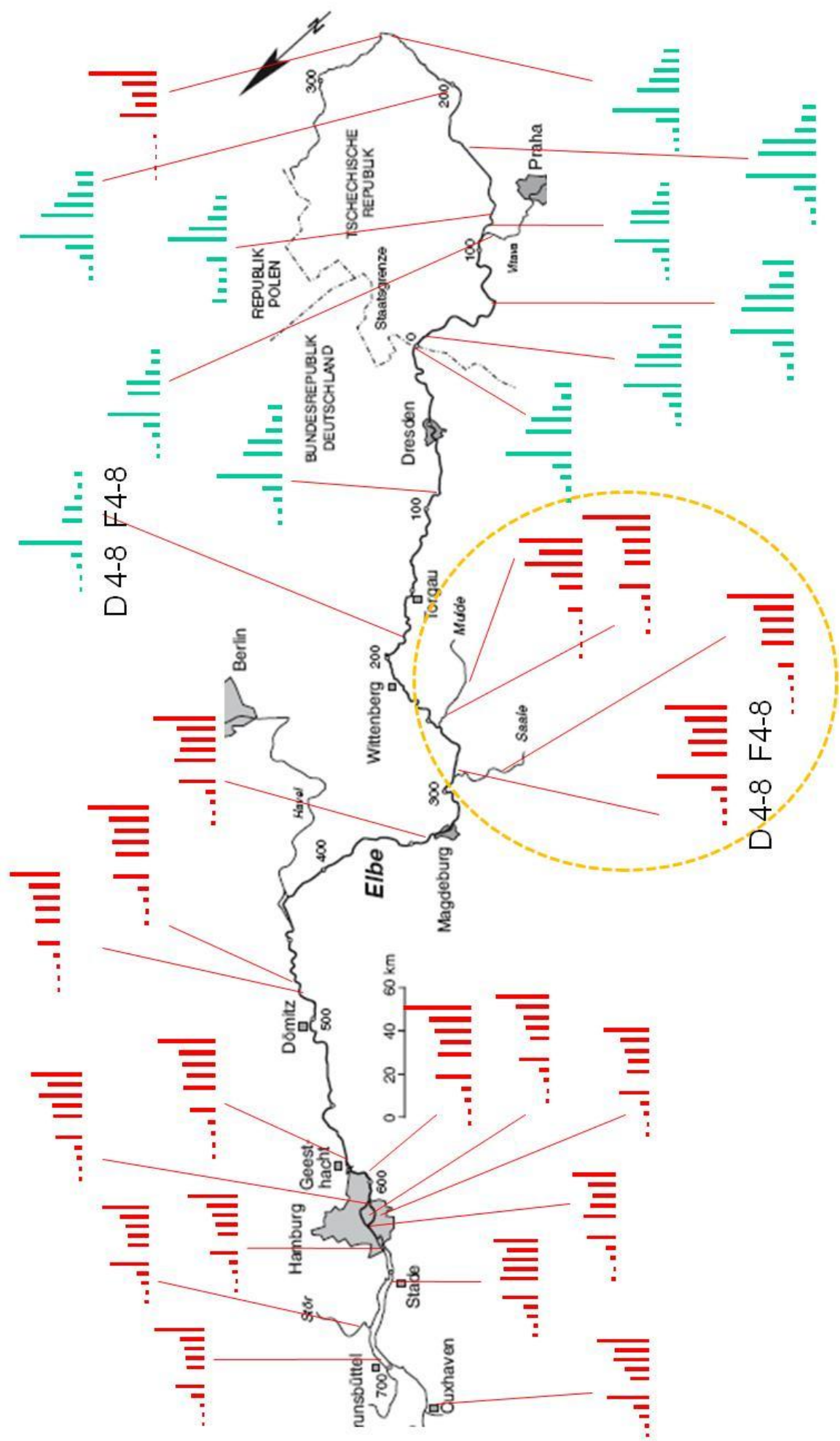


Figure 7: PCDD/F homologue pattern in solids along the Elbe catchment

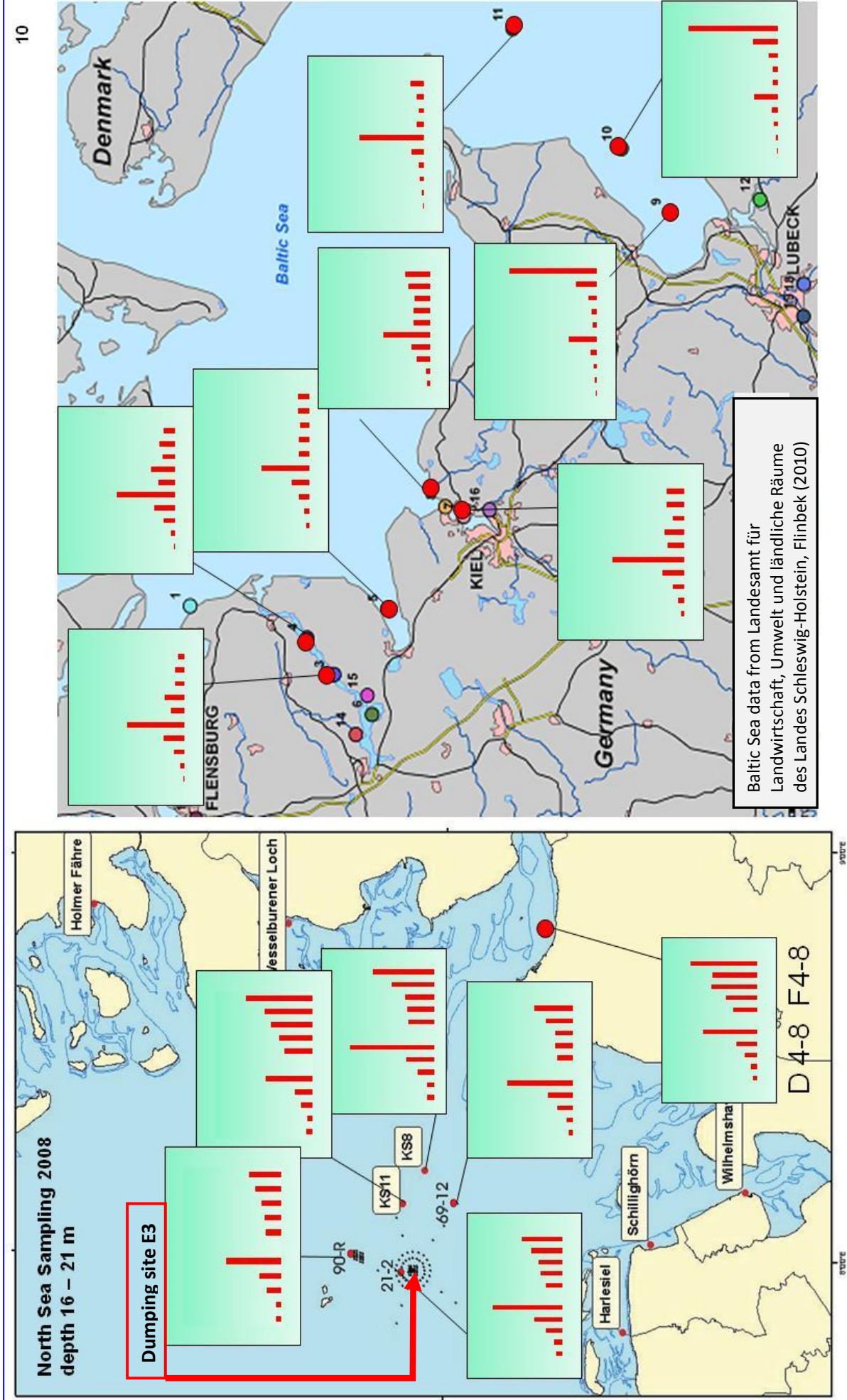


Figure 8: Comparison of PCDD/F homologous pattern in solids of the Elbe Estuary/North Sea and the Baltic Sea

PCB patterns

Sampling sites: 1=Pardubice-Semtin, 2=Valy, 3=Klavary, 4=Lysa nad Labem, 5=Cerínovsko, 6=Obristvy, 7=Vltava, Zelcin, 8=Zernoseky, 9=Decin, 10=Schmilka, 11=Zehren, 12=Dommitzsch, 13=Spittelwasser, 14=Mulde, Dessau, 15=Bode, Neugattersleben, 16=Saale, Rosenberg, 17=Magdeburg, 18=Cumlosen, 19=Schnackenburg, 20=Geesthacht, 21=Bullenhausen, 22=Bunthaus, 23=Süderelbe, 24=Köhlbrand, 25=Seemannshöft, 26=Wesel, 27=Grauerort, 28=Stör, Heiligenstedten, 29=Brunsbüttel, Elbehafen, 30=Cuxhaven, 31=North Sea KS8, 32=North Sea KS11, 33=North Sea sampling site 21, distance 2 km from dumping site E3, 34=North Sea sampling site 69, distance 12 km from dumping site E3, 35=North Sea sampling site 90, distance 10 km from dumping site E3 (reference area).

DL-PCB patterns

The congener distribution remains stable throughout a 51 km stretch of the Elbe between Pardubice-Semtin (km -237) and Klavary (km -186). Further downstream towards the North Sea and in the tributaries Vltava, Mulde, Spittelwasser, Saale, Bode and Stör there is some but no substantial variation in the congener pattern (Figure 9 and Appendix III). This indicates, as the decreasing concentrations in the German stretch as such, that the input from other sources downstream of the German border is low.

Indicator PCB patterns

At Pardubice-Semtin (km -237), Valy (km -228) and Klavary (km -186) specific congener patterns appear which only differ from each other slightly. Between Lysa nad Labem (km -151) and Obristvy (km -114) the patterns resemble each other closely. The influx of the Vltava near Zelcin (km -110) brings about no change, or very little, until Zehren (km 89.7). The pattern obtained for the Mulde is dominated by the influence of the Spittelwasser. The patterns from the Bode and Saale are very similar, and they remain stable until the Elbe sampling site at Magdeburg (km 318). From Magdeburg to the North Sea the patterns remain largely unchanged (Figure 10). In comparison with the PCDD/F and DL-PCB patterns, the indicator PCB patterns display frequent changes in the Czech section, an indication that their presence in the samples may be attributable to a range of different sources there.

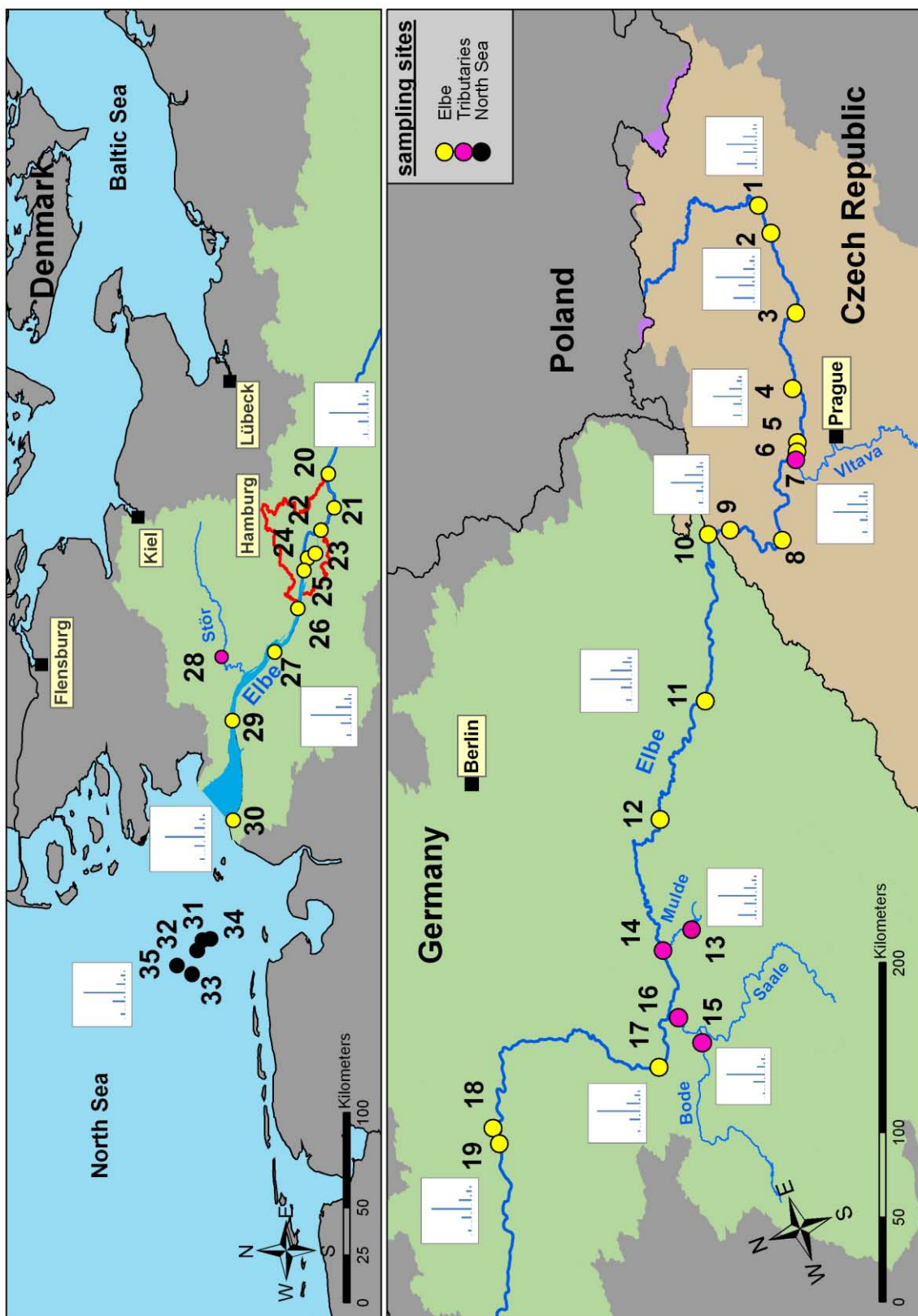


Figure 9: Selected DL-PCB patterns for the Elbe, its tributaries and the North Sea

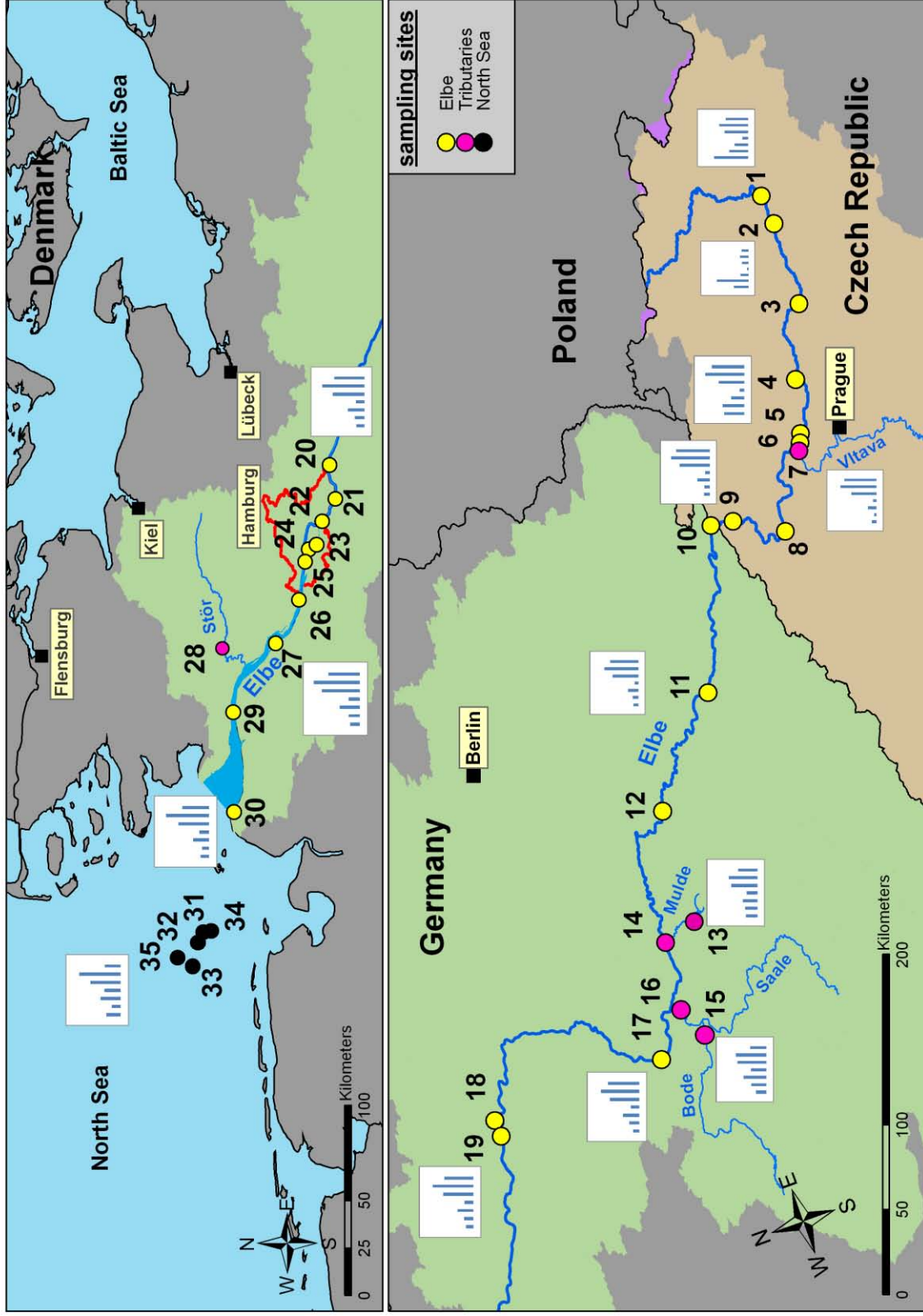


Figure 10: Selected Indicator PCB patterns for the Elbe, its tributaries and the North Sea

4.2 Bioassay-Tests

4.2.1 DR CALUX^R

As already described above, the DR CALUX^R bioassay-test determines the combinative effect of a mixture of dioxin-like chemicals, such as PXDD/Fs, PXBs, PXNs and X-PAK (X=Cl, Br, J, F), through the quantification of its reaction with the Ah-receptor. The test was carried out in addition to the chemical analyses for a subset of 25 samples selected from the present study. The results are shown in Figure 11 below (Behnisch et al. 2010).

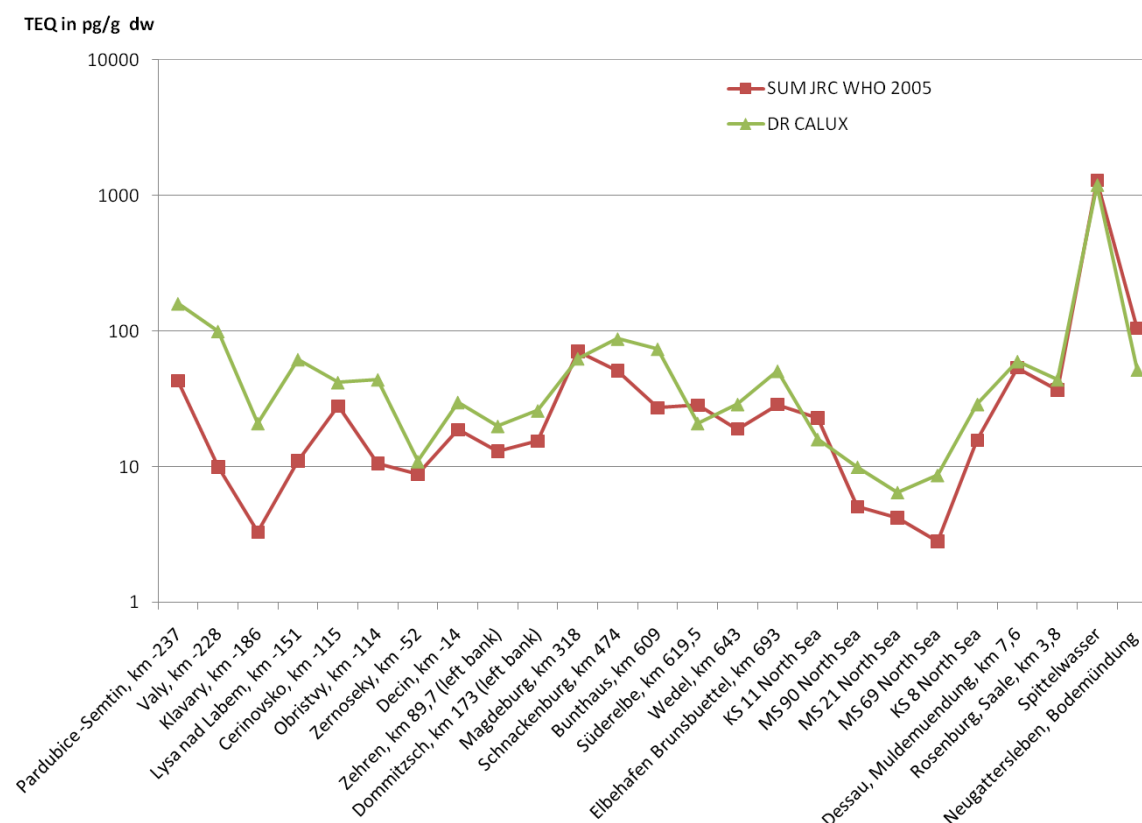


Figure 11: Comparison of the HRGC/HRMS results (*sum JRC TEQ-WHO₂₀₀₅*) with those of the DR CALUX^R test on sediments taken from the Elbe, its tributaries and the North Sea

In the German stretch the comparison shows a good level of correspondence between the TEQ values obtained respectively using the two different methods. However, in particular in the Czech section of the Elbe the bioassay resulted in distinctly higher TEQ values than the chemical analyses. This suggests a high additional portion of toxic potential in these solids, which is not explained by the PCDD/Fs and dioxin-like PCBs determined with the chemical analysis. Further investigations are necessary to identify/quantify the compounds responsible for this signal and to localize their sources. A more detailed discussion on this comparison is given by Behnisch et al. 2010.

4.2.2 EROD

Figure 12 shows overall higher Bio-TEQs in the Elbe solids after the confluence of the Mulde river. Also KS11, an area of former dumping site of treated sewage from Hamburg, showed elevated Bio-TEQ-values and might therefore reflect high dioxin-like potencies caused by legacy pollution (Eichbaum et al. 2011). Chem-TEQs – sum of dioxins (PCDDs), furans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs) determined in this study – only accounted for a small percentage of Bio-TEQs. Eichbaum et al. (2011) explained the notable divergence between EROD Bio-TEQs and Chem TEQs with the dioxin-like activities of polycyclic aromatic hydrocarbons (PAHs) and non-priority pollutants, which are not included in the present Chem-TEQs.

When compared to the DR CALUX^R bioassay, (which eliminates less persistent dioxin like compounds such as PAHs through the clean up applied) the EROD derived Bio-TEQs (where no clean up was used) are much higher. Dioxin-like activities of PAHs and other less stable pollutants, eliminated during the clean up (multilayer silica column, containing concentrated H₂SO₄) for the DR CALUX^R assay would explain this as well.

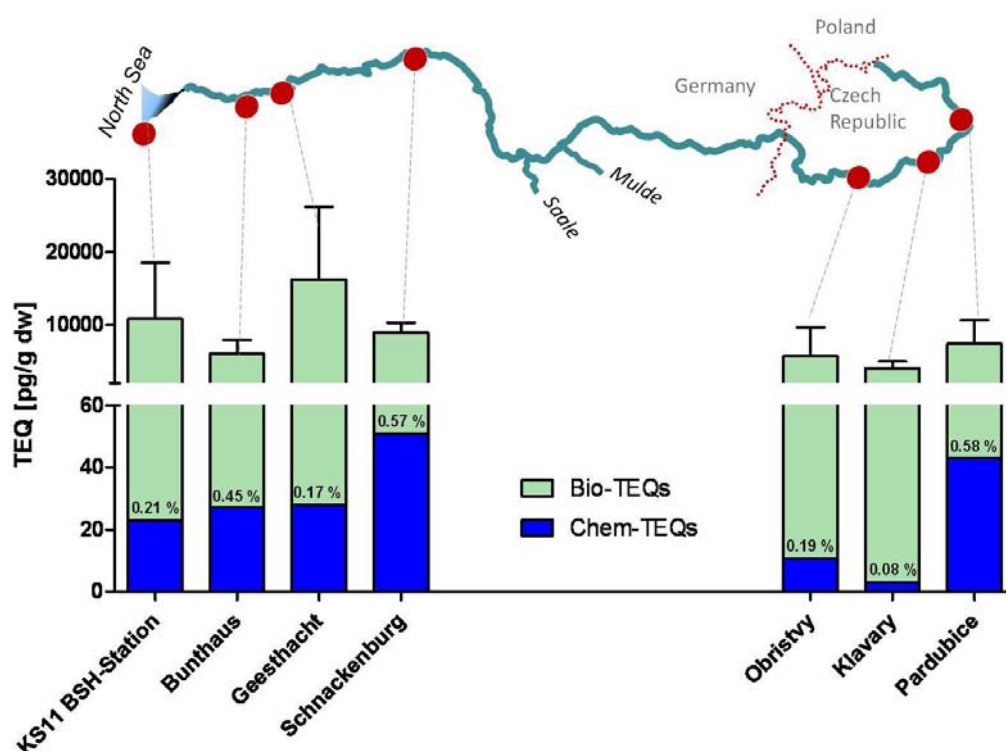


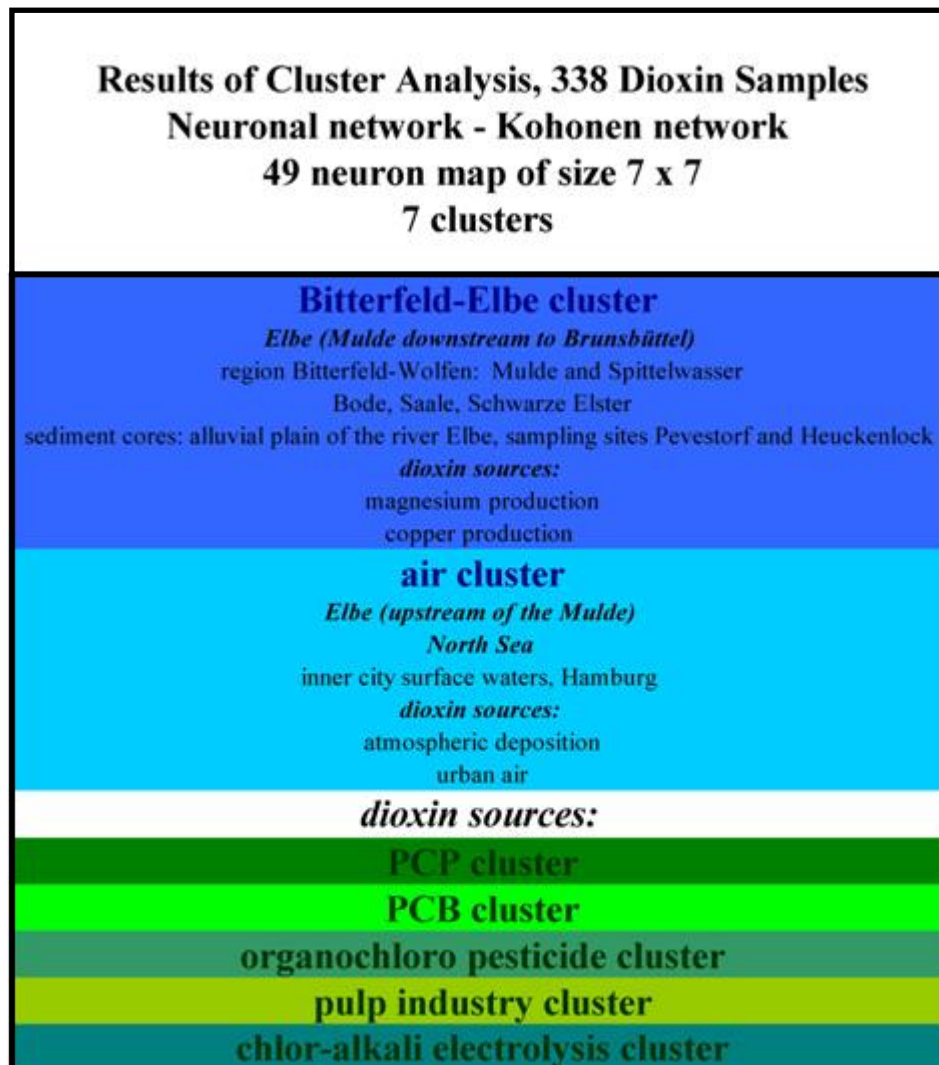
Figure 12: Comparison of Bio- and Chem-TEQs of Elbe sediment extracts (n=3), sampled in 2008 (Eichbaum et al. 2011)

Chem-TEQs (WHO₂₀₀₅-TEQs) include values for PCDD/Fs und DL-PCBs (this study). Percentages account for Chem-TEQ ratios in Bio-TEQs. Red dots on the map denote sampling sites in Germany and the Czech Republic.

4.3 Statistical analyses of Dioxin sources

Neuronal networks - Kohonen network and multivariate statistical methods

A dioxin data pool containing 338 dioxin samples was assembled for calculation purposes. The sample group from the Elbe consists of samples from the years 1998 to 2008. These include 30 dioxin samples (SPM, sediments originating from suspended matter, surface sediments) from the longitudinal Elbe profile (Elbe and tributaries) carried out in 2008 and five dioxin samples (surface sediment) from the North Sea, also taken in 2008. In two earlier investigations, cluster analyses were carried out using samples from the Elbe obtained up until 1995 (Götz and Lauer 2003; Götz et al. 2007).



In order to enable comparison with results obtained for the Elbe in the past – going back to the 1940 – dated sediment core samples taken from Pevestorf and Heuckenlock were integrated into the investigation as well.

The Bitterfeld group of data is based on 47 dioxin samples taken from the Spittelwasser and Mulde between 1992 and 2008. As a basis for a cause analysis supplementary dioxin samples were incorporated which can be assigned to the following primary dioxin sources: PCP (pentachlorophenol), PCBs, organochlorine pesticide production, cellulose industry, chlor-alkali electrolysis, magnesium and copper production. The dioxin sample groups ‘deposition’ and ‘atmosphere’ stand for the dioxin input via the atmosphere and thus a secondary dioxin source. Below the results of the Kohonen network analysis of the neuronal networks with 49 neurons (7 x 7) as well as the assignation of the individual dioxin sample groups to the resulting 7 clusters.

The samples from the section of the Elbe downstream of the Mulde to the sampling site at Cuxhaven taken from the 2008 longitudinal Elbe profile, the samples from the same section taken in previous years as well as those taken from the Bitterfeld-Wolfen region (Spittelwasser and Mulde) all belong to the Bitterfeld-Elbe cluster. The samples from the Bode and the Saale, too, are assigned to the Bitterfeld-Elbe cluster. This result supports the hypothesis that the Bitterfeld-Wolfen contamination – mainly introduced via the Spittelwasser and the Mulde – probably remains the fundamental source for dioxin pollution in the Elbe downstream of the Mulde to this day. Until 1993, the Spittelwasser – a tributary of the Mulde with a length of eight kilometres – was used for decades as an effluent channel for untreated industrial and domestic waste water (Fischer 2003, Lechner 2007).

The high dioxin concentrations found in the Spittelwasser-Mulde hydrological system and the dramatic increase in the dioxin levels of the Elbe downstream the Mulde confluence provide additional evidence to confirm the role of these rivers as a secondary source of dioxin contamination for the Elbe.

There are two possible mechanisms to account for the long-distance transport of dioxins from the Bitterfeld-Wolfen region to beyond Hamburg: These are transport via suspended particulate matter (with intermediate phases in which the suspended matter is deposited to become sediment and then reactivated through flow effects to continue on its way in suspension) and the transport of material in solution or in colloidal form in the water phase. There is a considerable bias in the equilibrium distribution of the dioxins away from the water phase in favour of the solids phase, resulting in the solid phase being greatly enriched and a very large proportion of the transport taking place via the solids phase. Investigations of the water phase in the Elbe returned extremely low concentrations (of the order of fg/L on a TEQ base) (Götz et al. 1995). If uncontaminated solid particles enter the Elbe (whether through phytoplankton production (plankton ‘bloom’) or from external sources), these particles adsorb dioxins as a result of the distribution mechanism mentioned above. Even in cases where the final equilibrium distribution is not actually reached, such previously uncontaminated particles are certainly subjected to a degree of dioxin enrichment.

The assumption in respect of the dioxin transport is supported by the fact that, following extreme flow conditions (Mulde floods of 1994, Elbe floods of August 2002) raised levels of dioxins were measured in the Elbe at Bunthaus-Hamburg (Hamburger Umweltberichte 57/99, Götz and Lauer 2003).

The similarity of the dioxin patterns and the dioxin concentration levels found in the dated sediment cores from the Elbe obtained from Pevestorf and Heuckenlock compared with the (undated) sediment cores from the Spittelwasser is indicative of a stable interrelationship over the course of a long period of time (Götz et al. 2007).

The dioxin sample groups for magnesium and copper production are also observed in the Bitterfeld-Elbe cluster. This identifies metal processing plants as being the probable cause of dioxin pollution in the Bitterfeld-Wolfen region. The magnesium production sample group contains sediment groups from the Grenlandsfjord in southern Norway near the Heroya magnesium smelting company. The data pool for the earlier cluster analyses contained five samples for the substance group magnesium production (Oehme et al 1989); the current pool was supplemented by a further 17 samples (Ishaq et al. 2009). The Heroya magnesium smelting plant was erected by experts from Bitterfeld, with construction beginning in 1941 (Fischer 2003). An overview of the various magnesium production plants in Bitterfeld can be found in Fischer (2003) and the Bitterfelder Chronik (1993).

Using a different mathematical approach, Uhlig et al. (2007) analysed dioxin congener patterns for suspended particulate matter and sediment samples from the Elbe, Spittelwasser, Mulde, Saale and Schwarze Elster. They came to the conclusion that 70 to 80 percent the dioxin contamination of the Elbe sediment in Hamburg can be attributed to sediments from the Mulde, whereby the study took account of both direct transport from the Mulde and also indirect transport via intermediate deposition.

Interestingly enough, the samples from the primary dioxin sources which can be attributed to the chlorine based production of PCPs, PCBs, and organochlorine pesticides form discrete clusters, showing no similarity to Bitterfeld and Elbe samples.

The PCP substance group was made up of the results of earlier investigations of the Elbe (Götz and Lauer 2003) supplemented by six samples (Masunaga et al. 2001; Seike et al. 2003) to a total of nine. With twenty samples, the organochlorine pesticide production substance group is also sufficiently numerous. The situation for the PCBs and chloralkali electrolysis groups is less favourable, with three and two samples respectively. It would have been helpful to have had access to more data in order to put the evaluation results on a firmer footing, but the authors have so far failed to find more relevant publications.

The cellulose and paper industry substance group (Rappe 1990) was adopted into the data pool in this study, although with only three waste water samples the data volume is meagre here, too. One sample is assigned to another cluster. Sundqvist et al. (2009a) point out that dioxin profiles for areas in the vicinity of cellulose and paper plants are very inhomogeneous.

Atmosphere cluster

The atmosphere cluster comprises deposition samples (dust precipitation) and ambient air samples (airborne dust and gas phase) from Hamburg, the sediment samples from the 2008 longitudinal profile of the Elbe upstream of the Mulde (Bitterfeld-Wolfen region) and from the North Sea as well as sediment samples from municipal waterways in Hamburg which are not influenced by the Elbe.

The fact that the Elbe samples from upstream of the Mulde (Germany and the Czech Republic) do not belong to the same cluster that contains the Bitterfeld-Wolfen samples is not surprising, as these sediments cannot be contaminated by the Bitterfeld-Wolfen sources. The cause for the dioxin contamination in the atmosphere cluster sediments appears to be, in the main, the secondary dioxin source atmospheric deposition.

The Elbe sediment sample from Pardubice-Semtin (1st Czech sampling site of the longitudinal profile of the Elbe) is not included in the atmosphere cluster, but in the Bitterfeld-Elbe cluster. It differs from the other samples taken from the Elbe upstream of the Mulde not only in respect of its dioxin pattern, but also in its relatively high PCDD/PCDF-WHO-TEQ content and a raised value for the PCDF/PCDD quotient. These characteristics are shared by the Elbe samples from the Bitterfeld-Elbe cluster. In contrast to these, however, the Pardubice-Semtin sample has a high level of DL-PCBs. It would appear that the Pardubice-Semtin sampling site is affected by dioxin sources in addition to the atmospheric input.

The four North Sea samples KS8, sampling site 21 (2 km from the dumping area E3), sampling site 69 (12 km from the dumping area E3) and sampling site 90 (10 km from the dumping area E3, reference area) are all included in the Bitterfeld-Elbe cluster. It may be that atmospheric deposition plays a role in this case.

Recent investigations with 146 sediment samples have provided some evidence that sediment samples in the offshore region off the Swedish coast in the Gulf of Bothnia and in the Baltic Sea may be influenced by atmospheric deposition (Sundqvist et al. 2009b).

In contrast to these four North Sea samples, the North Sea sample KS11, returned a raised level of dioxin contamination (considerably above the background level), and it is assigned to the Bitterfeld-Elbe cluster. At present no explanation for this result has been found. The area was still being used for dumping treated sewage sludge from Hamburg as recently as a few decades ago. In order to confirm the result, subsequent investigations were carried out at the sampling sites KS 8 and KS11.

With just ten dioxin investigations to date, the North Sea remains largely uncharted in respect of dioxin contamination. There is an urgent need for comprehensive investigations on dioxins, especially in the Wadden Sea.

4.4 Water regime and SPM associated PCDD/F loads

In this section we discuss the water discharge data and the suspended particulate matter (SPM) regime for different years for the Elbe, the Mulde and the Saale. On this basis an attempt is made to estimate the contamination loads.

The concentration data from three different matrices (SPM, settling material and surface sediments) were analysed, based on the assumption that the type of solid substance involved would have no major influence on the results and their interpretation. To substantiate this assumption, it would be necessary to generate corresponding data sets of parallel samples originating from different sampling methods. However, from the few sites where multiple matrices were sampled a sufficient conformity of the concentration data was observed (Figure 15). The contamination arises in the tributaries Saale and Mulde in particular, so that some attention is devoted to their PCDD/F loads. Not all of the available literature contains the concentration data for the individual congeners, thus it was not possible to convert the figures to PCDD/F WHO₂₀₀₅-TEQ used in this study. In such cases the original data format in I-TEQ is used.

4.4.1 Flow and freight volumes for 2008

In order to discuss the dioxin and PCB findings for 2008, it is necessary to take account of the surface water flow volumes and SPM regime, both for the Elbe and for the sampled tributaries. For instance, after the so-called ‘first flush’ of a flood event has taken its course, the hydraulic remobilisation of contaminated sediments can be expected to raise the freight levels for hazardous substances in the water column. Conversely, at times of low water level lower SPM quantities may be anticipated. However, in the aftermath of flood events that involve the Elbe floodplains, PCDD/Fs may be introduced into the Elbe through erosion of contaminated alluvial soils. It has been demonstrated, that floodplain soils are contaminated with PCDD/Fs at a level of approximately one order of magnitude higher than the recent sediments (Umlauf et al. 2005). Erosion of these soils that can occur at rapidly decreasing water levels after extreme events.

During the year 2008, the Elbe experienced flood conditions in the months of February, March and April, whereby the February and April floods peaked at about the same level (Figure 13). The water discharges close to the border, due to the low run offs from the various sub-catchments and relatively low (gauge Schöna, km 2.1). Further downstream larger tributaries cause marked increases in the flow volumes. Between June and the end of October the water discharges were significantly lower (the samples subject to this study were taken in September 2008), after which there was a slight increase in November and December (Figure 13). Table 1 displays the main hydrological characteristics for the year 2008 together with the long-term characteristics as a means of assessing the flow situation. These characteristics derive from statistics which are generally dependent on the respective gauge location, the actual water discharge and the frequency with which data is collected. At the time when the sampling was carried out in September 2008 the mean discharge lay between 120 m³/s (Usti

nad Labem) and 289 m³/s (Neu Darchau). Compared with the long-term average the year 2008 was rather dry, and there were no unusually high or low water discharges.

Table 1: Characteristic values for water discharges in the Elbe, Mulde and Saale

Gauge	river km	2008			Long term average since 1990	
		MQ m ³ /s	HQ m ³ /s	MQ Sept/Oct m ³ /s	MQ m ³ /s	MHQ m ³ /s
Usti nad Labem, Labe	-37 CZ	231	850	120	no data	no data
Schöna, Elbe	2.1	248	866	132	no data	no data
Wittenberg/L., Elbe	214.1	300	842	151	368	1480
Magdeburg-Strombrücke, Elbe	326.6	457	1350	224	558	1850
Neu Darchau, Elbe	536.4	643	1630	289	709	1980
Bad Döben, Mulde	68.1	59.5	480	21.7	64.0	488
Calbe-Grizehne, Saale	17.6	110	329	57.6	114	391

MQ=mean discharge in calendar year; HQ=maximum discharge; MHQ=mean maximum discharge in calendar year (values for specific dates); no data=figures unavailable.

For the Czech section of the Elbe there are no discharge data available apart from the gauge Usti nad Labem (37 km upstream of Hrensko). The maximum discharge value measured at Usti nad Labem, 850 m³/s, differs only a little from the corresponding value measured at the Schöna gauge further downstream: 866 m³/s (Table 1).

The tributaries Mulde and Saale also experienced high discharge rates in the months of February, March and April. In February, a peak value of 480 m³/s was measured at the Bad Döben gauge (km 68.1) of the Mulde. The peak value in the Saale measured at Calbe (km 17.6) was 329 m³/s, also in February. From June until the end of October the discharge rates fell to mean values of 22 m³/s (Mulde) and 57 m³/s (Saale), after which the flow levels rose again in November and December. As was the case for the Elbe, 2008 was quite a dry year for both tributaries in comparison with the long-term average, and there were no remarkably high or low water events.

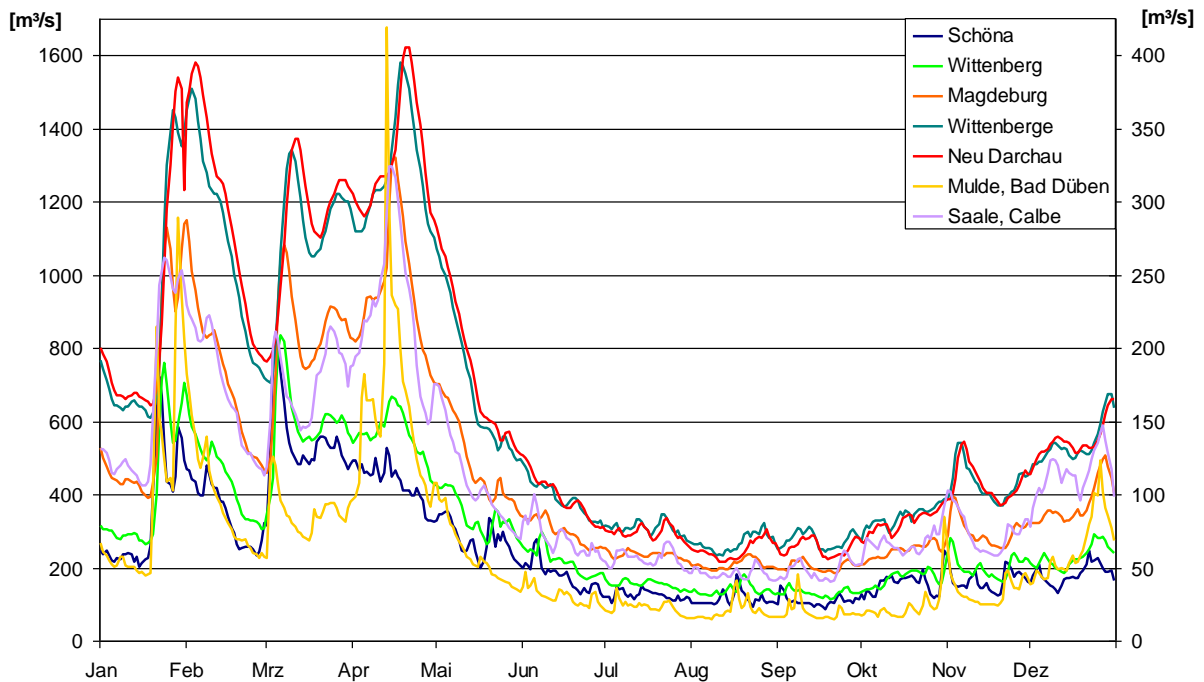


Figure 13: Daily mean values for the water discharges in the Elbe (l.h. ordinate), Mulde and Saale (r.h. ordinate) in the year 2008

Schöna km 2.1; Wittenberg km 214.1; Magdeburg km 326.6; Wittenberge km 453.9, Neu Darchau km 536.4; Mulde Bad Düben km 68.1; Saale Calbe km 17.6.

4.4.2 The SPM regime and an estimate of the PCDD/F loads in September 2008

The description of the SPM regime is provided by the concentrations of filterable substances (daily values). The SPM loads are displayed in Figure 14, based on a procedure in common use in the FGG Elbe. It should be noted that in comparison with the water discharge values (Figure 13), the data density for these measurements is much lower – in some cases only monthly values were available.

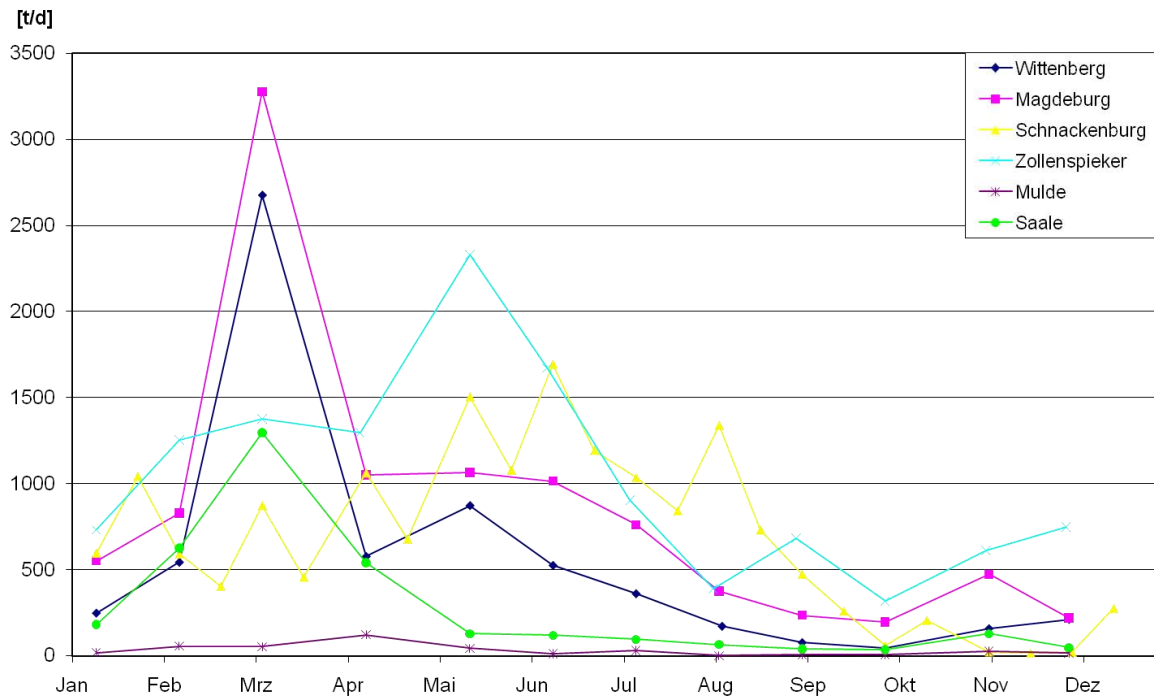


Figure 14: SPM loads in the Elbe, Mulde and Saale in the year 2008

Wittenberg km 214.1, Magdeburg km 318, Schnackenburg km 474, Zollenspieker km 498.7, Mulde km 7.6, Saale km 4.5.

Peaks in the SPM loads can be seen for the months of March and May, probably caused by periods of high water discharges from the Saale and Mulde catchment, which remobilized Elbe sediments. Interestingly, the March SPM load in the Saale is greater than that of the Elbe at Schnackenburg, suggesting sedimentation of the Saale solids downstream its confluence with the Elbe. In contrast, the SPM loads in the Mulde are low in March and May, although the discharges in the Mulde were enhanced as well. This is most likely due to the trapping of suspended solids in the Mulde Barrier Lake (6.3 km², finished in 1975, estimated 400.000 t/a sedimentation⁴), which would explain the overall low SPM concentrations of the Mulde at km 7.6 (downstream the Mulde Barrier Lake) when compared to Saale and Elbe.

The SPM load levels determined at the time of sampling in September are roughly the same as in February. The SPM loads in the Elbe, Mulde and Saale for 2008 were similar to those of the previous years, as were the water discharge figures.

Based on the SPM loads and the PCDD/F concentrations in SPM determined in this study, the following passage provides estimated TEQ loads for certain reference gauges in the Elbe, the Mulde and the Saale associated with the respective sampling date. The actual SPM figures used are the mean values obtained from the SPM loads measured for 03 September and 01 October 2008.

⁴ <http://de.wikipedia.org/wiki/Muldestausee>, 1. September 2011

In the Mulde the SPM load amounted to 190 t/month (sampling site Dessau) and the PCDD/F concentration was around 52 µg WHO₂₀₀₅-TEQ/t. This is equivalent to a total load of 9.9 mg WHO₂₀₀₅-TEQ/month. For the Saale the figures are: SPM load = 1164 t/month; PCDD/F concentration 34.8 µg WHO₂₀₀₅-TEQ/t, resulting in a total load of 40.5 mg WHO₂₀₀₅-TEQ/month. For comparison: In the same period of time the Elbe had a considerably higher SPM load, namely 7562 t/month Elbe at Schnackenburg. With a concentration of 48.8 µg WHO₂₀₀₅-TEQ/t, this amounts to a total load of 369 mg WHO₂₀₀₅-TEQ/month. It should be borne in mind that these estimates are necessarily very approximate. In order to increase the reliability of such figures for PCDD/F loads, sampling must be carried out at more frequent intervals.

These estimates indicate that in the Elbe near Schnackenburg the SPM associated transport several times larger than those of the Mulde and Saale. The cause for this can probably be seen in the remobilisation of old sediments which are swept into the main flow channel (from, amongst other sources, groyne fields). The main reason for the low SPM load in the Mulde is likely to be the retentive effect of the Mulde reservoir near Bitterfeld, where the main part of the contaminated SPM settles and thus fails to enter the lower reaches of the Mulde. Investigations confirm the Mulde reservoir's capacity to retain contaminants (Klemm et al. 2005).

4.4.3 High water events

The description of the water discharges and the SPM regime in the Elbe, Mulde and Saale presented above refers to the sampling year 2008, so it is not representative of the long-term discharge situation and can therefore shed only a limited amount of light on the causes behind the decades long history of dioxin contamination in the Elbe. As a further step in this direction, it is necessary to take account of flood events and their effects on the SPM dynamics, their role in shifting contaminated solids and thus on the contaminant immission situation of the Elbe in general.

High water levels and flood events in the Upper and Middle Elbe are brought about by the yearly snow melt in the Krkonoše or Riesengebirge, a range of mountains in the northern part of the Czech Republic, as well as – increasingly – periods of extreme precipitation. As a result, parts of the catchment area are regularly flooded and both contaminated and uncontaminated particles are introduced into the river system.

The progress of an event is determined by the hydrological situation prevailing beforehand, the way the wave peaks, the type of event and also anthropogenic construction measures (regulation, artificial channels, dykes). According to the specific situation, large or smaller areas of alluvial soils may be flooded. The resulting deposition of contaminated substances can lead to the impairment of agricultural land (Hanisch et al. 2005). In addition to the hydro-mechanical conditions, an important factor influencing the degree of contamination may be seen in the origin and character of the SPM. This question has been more thoroughly investigated in the Rotmain, a small river in Northern Bavaria, Germany). Symader et al. (1991) investigated the course of a summer high water event in the Rotmain. Peaks for Ca,

Fe, Mn and phosphates were examined before, during and after the peak wave in respect of their origins. Surface run-off proved to be a relevant source for solid material input. It has been demonstrated that superficial run off represented a significant source for the transported solids. In situ investigations of various SPM sample fractions taken from the Rotmain showed that approximately 60% of the total PAH load is transported via medium grained silt. Lindane, on the other hand, with a lower distribution coefficient compared with the PAHs, is transported mainly via the aqueous phase (Umlauf and Bierl 1987).

It goes without saying that the results obtained from a small river such as the Rotmain may not be applied whole scale to the Elbe. Nevertheless, the results indicate that in conjunction with other hydrological conditions certain processes such as the scouring of particular soil layers could also play a role for the Elbe during high water events – especially in respect of soils being washed out of the highly contaminated alluvial soils.

The present level of knowledge in this area precludes the possibility of making generally valid forecasts for the spatial and temporal movement of contaminants with floodwaters. The following passage contains an overview of water discharge figures and SPM loads for the Elbe, Mulde and Saale over a longer period of time, from 1996 to 2006. Table 2 includes computed results for the mean yearly maximum discharge and the SPM load for a given high water event. The mean values are generated using the values before and after the event in the respective discharge year. It should be borne in mind that in some cases only a small data pool is available, so the computed figures are only indicative.

Table 2 shows water discharge amounts and SPM loads for the Elbe, Saale and Mulde in the years 1996 to 2006. It is readily apparent that in extreme cases both parameters can attain values dramatically in excess of the normal quantities. The high water events shown led to an increase in the water discharge rate by factors ranging from 2 to 7, whilst the corresponding SPM loads increased over proportional by between 4 and 28 times the mean values.

As an example, the disastrous flood, which occurred in August 2002 is discussed in more detail in the following passage. After torrential precipitation in Austria, the Czech Republic, Slovakia and the eastern part of Germany, large stretches of countryside were flooded. Municipal and industrial waste water treatment plants, agricultural land and residential areas were affected. Public attention was focussed on the Spolana chemical plant in view of the possibility that large quantities of dioxins could be released into the environment. In August 2002 the catchments of the Saale and the Schwarze Elster were less affected by precipitation.

The high SPM load calculated for the Mulde, with a peak of approximately 10000 kg/d, indicates that the SPM load in Magdeburg could have originated largely from the Mulde.

The large amounts of SPM of about 10000 t/d in the Mulde at Dessau underline the high remobilization potential from the Mulde catchment in spite of the retention of solids in the Mulde barrier lake (Junge et al. 2004).

Table 2: Water discharges (HQ) and SPM loads from the Elbe, Mulde and Saale

River	Sampling point	Time period	HQ mean value (m ³ /s)	SPM load mean value (t/d)	HQ high water (m ³ /s)	SPM load high water (t/d)
Elbe	Wittenberg/L. km 214	03.01.96-18.12.96	334	818	1271	10762
Elbe	Wittenberg/L. km 214	04.01.00-20.12.00	295	699	1900	11655
Elbe	Wittenberg/L. km 214	09.01.02-18.12.02	968	2048	3236	28252
Elbe	Wittenberg/L. km 214	18.08.02	no data	no data	3990*	55158*
Elbe	Wittenberg/L. km 214	22.01.03-17.12.03	267	599	2080	16893
Elbe	Wittenberg/L. km 214	01.02.06-06.12.06	351	588	1000	10368
Elbe	Magdeburg li km 318	14.02.96-18.12.06	550	1193	1390	7791
Elbe	Magdeburg li km 318	04.01.00-20.12.00	457	1192	1920	4636
Elbe	Magdeburg li km 318	09.01.02-18.12.02	1417	1900	3306	9490
Elbe	Magdeburg li km 318	19.08.02	no data	no data	4010*	11756*
Elbe	Magdeburg li km 318	22.01.03-18.12.03	429	1026	2900	10273
Elbe	Magdeburg li km 318	01.02.06-06.12.06	469	781	1310	15814
Saale	Rosenburg [§] km 4.5	22.05.96	no data	no data	174*	1222*
Saale	Rosenburg [§] km 4.5	29.03.06	no data	no data	378*	10950*
Mulde	Dessau ^{&} km 7.6	08.05.96-18.12.96	65	41	99,9	133
Mulde	Dessau ^{&} km 7.6	04.01.00-20.12.00	65	59	313	707
Mulde	Dessau ^{&} km 7.6	09.01.02-18.12.02	109	99	398	2377
Mulde	Dessau ^{&} km 7.6	16.8.02	no data	no data	678*	9751*
Mulde	Dessau ^{&} km 7.6	22.01.03-17.12.03	38	27	197	346
Mulde	Dessau ^{&} km 7.6	04.01.06-06.12.06	44	32	596	3000

*=maximum value; §= gauge Calbe-Grizehne; &= gauge Bad Döben.

It is worthy of note that the areas behind the dykes which were flooded on account of breaches in the dykes displayed low dioxin concentrations (Umlauf et al. 2005). This indicated an overall low impact of the 2002 flood event on the total PCDD/F contamination of the alluvial soils.

It should be borne in mind that approximately 45 km upstream of the Mulde the Elbe already contained a high load of SPM (Wittenberg/Lutherstadt gauge, km 214). On the basis of measured SPM deposits on the floodplains of the Elbe, together with analysis results (median value 52 pg WHO₁₉₉₈-TEQ/g), it is estimated that the contamination of the flooded soils was increased to a degree lying between 4.3 g and 6.5 g WHO₁₉₉₈-TEQ/g. Between 3.1 and 4.6 g WHO₁₉₉₈-TEQ/g of PCDD/Fs were transported towards the North Sea over the weir at Geesthacht (Stachel et al. 2006). These figures give an impression of the amount of contaminated material which such events introduce into the Elbe, particularly from the catchment area of the Mulde. There is clear evidence that especially the high water events, which occur several times every year are responsible for a large part of the still high degree of contamination with dioxins to be found in the Elbe and its tributaries on account of the erosion or remobilisation of historic sediments from the floodplains. In comparison, relatively small quantities of dioxin are introduced via the tributaries under normal discharge conditions as we encountered during the 2008 investigation.

The main hazard with respect to dioxin contamination in the Elbe are high water events occurring in the Spittelwasser-Mulde-Saale system. Consequently, an improvement in the immission situation for the Elbe can only be expected after the corresponding sources have been adequately cleaned up. A reduction in the pollutant loads in the Elbe would have a positive effect on the immission situation in the coastal parts of the North Sea as well.

4.5 PCDD/Fs – further discussion

The PCDD/F results are shown in WHO₂₀₀₅-TEQ in Figure 3. As a benchmark to evaluate the risk arising from the PCDD/Fs and PCBs in the sediment, the following orientation values for sediments can be compared. The FGG Elbe and the Hamburg Port Authority specify a limiting concentration of 5.5 pg WHO-PCDD/F-TEQ-2005/g for suspended matter in respect of fish stocks for human consumption (Heise et al. 2008). The ‘safe sediment value’ of 20 pg PCDD/F-I-TEQ/g (Evers et al. 1996) is based on biomagnification of PCDD/Fs in seabirds. Calmano (2001) specified a precautionary value of 5 pg/g, a testing value of 15 pg/g and a threshold value for undertaking precautionary measures of 100 pg/g for summed WHO-PCDD/F+PCB-TEQ values. These values have also been published in Henschel et al. (2003), *Handbuch für Angewandte Limnologie*. A ‘national environmental quality standard for dioxins’ for Japanese river sediments and ocean sediments amounting to 150 pg TEQ/g has been published (Uchimiya et al. 2007). A considerably higher value has been specified in connection with the cleaning-up of contaminated sediments in the Australian harbour of Port Jackson, namely 1000 pg WHO-PCDD/F/g (Birch et al. 2007). For the sum of the 7 indicator PCB congeners guideline values of 10 ng/g (OSPAR 2000), 20 ng/g for marine sediments and 30 ng/g for terrestrial sediments are given (Swedish EPA 2008).

As already indicated in Chapter 4.1.2, the PCDD/Fs levels in the Elbe solids upstream of the Mulde are generally relatively low. Downstream of the Mulde there is a significant increase in concentration (12 pg WHO₂₀₀₅-TEQ/g upstream of the Mulde near Dommitzsch; 68 pg WHO₂₀₀₅-TEQ/g downstream of the Mulde near Magdeburg). Downstream from that site the concentrations decline steadily. The highest dioxin concentration was returned by the Spittelwasser: 1260 pg WHO₂₀₀₅-TEQ/g. Spittelwasser sediments data originating from SPM dating from 1998-2009 (Figure 20) yielded a concentration range of 347-6320 pg I-TEQ/g, whereby the high values were measured in samples from 1998 and 1999. Thus the individual value of 1260 pg WHO₂₀₀₅-TEQ/g measured in the Spittelwasser solids in 2008 agrees well with the range of earlier results.

102 pg WHO₂₀₀₅-TEQ /g suspended matter were found in the Bode, a tributary of the Saale. Further individual concentration values for samples taken from the Bode between 2007 and 2008 range between 35 pg I-TEQ/g and 140 pg I-TEQ/g (Figure 23), a range which again accommodates the current value for 2008: There is therefore no indication that the dioxin concentrations are becoming significantly less for this tributary, either.

The longitudinal profile of the Elbe for dioxins (and DL-PCBs) for 2008 displays marked discontinuities in the data series occurring downstream of the sites where the Mulde and Saale enter the Elbe. They can be observed in the dioxin concentrations, the quotients PCDF/PCDD and (PCDD+PCDF)/DL-PCB as well as in the dioxin patterns. Similar jumps were registered in earlier investigations involving dioxin analyses of samples from the Elbe from the years 1989 to 1995 (Götz et al. 1995, Götz et al. 1998a, Götz et al. 1998b, Götz and Lauer 2003). In that period, the dioxin concentrations in the Mulde amounted to as much as 550 pg WHO-TEQ/g, considerably more than today. Already from these earlier investigations the region Bitterfeld-Wolfen (via the Spittelwasser and Mulde) had been suggested as probable main source for the dioxin contamination in the Elbe downstream of the Mulde.

4.5.1 The Elbe at Neratovice

In Neratovice, about 25 km north of Prague and 12 km upstream of the tributary Vltava, the Spolana chemical plant produced the herbicide 2,4,5-T between 1965 and 1968. This substance was used as a constituent of the total herbicide Agent Orange. It may be assumed that during production large quantities of dioxins were generated which have contaminated the factory premises and the neighbourhood.

The PCDD/Fs, expressed as WHO₂₀₀₅-TEQ/g, return concentrations of 2 pg/g (Klavary) and 23 pg/g (Pardubice-Semtin) in the Czech section. A small increase in the concentration could be attributable to the Spolana plant: In samples taken downstream the plant (Cerinovsko at 3 km and Obristvy at 4 km), only the Cerinovsko sample result (21 pg/g) showed an increase by a factor of approximately 2.5 compared with the sampling site Lysa n. L. The latter sampling site is 37 km upstream of the Spolana plant. 2,3,7,8-TCDD is the dominant congener which emerges from the production of the chlorinated compound 2,4,5-T. There are arguments for assuming a connection with the Spolana plant, because a significant increase in the concentration of 2,3,7,8-TCDD from 0.18 pg/g at Lysa n. L. to 4.9 pg/g at Cerinovsko was

found (Appendix II). The sampling site Obristvy is one kilometre further downstream; the sample taken there returned 1.2 pg/g 2,3,7,8-TCDD. However, in respect of the total dioxin contamination situation of the Elbe, no significant contribution can be established from the solid matter samples taken from around the Spolana plant.

4.5.2 The Elbe at Magdeburg

In order to illustrate the progression of the dioxin concentrations near Magdeburg between 2005 and 2008, the following figure shows the data available for the sampling site Magdeburg (km 318, left bank) (Figure 15).

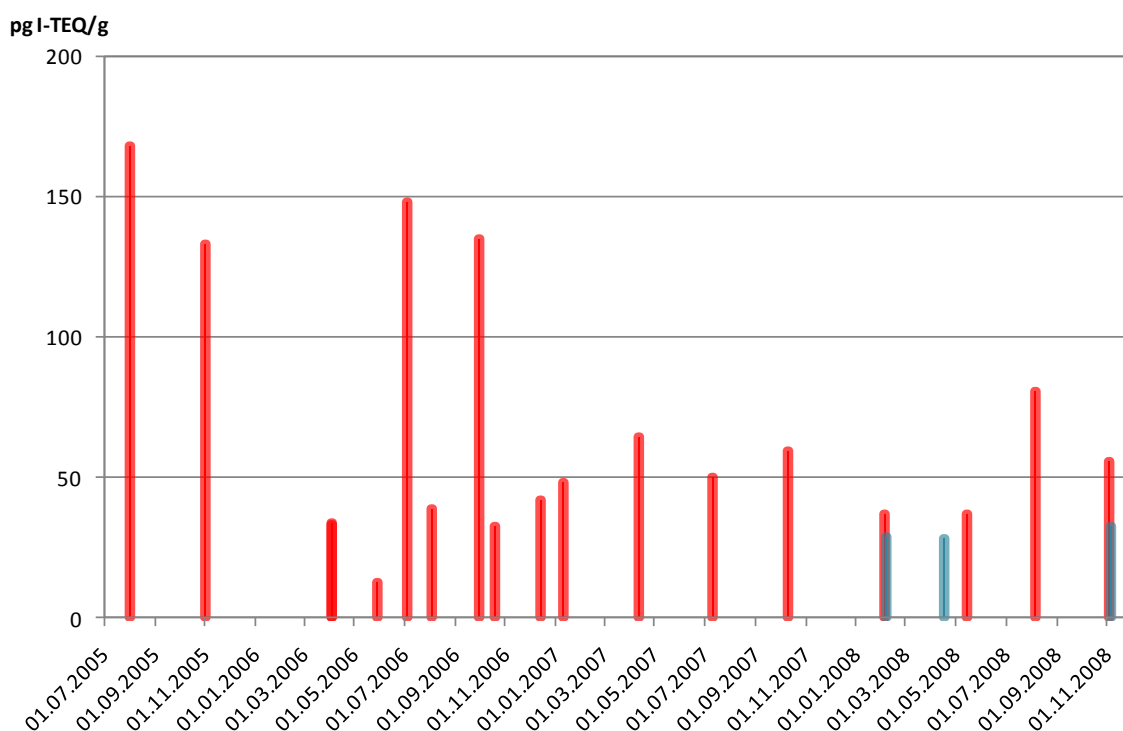


Figure 15: PCDD/F concentrations in solid matter sample at the sampling site Magdeburg (km 318, left bank).

The SPM was sampled from the Sternbrücke (bridge), LHW 2010. Red bars=freshly deposited sediments (four weeks composite samples), blue bars=SPM (continuous centrifuge).

In 2005 and 2006 relatively high PCDD/F concentrations were found. The highest values from these years lay between 148 (2006) and 170 pg I-TEQ/g (2005). In the months that followed the concentrations decreased, with values around 50 pg I-TEQ/g. The value obtained for the 2008 sampling series of 68 pg WHO₂₀₀₅-TEQ/g (Figure 3), agrees well with the earlier series.

In 2005, three SPM samples were obtained from Magdeburg harbour which returned the values 485, 766 and 867 pg I-TEQ/g (LHW 2010). This shows clearly that the harbour functions as a contaminant sink. Both flood events and dredging operations which have to be carried out to ensure that the harbour remains deep enough for shipping can cause contaminated sediments to be returned to the Elbe.

4.5.3 The Elbe at Bunthaus, Hamburg

The sampling site Bunthaus in Hamburg (km 609) has been used for the generation of a PCDD/F large data set since 1990, which allows an assessment of the contamination situation at this site (Figure 16). Analyses were performed on surface sediments, freshly deposited sediments (FDS) originating from SPM as well as SPM itself, which was collected by a continuous centrifuge. FDS composite sampling time was 4 weeks.

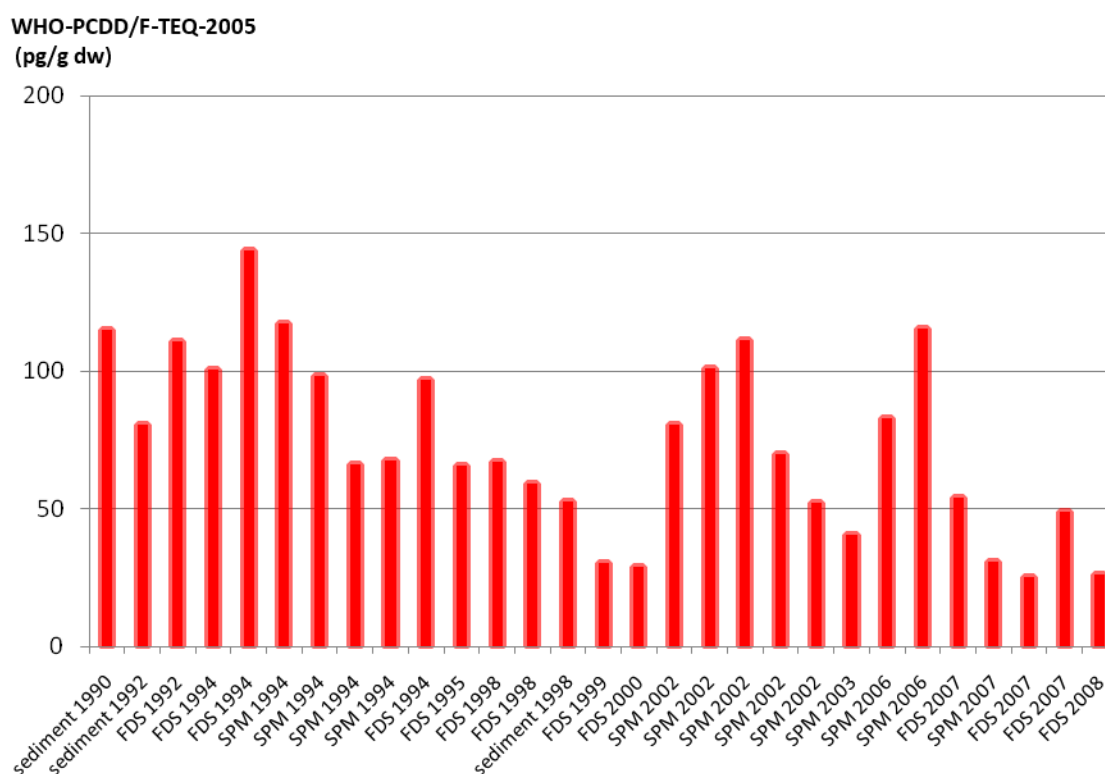


Figure 16: Progression of the PCDD/F concentrations at the sampling site Bunthaus (km 609), Hamburg (km 609).

SPM=suspended particulate matter, FDS=freshly deposited sediment samples (4 weeks composite sample), sediment=surface sediment sample.

The results show that the PCDD/F concentrations vary considerably throughout the course of the period between 1990 and 2008. The concentration peaks in the years 2002 and 2006 could result from the high water events which occurred in those years (see Table 2). In view of the inhomogeneity in the results, there are at present no reasons for assuming that the PCDD/F levels at the Bunthaus sampling site have become lastingly less.

4.5.4 The floodplains of the Elbe

The displacement of polluted old sediments from oxbow lakes, backwaters, flood channels and ditches in the recent floodplains, as well as contaminated soil from the floodplains must be seen as a potential source of contamination of the river. The fact that a huge contamination potential has built up in the course of many years and decades has been confirmed by the high – in some cases extremely high – dioxin levels found in sediment cores (Götz and Lauer

2003). The fact that the sediments still return maximum values at the point where the Mulde enters the Elbe shows that the Mulde contaminates the Elbe sediments during high water events. In addition, contaminated solids are transported from the alluvial soils into the Elbe. We may assume that the soil erosion from the water meadows and the contribution from the Mulde combine to produce the jump in PCDD/F concentration in the alluvial soil downstream the Mulde confluence (Umlauf et al. 2005). Thus these areas may also contribute to the sudden increase in the dioxin levels downstream of the Mulde, as the longitudinal soil sample profile for the Elbe floodplain taken in 2003 also returned a corresponding jump in the concentrations (Umlauf et al. 2005). However, the highest dioxin concentrations in soil samples were recorded further downstream (Figure 17: immediately downstream of the Mulde 665 pg WHO-TEQ/g; near Schnackenburg 2079 pg WHO-TEQ/g; somewhat upstream of Hamburg 1198 pg WHO-TEQ/g).

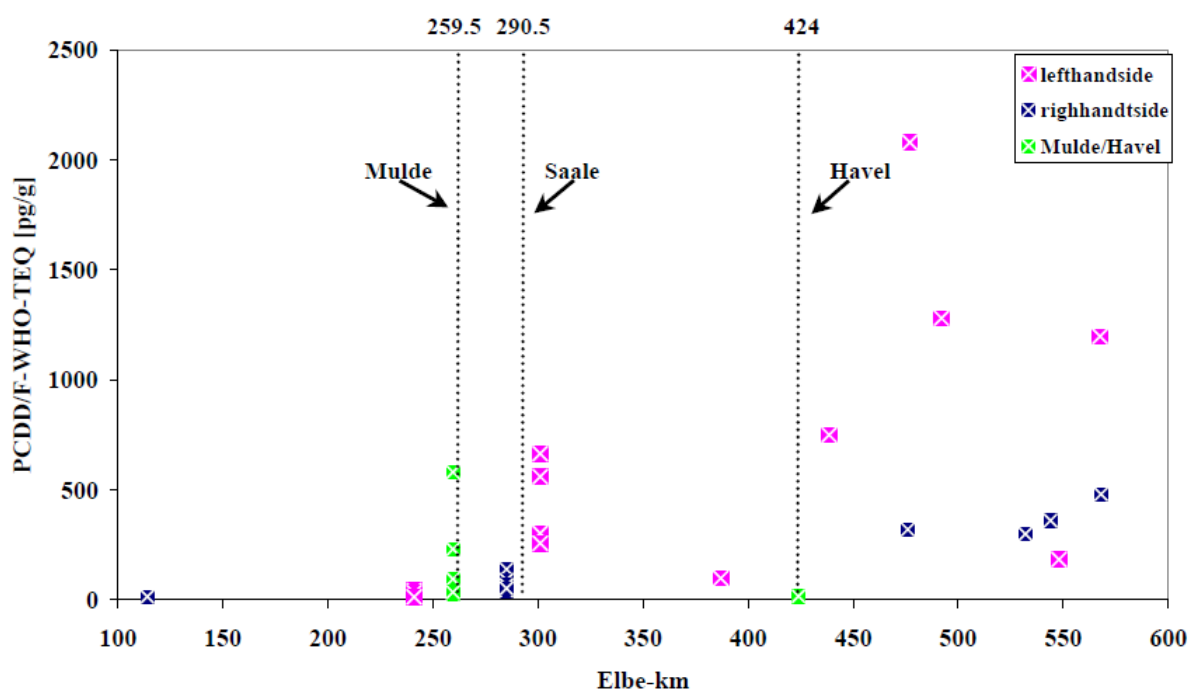


Figure 17: PCDD/F concentrations measured in soil samples taken from the ancient and recent floodplains of the Elbe (2003)

This spatial distribution maximum in the soils, located more downstream when compared to the sediments (Figure 3), suggests that the periodic floods since the closure of the Magnesium production have dislocated the high historic PCDD/F loads present in the floodplains further downstream of their initial discharge into the Elbe. Notably the left-hand side floodplains carry more PCDD/Fs, illustrating again the introduction from the left-hand side confluence of the Mulde/Saale catchments.

In 1993, soil samples taken from floodplains of the Elbe in Lower Saxony from the area of Gorleben (approx. river km 490) to Rönne (opposite Geesthacht, river km 585) were analysed for dioxins (Niedersächsischer Untersuchungsbericht 1993). With up to 2300 pg WHO-TEQ/g, the results were comparable with the high concentrations found in 2003.

Very high dioxin concentrations – 6880 pg WHO-TEQ/g and 2050 pg WHO-TEQ/g – were found in dated Elbe sediment cores taken from Pevestorf (km 485) and Heuckenlock/Hamburg which could be assigned to the 1950s and 1940s (Götz et al. 2007). Undated sediment cores from the Spittelwasser also yielded extremely high dioxin concentrations: 14500 pg WHO-TEQ/g (Götz and Lauer 2003) and 11790 pg WHO-TEQ/g (Schwartz et al. 2006). One soil sample taken near the Spittelwasser returned an extreme value of 157,000 pg WHO-TEQ/g (Götz et al. 1996).

With the aid of previous cluster analyses it was possible to show that suspended particulate matter samples, sediment samples and sediment core samples taken from the river system Spittelwasser - Mulde - Elbe (downstream of the Mulde) and the soil samples with high dioxin concentrations taken from floodplains of the Elbe display similar dioxin patterns (Götz and Lauer 2003, Götz et al. 2007). The dioxin pattern and the dioxin concentrations indicate that the Elbe (downstream of the Mulde) has been contaminated via the Mulde since the 1940s, whereby not only direct introduction, but also mechanisms such as sedimentation and remobilisation in still water zones probably also play a role (Schwartz et al. 2006a). Furthermore, the high degree of contamination found in floodplains of the Elbe at present can probably also be attributed to the deposition of these older sediments.

The results of these and earlier cluster analyses (neuronal networks – Kohonen network as well as multivariate statistical methods) suggest that the dioxin contamination has arisen on account of metal processing operations (Götz et al. 1996, Götz and Lauer 2003). Some recent publications emphasise the importance of magnesium production in Bitterfeld-Wolfen in particular for the dioxin contamination (Bunge et al. 2007, Lechner 2007).

4.5.5 The Mulde-Spittelwasser system

As a result of operations for the manufacture of chemical goods and raw materials which began over one hundred years ago in the region of Bitterfeld-Wolfen, both the sites of abandoned chemical works and the groundwater have become contaminated. In some cases, chemical production waste (such as HCHs, hexachloroethane, DDT slurry as well as other chlorinated slurries and distillation residues (aliphatic VCH, alkalis and salts) was dumped in disused lignite mines. The contamination affects part of the area surrounding Bitterfeld-Wolfen, such as approximately 60 km² of lowlands known as the ‘Spittelwasser’, including the villages of Greppin and Jeßnitz. When flooded, the Spittelwasser lowlands turn into a large lake between 10 and 30 km² in size (ConSoil 2000).

The main sources for the dioxin contamination were probably a number of metal processing plants which produced amongst other things magnesium before, during and after the second world war (Bitterfelder Chronik 1993, as cited in the Hamburger Umweltberichte, Hamburg

Environmental Report 57/99). The production process, the so-called smelting flux or *fused salt electrolysis* process, is known to cause high dioxin emissions. Thus according to the Dioxin Toolkit issued by the UNEP (2005) for one ton of magnesium produced using this method 9 mg I-TEQ are introduced into the environment via waste water. This represents an estimated 3 kg I-TEQ for the duration of the Second World War. After crossing the state border between Saxony and Saxony-Anhalt the Mulde flows into the Mulde-reservoir. Downstream of the reservoir it is augmented by its main tributaries the Leine and the Spittelwasser. The Schachtgraben discharges into the Spittelwasser (Figure 18).

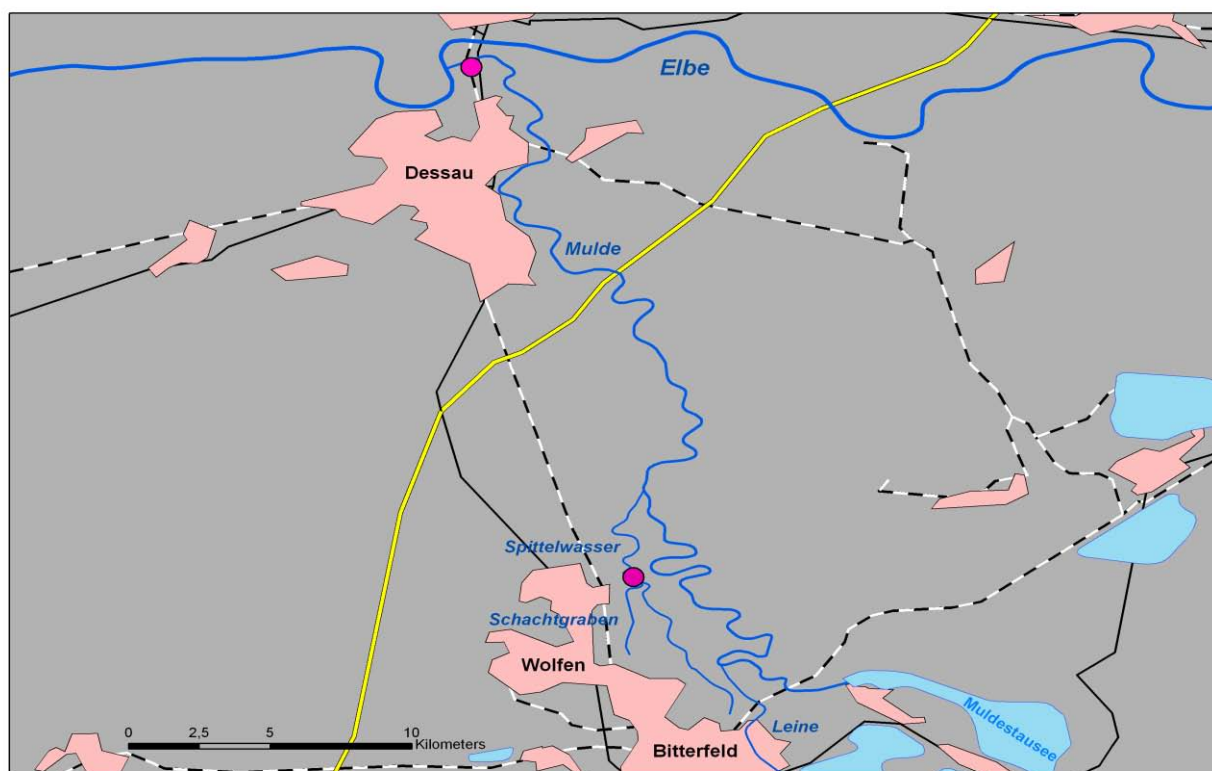


Figure 18: The Spittelwasser-Mulde system

4.5.6 The Mulde

The Mulde, which is also known as the ‘Vereinigte Mulde’ (‘United Mulde’), originates in Saxony at the confluence of the Zwickauer Mulde and the Freiburger Mulde south-west of Leipzig near Großbothen. It has a length of 124 km (290 km including the Zwickauer Mulde), and it joins the Elbe at Dessau-Roßlau.

Especially at times of high water discharge, the Mulde with its catchment area plays a decisive role in respect of the contamination of the Elbe with dioxins.

Dioxin data from SPM-generated and surface sediments are collected regularly by the Landesbetrieb für Hochwasserschutz (State Agency for Flood Protection, Saxony-Anhalt,

LHW) from the Mulde at the monitoring station Dessau (Figure 19). The sediment values dating from 1992 were measured by the former Hamburg environment authority.

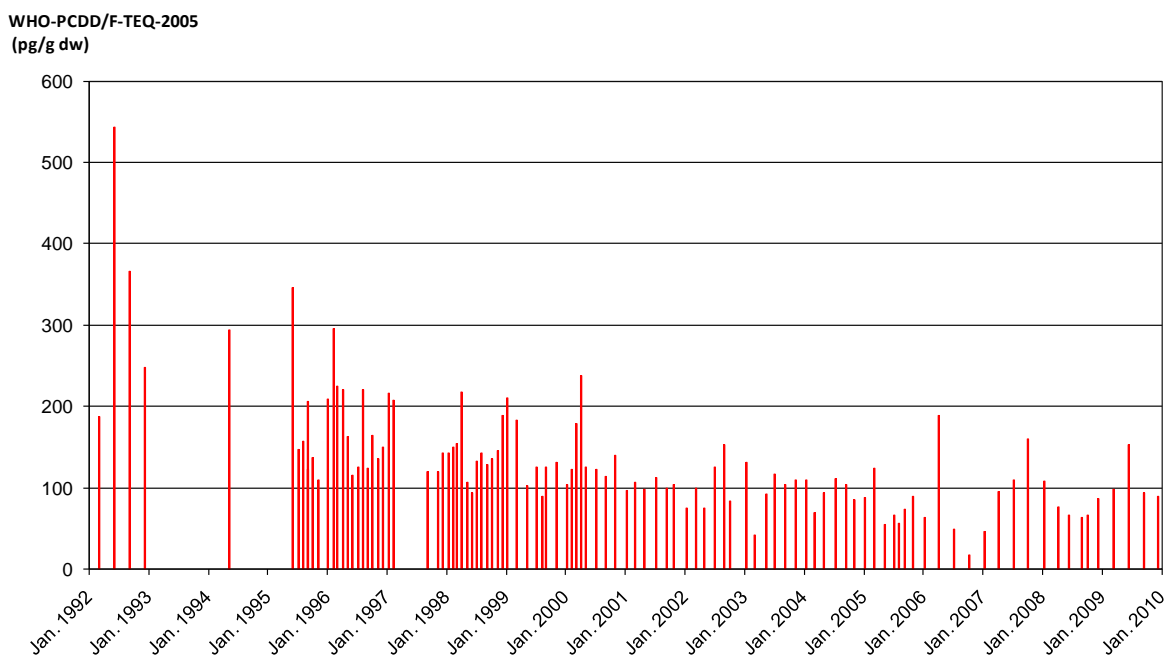


Figure 19: Progression of PCDD/F concentrations in solid matter taken from the Mulde.

Monitoring station Dessau, Elbe km 214.1. Data 1992: sediment sample.

The results shown in Figure 19 reveal that the PCDD/F contamination of the Mulde was higher from 1992 until around 1995 than was the case in subsequent years. Under normal discharge conditions the SPM load is relatively low, indicating that the Mulde transports only small dioxin quantities into the Elbe. However, significant high water events lead to contaminated material being washed out of the Mulde into the Elbe.

4.5.7 The Spittelwasser

The Spittelwasser is a creek only 8 kilometres long, and yet it represents the most important tributary of the Vereinigte Mulde as far as the pollution load with PCDD/Fs is concerned. It flows along the eastern edge of the region with a high density of chemical plants. The Leine, a small creek which flows into the Mulde (Figure 18), is already highly contaminated with dioxins. Measurements conducted by the State Agency for Flood Protection, Saxony-Anhalt, in 2007 near Bad Döben show that where the Mulde flows through the State of Saxony the dioxin concentrations are still low. Before it enters the Mulde, the Leine solids are already contaminated with dioxins up to approximately 600 pg I-TEQ/g, and the dioxin load transported by the Schachtgraben near Jeßnitz is approximately 1000 pg I-TEQ/g (LHW 2010).

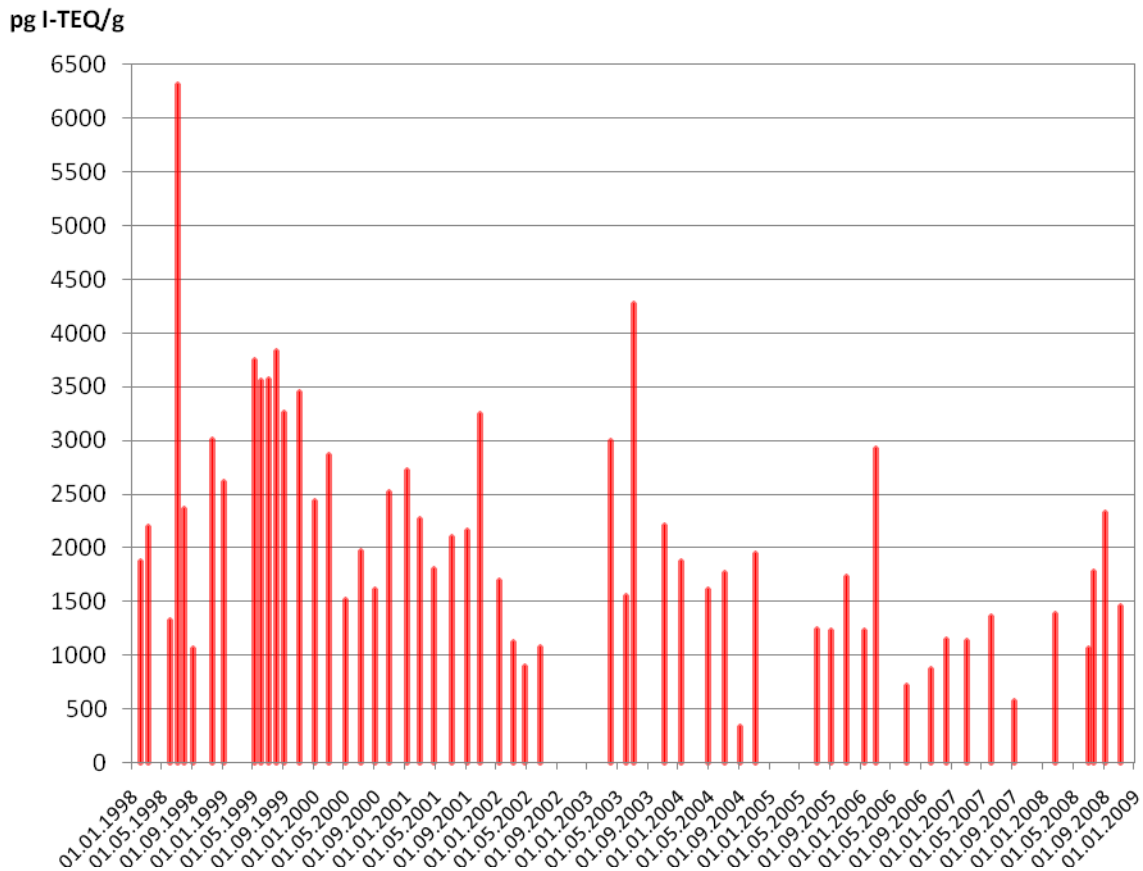


Figure 20: PCDD/F concentrations in SPM at the Spittelwasser sampling site

Figure 20 shows peak concentrations of 6320 pg I-TEQ/g and 3840 pg I-TEQ/g occurring in 1998 and 2003 respectively. The trend is towards decreasing peak values from 2003 to 2009. The dioxin concentrations frequently lie in the range 1000 to 2000 pg I-TEQ/g. Thus the SPM transported by the Spittelwasser represent a major source of contamination for this river system which needs to be subjected to adequate decontamination measures (ConSoil 2000). Experts are elaborating recommendations for such measures in order to decontaminate the extremely polluted sediments of the Spittelwasser (amounting to about 20,000 m³) together with the areas which it floods at times of high water (Förstner 2010).

4.5.8 The Saale

With a length of 413 km, the Saale is the second longest tributary of the Elbe after the Vltava (Moldau). Its source is near Zell in the Fichtelgebirge mountains and it joins the Elbe at Barby. It has a catchment area of 24,100 km² (IKSE 2005). A number of chemical plants are situated on the Weiße Elster, a river which enters the Saale on its right bank. Figure 21 shows the results of analyses performed on SPM-generated sediments taken from the Saale near Groß Rosenberg from 2005 to 2008.

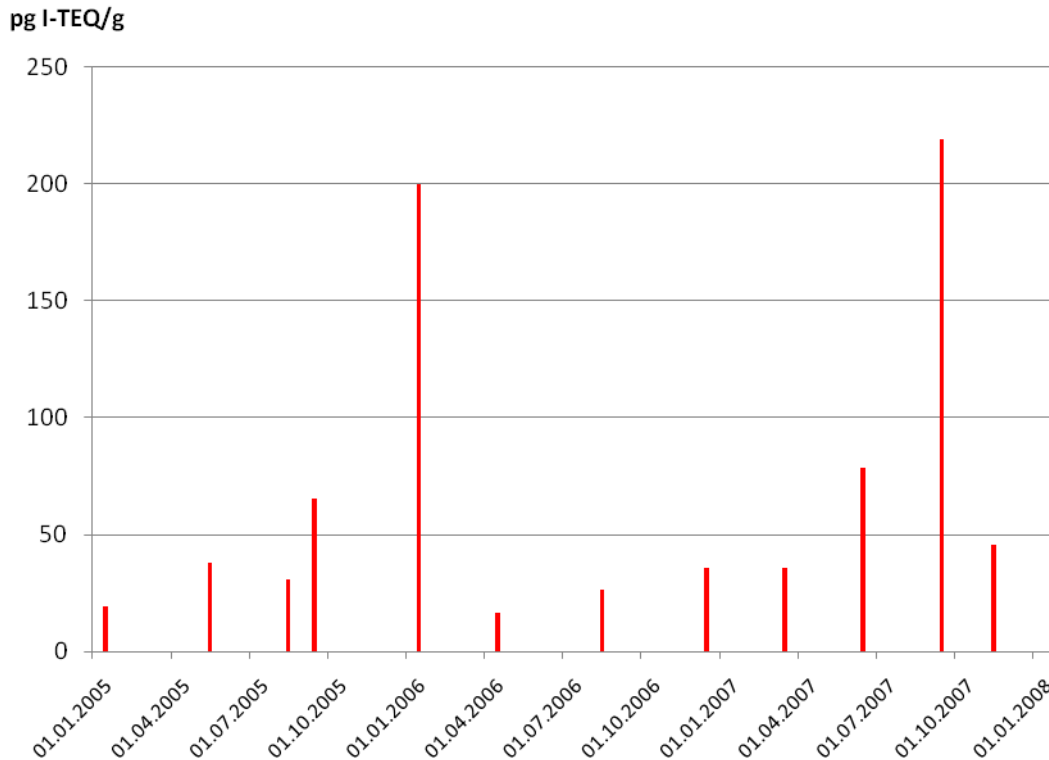


Figure 21: PCDD/F concentrations in solid matter from the Saale near Groß Rosenberg

Data from the State Agency for Flood Protection, Saxony-Anhalt, LHW).

Figure 21 shows that concentration levels in solid matter samples from the Saale generally lie below 50 pg I-TEQ/g. Conspicuous exceptions are the values 200 and 219 pg I-TEQ/g from 2006 and 2007. As a result of the cluster analysis (neuronal networks) for this series of investigations the respective individual sample was assigned to the Bitterfeld-Elbe cluster, indicating a connection with thermal metal production processes (Chapter 4.3). SPM collected near Groß Rosenberg using a continuous centrifuge return values ranging from 15 to 60 pg I-TEQ/g (mean value=38 pg I-TEQ/g). The evaluation of the congener distribution carried out by the State Agency for Flood Protection, Saxony-Anhalt (LHW), reveals a significant correspondence with the patterns obtained for the Bode (LHW 2010).

SPM taken from the Weiße Elster near Halle-Ammendorf/Burg in 2008 yield a range from 19 to 25 pg I-TEQ/g, with a mean value of 23 pg I-TEQ/g (n=4). These results show that the Weiße Elster also contributes to the dioxin load transported by the Saale. The State Agency for Flood Protection plans further investigations on solid matter from the Weiße Elster.

4.5.9 The Bode

The Bode joins the Saale near Nienburg, entering on its left bank. It is 169 km long and has a catchment area of 3300 km² (IKSE 2005). SPM samples were obtained from the vicinity of Neugattersleben (Figure 22). Figure 23 shows the results for 2007 to 2008.

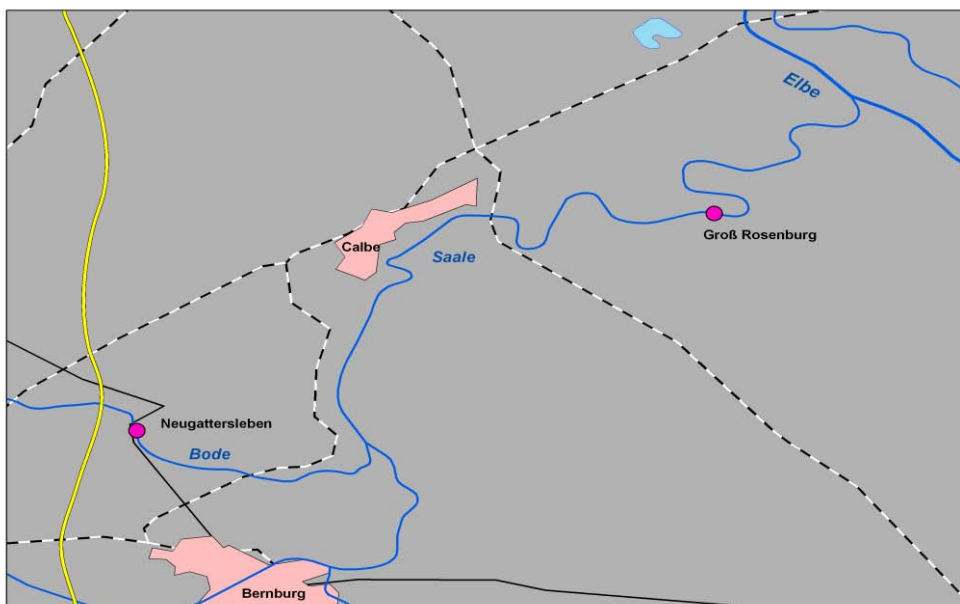


Figure 22: Sampling sites for sampling SPM with continuous centrifuge

Data from the State Agency for Flood Protection, Saxony-Anhalt (LHW), 2010.

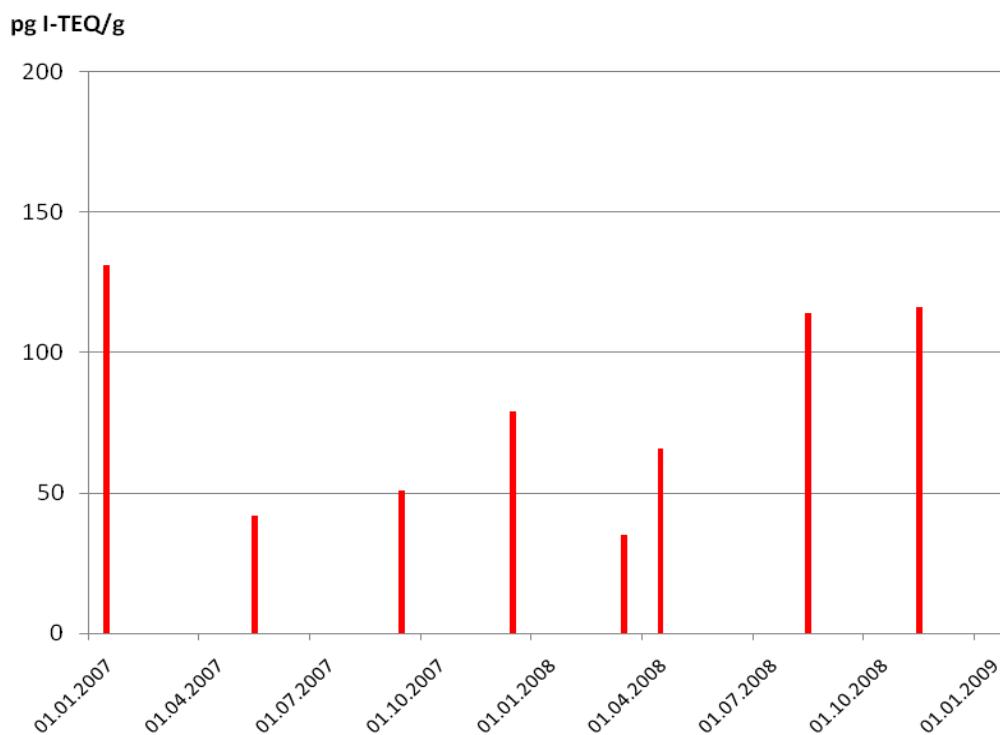


Figure 23: PCDD/F concentrations in SPM samples from the Bode

Data from the State Agency for Flood Protection, Saxony-Anhalt (LHW), 2010.

The SPM taken from the Bode for this study contained 102 pg WHO₂₀₀₅-TEQ/g. Other individual measurements of samples taken from the Bode between 2005 and 2008 returned a concentration range from 35 pg I-TEQ/g to 154 pg I-TEQ/g (LHW 2010). As is the case for

the Saale, the results for this tributary cannot be taken as indicative of significant reductions in the dioxin levels in recent years.

Downstream of Staßfurt a tributary of the Bode, the Liethe, flows close to the urban part of the community of Leopoldshall. Various metal processing plants are located on the Liethe which are still working. It is possible that certain production processes contribute to the dioxin contamination (LHW, No. 1/2010). The State Agency for Flood Protection, Saxony-Anhalt, is planning further sampling to investigate this possibility.

4.5.10 Comparison of the longitudinal PCDD/F profiles from 2002 and 2008

In August 2002, extreme and long-lasting precipitation in the Czech Republic and in the eastern part of Germany caused a flood disaster affecting the Upper and Middle Elbe, the Vltava and the Mulde. Dykes broke, and many factories (including the Spolana chemical plant) as well as municipal and industrial sewage treatment works were flooded. There was great concern that contaminated soil and remobilised contaminated sediments from backwaters could be introduced into the Elbe and its tributaries, and this was indeed the case.

In order to gather information about the effects of the flooding on the dioxin immission situation in the Elbe, 37 surface sediment samples were taken four weeks after the main flood from sampling sites starting at Obristvy to Trischendamm in the Wadden Sea. The samples were analysed for a number of organic pollutants (Stachel et al. 2005). A comparison of the two longitudinal profiles obtained in the year 2003 and 2008 display some interesting analogies with respect to the presence of dioxins in the Elbe.

Figure 24 shows PCDD/F concentrations in the Elbe. Despite the differences between the two studies, such as the samples themselves, the time period between them and the differing discharge situations (disastrous flood in 2002 versus low water event in September 2008), the two datasets are quite similar. Both longitudinal profiles reveal significantly lower PCDD/F concentrations upstream of the Mulde confluence. In 2002, a very pronounced peak was recorded at the sampling site Breitenhagen about 30 km downstream of mouth of the Mulde. In both cases, a continual reduction in the PCDD/F levels can be seen in the remaining course of the river. Overall levels are in a similar range with a tendency of a shift of PCDD/Fs from the Mulde confluence towards the tidal Elbe. This would indicate an overall translocation of the Elbe sediments but more data are needed to evaluate this hypothesis. In addition, the good match of the two concentration profiles demonstrates that the use of standardized analysis procedures allows reliable comparison of results. The sample analyses for the longitudinal profile conducted in 2002 were performed by the Umweltbundesamt (Federal Environment Agency) at its subsidiary laboratory in Langen, while the 2008 series was analysed at the JRC Ispra.

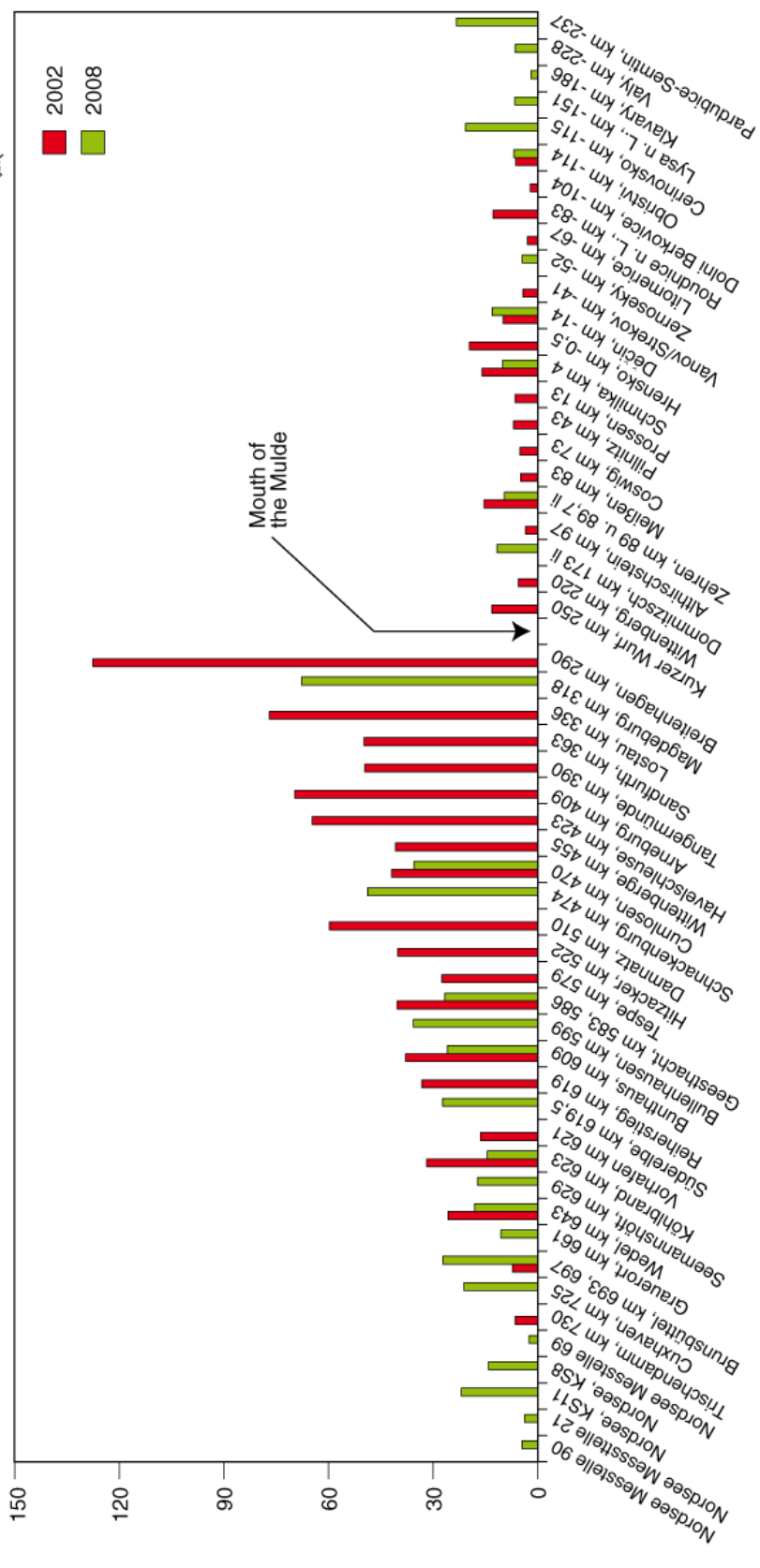
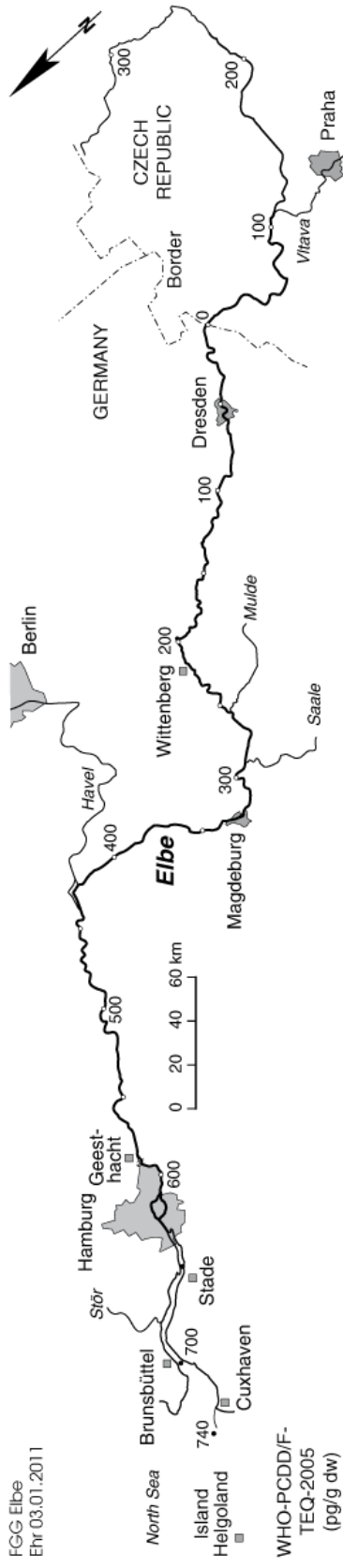


Figure 24: Comparison of the longitudinal PCDD/F profiles of the Elbe from the years 2002 and 2008

4.5.11 Comparison with other water bodies – Danube

The Danube is the second longest river in Europe after the Volga. It is about 2800 kilometres in length and has a catchment area of 795,690 km² (ICPDR 2004). It is approximately three times as long as the Elbe and its catchment area is about five times greater. As the Elbe, it got stretches of near-natural conditions and flow through biosphere reserves.

In order to establish the extent to which the Danube is contaminated with PCDD/F the JRC took sediment samples from the left and right river banks in September 2007. The samples were taken from immediately downstream of the river's source in the Black Forest to the point where it enters the Black Sea, and then analyzed for the 17 WHO congeners (Umlauf et al. 2008). Figure 25 shows the results of this investigation.

The PCDD/F concentrations in the samples range from 2 pg WHO₁₉₉₈-TEQ/g to a maximum of 21 pg WHO₁₉₉₈-TEQ/g. These concentrations are significantly lower than those found in the Elbe and its tributaries (see Figure 3). The right bank does not show big differences. The maximum value is an exception found in a sample taken from the left bank a short way downstream of Pancevo (Serbia). Since the confluence of tributaries Drave and Save (both low in concentration and entering from the right bank) cannot explain this, it is suggested that the source is Pancevo itself, where chemical industry had been destroyed during the Balkan war.

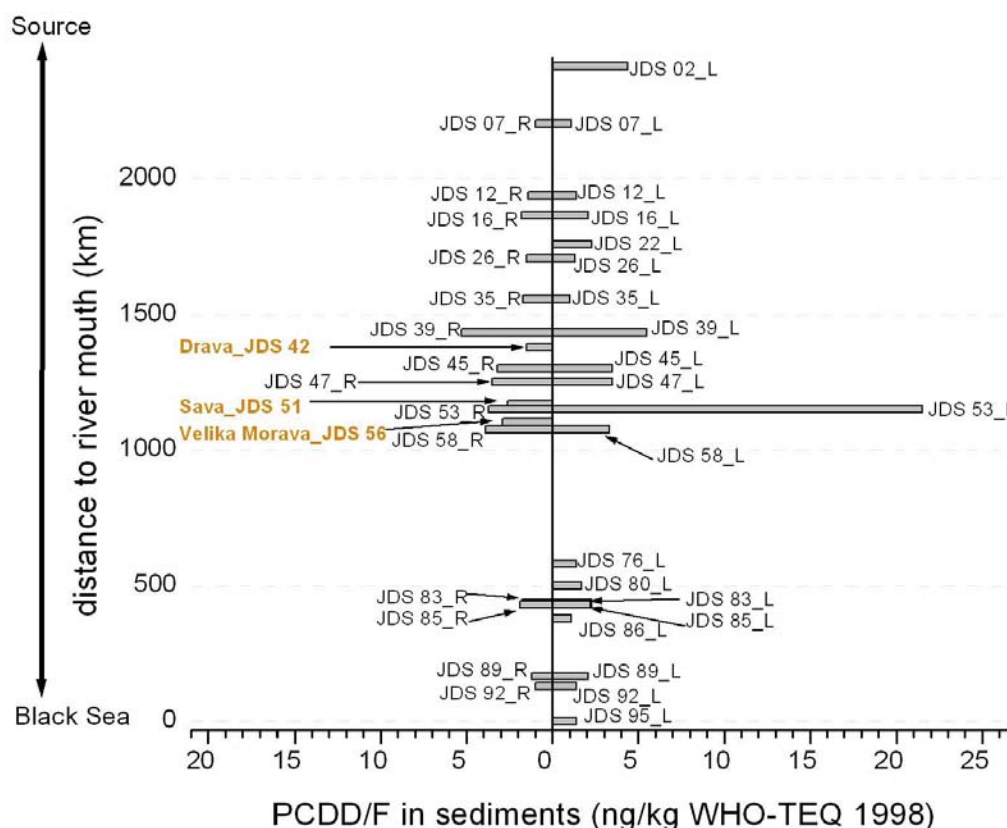


Figure 25: PCDD/F concentrations in sediments from the Danube

L=left bank, R=right bank; JDS=joint dioxin survey. Data from Umlauf et al. 2008.

4.5.12 Comparison with other water bodies - the Baltic Sea

The Baltic Sea represents another large, open body of water. The results of a comprehensive Swedish study show that relatively high dioxin concentrations can be found in some parts of the Baltic Sea as well.

Sundqvist (2009) and Sundqvist et al. (2009a and 2009b) carried out wide-ranging investigations in near-surface sediments taken along the Swedish coast and also from offshore sampling sites. PCDD/Fs and the non-ortho PCBs TeCB-77, TeCB-81, PeCB-126 and HxCB-169 as well as further chlorinated hydrocarbons were determined for nearly 150 samples. The results for the PCDD/F varied a great deal. In the coastal regions, the WHO-TEQ lay in the concentration range 0.85 to >1000 pg/g, whereby the substances were introduced mainly via point sources (wood conservation using PCP, pulp/paper production). Atmospheric deposition was identified as a significant source of contamination in offshore regions.

Sediments samples taken from the Gulf of Finland also returned high dioxin concentrations. Maximum values of 648 and 750 pg I-TEQ/g are indicative of the high degree of contamination in sediments from southern Finland (SCALE 2004). The dioxin contamination can be attributed to the paper and cellulose industry.

4.6 PCBs – further discussion

4.6.1 Spatial distribution and potential sources

The concentrations found for PCBs are higher in the upper sections of the river than further downstream, where the levels decline steadily (Figure 4 and Figure 5). The maximum DL-PCB value was found in the samples from Pardubice-Semtin (21 pg WHO₂₀₀₅-TEQ/g) and the Spittelwasser (35 pg WHO₂₀₀₅-TEQ/g). DL-PCB samples from 2008 returned a range of values for the Spittelwasser from 34 to 46 pg WHO-TEQ/g (LHW 2010). However, the Spittelwasser is only a small creek with considerably low discharge, and is therefore negligible in the PCB budget of the river Elbe.

In contrast, the PCB values in the Czech stretch of the River Elbe are of concern.

The sum of the 7 indicator PCB concentrations in excess of 100 ng/g were measured at the sampling sites Valy, Lysa nad Labem, Cerinovsko, Obristvy, Decin and Schmilka as well as in the Vltava (Moldau). In this respect it is worthy to note that in comparison with PCDD/Fs, PCBs accumulate in biota considerably more readily (Nimii 1996). The results found for eels, where the PCB toxicity exceed the PCDD/F concentrations confirm this (Figure 1).

Both the available orientation values for indicator PCBs in sediments, namely 10 ng/g (OSPAR 2000) and 20 ng/g (Swedish EPA 2008) were significantly exceeded, in one case by a factor of approximately 20 (Decin).

The geographical distribution of PCBs in the Elbe solids is in line with the comparably high human PCB exposure of the Czech population (Van Leeuwen and Malisch 2002; WHO 1996).

Possible sources for PCB emissions are dumps containing industrial waste along the Czech section of the river. For instance, only 3 km upstream of the sampling site Pardubice-Semtin (km -237) near Rybitvi (km -234, District of Pardubice) there is a landfill site containing chemical industrial waste (IKSE 2000, Heinisch et al. 2007). The high PCB contamination near Decin (Figure 5) could be attributed to discharges from the industrial region of Usti nad Labem (Heinisch et al. 2007). Further sources may be anticipated in recycling plants for processing shredded materials. As there are a number of metal processing plants along the Czech section of the river Elbe, it is possible that individual plants may be responsible for the emission of contaminants. Especially facility buildings which are not provided with a protective housing release gaseous and particle-bound PCBs and PCDD/Fs into the atmosphere and can therefore present an environmental hazard through wet and dry deposition (Bayerisches Landesamt für Umwelt 2009).

Nondek & Frolikova (1991) published the results from an Elbe screening of more than 200 sites in the former Czechoslovakia executed during 1987-1990. They identify waste waters from chemical factories in Pardubice, Kolin, Neratovice, Steti, Lovosice and Usti nad Labem as contamination sources of POPs. In particular the Skoda car factory at Mlada Bolesav and an industrial dumping site upstream of Mlada Bolesav were identified as the main PCB sources. Mlada Bolesav (resp. the confluence of the associated Elbe tributary) is located between the 2008 sampling sites Lysa nad Labem and Cerinovsko.

The high levels of PCBs in the Vltava cannot be explained as yet. In order to be able to locate possible sources, Povodi Vltava (Prague) is carrying out further research. The PCBs may well be introduced via the river Zakolansky, which drains the region surrounding the town of Kladno. In the past, this was the location of one of the largest Czech metal factories, and this site also housed a shredder plant (Jan Valek, personal communication 2010).

4.6.2 Comparison with other water bodies – Danube

Compared to the average DL-PCB levels in the Danube sediments (Figure 26) as determined in 2007 (0.6 pg WHO₁₉₉₈-TEQ/g), the German stretch of the Elbe, shows levels of about three times higher the while in the Czech stretch the average DL-PCB levels were about average ten times higher. The maximum level in Pardubice-Semtin of around 20 pg WHO₁₉₉₈-TEQ/g exceeds the Danube maximum by a factor of 7.

The comparison of the indicator PCBs⁵ (Figure 27) shows a similar differences between the two rivers, again with PCB levels in the Czech stretch exceeding the Danube PCB average (around 6 ng/g) by a factor of ten.

⁵ From the Danube study only 6 marker PCBs are reported for comparison with the 7 marker PCBs of the Elbe study. However, PCB 118, not included in the Danube data accounts to less than 15% to the sum of 7.

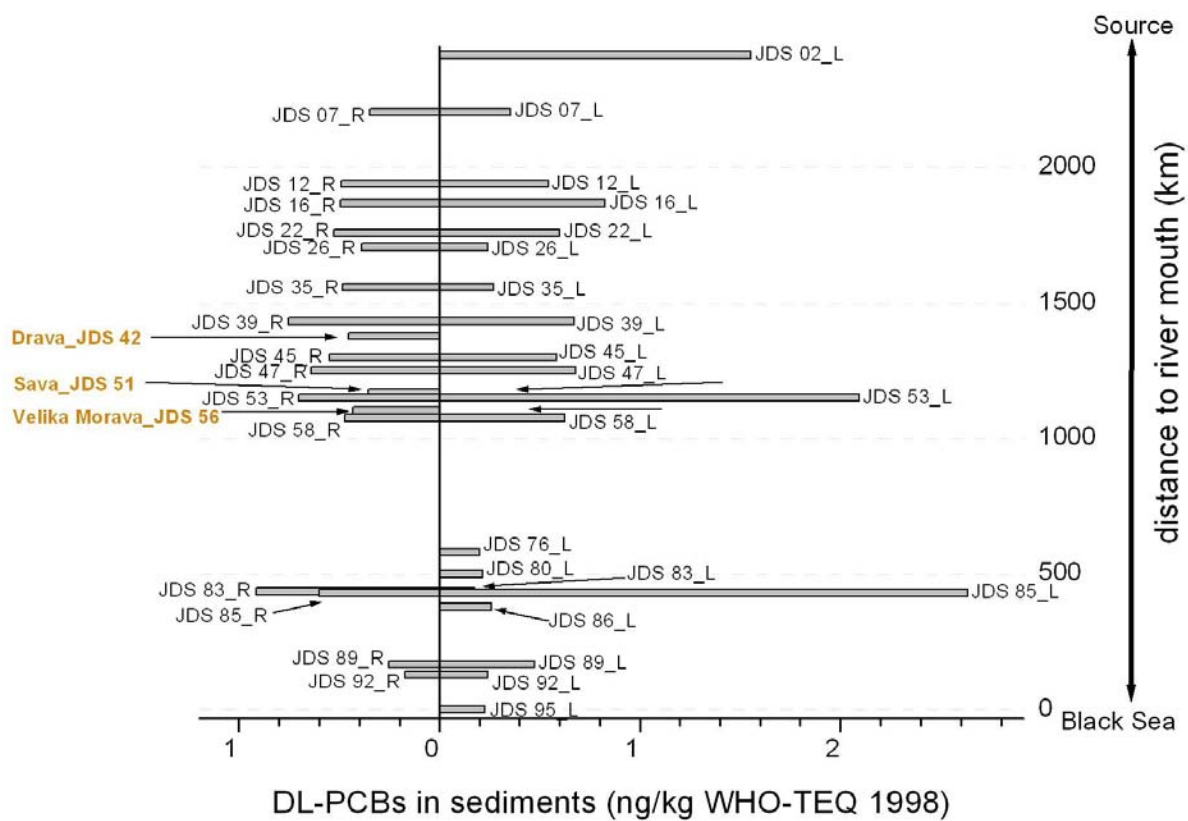


Figure 26: Dioxin-like PCBs concentrations in sediments from the Danube

L=left bank, R=right bank; JDS=joint dioxin survey (Umlauf et al. 2008).

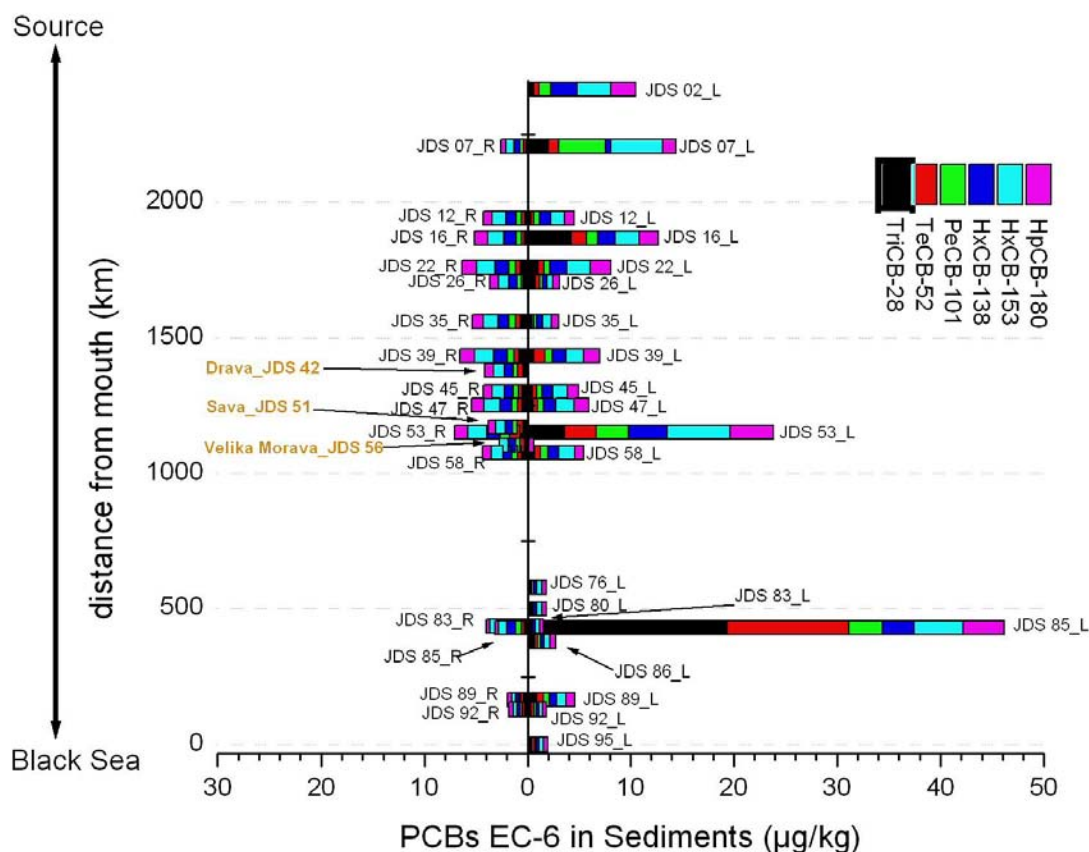


Figure 27: Indicator PCB concentrations in sediments from the Danube

L=left bank, R=right bank; JDS=joint dioxin survey (Umlauf et al. 2008).

5 Conclusions

Solid materials transported by the Elbe and its relevant tributaries the Vltava, the Spittelwasser, the Mulde, the Bode, the Saale and the Stör are in some cases highly contaminated with dioxins and PCBs. This could be an explanation why eels caught in the lower Elbe are seriously contaminated with PCDD/Fs and especially with dioxin-like PCBs. However, the spatial distribution of PCDD/Fs and PCBs is very different, and measures to reduce their occurrence in the Elbe ecosystem need to address the two compound groups separately and at different origins.

PCDD/Fs: PCDD/Fs are phenomena mainly of the German stretch of the Elbe, in particular after the confluence of the Rivers Mulde and Saale. Upstream of the Mulde confluence the concentrations are relatively low; immediately downstream of the confluence they increase significantly, after which they decline steadily until the Hamburg region. Thereby the concentration levels as well as the downstream profile from 2002 and 2008 were rather similar, indicating minor change of the overall situation since 2002. The dominant influence on the PCDD/F contamination in the Elbe comes and came from the river Mulde, more specifically the Spittelwasser-Mulde system, where the highest levels were found, and to

some extent from the catchment area of the Saale. High flood events lead to high soil erosion of the contaminated sites at the Mulde region and reach the Elbe River at least.

The results of the cluster analysis (neuronal networks) provide evidence for the influence of former metal producing plants in the Bitterfeld-Wolfen region and possible near Staßfurt on the river Bode, a tributary of the Saale.

Especially during extreme precipitation events the highly contaminated Spittelwasser solids can enter the Elbe unhampered. Besides the secondary PCDD/F reservoirs in the tributary catchments also the historically contaminated alluvial soils and slack water zones of the Elbe itself can remobilize PCDD/Fs into the water column in the case of flood events.

The time series for dioxin concentrations for solid matter from the Mulde between 1992 and 2009 shows that dioxins continue to be introduced into the Elbe via the Mulde. This can be attributed to historical sources located in the Bitterfeld-Wolfen region and the catchment area of the Bode (thermal metal production processes). The contaminated, remobilized material is transported into the Elbe and hence into the North Sea every time the region undergoes flooding. The PCDD/F fingerprint in the Czech section of the Elbe at Neratovice suggests only a minor local impact from the production of 2,4,5-T at the Spolana chemical plant in the past, with no significant impact on the overall contamination of the Elbe with PCDD/Fs.

A comparison with orientation values for dioxins and indicator PCBs for sediments obtained from relevant studies suggest hazards for aquatic organisms and humans. Sediments in the Danube, which like the Elbe flows through large areas designated as nature reserves and biosphere reserves, are significantly less contaminated with dioxins and PCBs than those of the Elbe.

Higher levels of dioxins (as compared with a neighbouring reference area) were found offshore in the North Sea South of Helgoland in the area previously used for dumping treated sewage from Hamburg. However, the PCDD/F fingerprints found there point to the Bitterfeld-Wolfen region rather than to impacts from both sewage dumping. Also the current dumping of sediments at another North Sea site had little impact, also here, as in all sites sampled in the North Sea, the Bitterfeld-Wolfen fingerprint was dominant.

The spatial information on the occurrence of PCDD/Fs, as well as the fingerprint based source apportionments suggest the need to inhibit further remobilization from the Spittelwasser, adjacent historic production sites and from secondary reservoirs in the contaminated alluvial soils and the slack water zones.

PCBs: In contrast to the PCDD/Fs, PCBs are mainly present in the Czech section of the Upper Elbe. After the German border PCBs display an overall decrease. Other than PCDD/Fs, PCB emissions into the Elbe cannot be attributed to a dominant source or area. Indicator PCBs did rise more or less constantly in concentration until the German border, suggesting a variety of cumulative emission sources along the whole Czech catchment. Thus, no specific recommendation on how to decrease the PCB pressure on the River Elbe can be given on the basis of the data acquired in this study. Detailed regional scale monitoring in the Czech stretch, together with the evaluation of production statistics regarding potential PCB sources

are needed here. After all the PCB toxicity in eel is exceeding that of PCDD/F up to one order of magnitude.

Other dioxin-like compounds: As an amendment to the chemical analyses, two Ah-receptor based bioassays (DR CALUX^R and EROD), which display the dioxin-like activity of all pollutants present, was performed on a subset of the samples (blind study). For the DR CALUX^R the comparison revealed a good agreement between the HRGC/HRMS results on dioxins and dioxin-like PCBs along the German stretch and the bioassay. However, along the Czech section of the Elbe the DR CALUX^R displayed a 10 times higher dioxin-like activity than the chemical analyses. This suggests that the solid material in the Czech section contains additional persistent dioxin-like acting pollutants. In comparison to the DR CALUX^R test, the EROD assay displayed even higher dioxin-like activities, less than 1 % of the observed signal could be explained by the PCDD/Fs and dioxin like PCBs quantified. The differences can be explained by the fact that the clean up procedure for the DR CALUX^R destroyed the less persistent organic pollutants in the extract, while the EROD procedure remained sensitive to those. More research is needed to identify the compounds behind the so far unexplained signal of the bioassays and to localize their emission sources.

6 Outlook

A description of transport mechanisms for dioxins in the limnic Elbe with special emphasis on the movement of substances out of groyne fields is the subject of a thesis at the Technical University Hamburg-Harburg. Computational models which are planned as part of the EU Interreg IVB project DiPol are to portray the probable distribution of contaminants in the tidal Elbe and the North Sea coast. These models will be computed by DELTARES (NL).

Finally, the JRC of the European Commission – Institute for Environment and Sustainability, Ispra, Italy, is currently supplementing the study with data on organohalogen pesticides and polybrominated diphenyl ethers determined in the solid samples presented in this report.

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Appendices

- I Sampling sites: location, TOC and grain size fraction $<20 \mu\text{m}$
- II Analysis results: PCDD/F
- III Analysis results: DL-PCB
- IV Analysis results: indicator PCB
- V Quality control
- VI Analysis method
- VII Sampling devices

Appendix I

Sampling sites: location, TOC and grain size fraction <20 µm

Sample site	River km	Latitude [decdeg]	Longitude [decdeg]	Sample	TOC [% dw]	Faction <20µm [% dw]
Pardubice-Semtin, rechts	-237,0	15,77804	50,04433	sediment, EP	3,2	nd
Valy, links	-228,0	15,61820	50,03330	FDS	7,7	4,3
Klavary, links	-186,0	15,17367	50,05415	sediment, EP	3,7	
Lysa nad Labem, rechts	-151,0	14,80255	50,20788	FDS	6,9	3,3
Cerínovsko, rechts	-115,0	14,52608	50,27922	sediment, EP	31	
Obristvy, links	-114,0	14,48090	50,29893	FDS	5,6	4,4
Vltava, Zelcin, links	-110,0	14,44207	50,31853	FDS	0,01	nd
Zernoseky, rechts	-52,0	14,06732	50,53216	sediment, EP	11	nd
Decin, rechts	-14,0	14,21166	50,77420	FDS	7,1	6,8
Schmilka, rechts	4,0	14,23017	50,89130	FDS	7,1	78
Zehren, links	89,7	13,40406	51,20933	FDS	6,2	82
Dommitzsch, links	173,0	12,89514	51,64857	FDS	6,1	68
Spittelwasser	nd	12,28882	51,69216	FDS	7,9	86
Mulde, Dessau	7,6	12,23733	51,87168	FDS	7,7	49
Bode, Neugattersleben	nd	11,70624	51,84576	SPM	12	71
Saale, Rosenberg	3,8	11,87469	51,91684	FDS	4,8	68
Magdeburg, links	318,0	11,66252	52,10583	FDS	5,7	69
Cumlosen, rechts	470,0	11,66073	53,04169	FDS	6,4	nd
Schnackenburg, links	474,0	11,56971	53,03824	FDS	5,8	46
Geesthacht, rechts	586,0	10,33775	53,42354	FDS	5,6	nd
Bullenhausen, links	599,0	10,07021	53,45903	sediment, EP	3,9	70
Bunthaus, rechts	609,0	10,17830	53,39691	FDS	4,8	45
Süderelbe, rechts	619,5	9,96075	53,48710	sediment, EP	3,4	40
Köhlbrand, links	623,0	9,93986	53,52372	sediment, EP	3,1	29
Seemannshöft, links	629,0	9,88067	53,54027	FDS	3,6	67
Wedel, rechts	643,0	9,70065	53,56979	FDS	2,2	37
Grauerort, links	661,0	9,49529	53,67791	FDS	1,7	23
Stör, Heiligenstedten, rechts	nd	9,47034	53,93081	sediment, EP	3,4	29
Brunsbüttel, Elbehafen, rechts	693,0	9,16861	53,87951	sediment, EP	1,7	26
Cuxhaven, links	725,0	8,70128	53,87793	SPM	4,6	51
Nordsee KS 8 (BSH)	0,0	8,12500	54,02000	sediment, EP	1,8	nd
Nordsee KS 11 (BSH)	0,0	8,07500	54,04000	sediment, EP	2,2	nd
Nordsee Messstelle 21, 2 km von Verklappstelle E3	0,0	7,96702	54,06966	sediment, EP	1,1	41
Nordsee Messstelle 69, 12 km von Verklappstelle E3	0,0	8,13482	53,98465	sediment, EP	0,73	33
Nordsee Messstelle 90, Referenzgebiet	0,0	8,00925	54,14245	sediment, EP	0,88	34

EP = single sample

FDS = freshly deposited sediments, composite sample

SPM = suspended particulate matter

nd = not determined

Appendix II

Analysis results: PCDD/Fs

Lab. Code:	DP-08-251-070409-11	DP-08-271-200409-8	DP-08-253-120509-5B	DP-08-272-200409-9	DP-08-252-070409-12
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Pardubice Semtin, km -237	Valy, km -228	Klavary, km -186	Lysa nad Labem, km -151	Cerinovsko, km -115
Sampling	30.09.2008	28.08.-02.10.08	30.09.2008	28.09.-01.10.08	30.09.2008
Type of sample:	Sediment, EP	FDS	Sediment, EP	FDS	Sediment, EP
Mass Analysed:	5,02	5,04	5,01	5,05	5,05
Data analysed:	25.04.2009	01.05.2009	26.05.2009	01.05.2009	25.04.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
2,3,7,8 - substituted PCDD/Fs					
2378-TCDD	0,19	0,22	0,09	0,18	4,94
12378-PeCDD	1,78	1,33	0,20	1,18	4,46
123478-HxCDD	0,42	1,04	0,15	0,83	1,44
123678-HxCDD	1,06	1,92	0,47	1,88	2,69
123789-HxCDD	0,43	1,93	0,53	1,38	2,03
1234678-HpCDD	5,84	23,54	7,00	22,74	18,10
OCDD	29,08	147,05	39,17	148,42	86,08
2378-TCDF	6,56	5,32	2,30	8,48	25,98
12378-PeCDF	2,73	2,96	0,94	3,39	13,93
23478-PeCDF	22,78	5,18	1,96	6,58	11,93
123478-HxCDF	67,73	5,45	2,05	5,98	18,37
123678-HxCDF	10,40	4,23	0,99	3,35	7,76
234678-HxCDF	9,10	5,94	0,92	4,16	6,10
123789-HxCDF	19,99	1,24	0,58	1,01	2,85
1234678-HpCDF	211,54	23,80	5,06	16,37	33,93
1234789-HpCDF	42,08	3,38	0,99	2,86	5,65
OCDF	673,84	33,72	9,56	27,81	45,51
WHO-TEQ-2005	23,27	6,46	1,85	6,62	20,73
Homol. ΣPCDD/Fs					
TCDD	14,54	10,21	2,35	8,45	63,63
PeCDD	18,91	12,75	2,35	12,57	39,72
HxCDD	12,79	13,64	7,12	24,03	33,74
HpCDD	11,87	51,73	14,80	46,76	35,29
OCDD	29,08	147,05	39,17	148,42	86,08
TCDF	363,84	93,19	28,02	122,61	251,85
PeCDF	205,41	66,99	21,12	113,77	161,62
HxCDF	243,16	57,61	13,90	45,31	80,77
HpCDF	345,11	40,28	8,53	30,53	55,18
OCDF	673,84	33,72	9,56	27,81	45,51
Total PCDDs	87,19	235,37	65,78	240,22	258,46
Total PCDFs	1831,36	291,79	81,14	340,03	594,93
Total PCDD/Fs	1918,55	527,16	146,91	580,25	853,39

Lab. Code:	DP-08-270-120509-9	DP-08-268-200409-5	DP-08-254-070409-14	DP-08-269-200409-6	DP-08-246-070409-6
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Obristvy, km -114	Vltava, Zelcin, km -110	Zernoseky, km -52	Decin, km -14	Schmilka, km 4
Sampling	26.08.-23.09.08	26.08.-30.09.08	30.09.2008	28.08.-02.10.08	01.09.-29.09.08
Type of sample:	FDS	FDS	Sediment, EP	FDS	FDS
Mass Analysed:	5.0	5.0	5.0	5,02	5.0
Data analysed:	23.05.2009	01.05.2009	25.04.2009	01.05.2009	25.04.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
2,3,7,8 - substituted PCDD/Fs					
2378-TCDD	1,17	0,14	0,54	2,40	1,88
12378-PeCDD	0,55	0,59	0,56	1,50	1,33
123478-HxCDD	0,68	0,37	0,24	1,28	1,01
123678-HxCDD	1,55	0,92	0,44	2,79	2,13
123789-HxCDD	1,28	0,60	0,41	2,57	2,22
1234678-HpCDD	19,91	14,97	5,16	24,65	22,41
OCDD	136,39	99,52	37,65	154,87	160,00
2378-TCDF	7,31	5,54	5,64	16,53	12,72
12378-PeCDF	3,76	2,34	2,41	8,53	6,64
23478-PeCDF	7,00	3,87	5,28	11,57	8,16
123478-HxCDF	6,52	3,51	5,45	13,78	9,81
123678-HxCDF	3,03	2,16	1,17	4,65	3,68
234678-HxCDF	3,62	2,67	1,77	4,86	4,09
123789-HxCDF	1,26	0,75	0,46	2,34	1,63
1234678-HpCDF	13,26	10,32	4,53	19,53	13,75
1234789-HpCDF	2,32	1,32	0,88	4,56	2,71
OCDF	22,60	16,24	7,32	76,66	39,40
WHO-TEQ-2005	6,86	3,91	4,44	13,07	10,03
Homol. ΣPCDD/Fs					
TCDD	7,79	6,69	2,31	15,06	13,04
PeCDD	10,13	6,88	2,90	16,63	13,30
HxCDD	18,46	14,98	5,82	31,66	26,20
HpCDD	41,05	32,37	10,78	51,03	46,63
OCDD	136,39	99,52	37,65	154,87	160,00
TCDF	98,13	61,55	42,41	126,24	111,79
PeCDF	95,14	64,07	46,08	119,81	97,06
HxCDF	42,10	28,60	21,17	58,88	44,96
HpCDF	31,67	18,01	7,58	34,69	24,60
OCDF	22,60	16,24	7,32	76,66	39,40
Total PCDDs	213,82	160,45	59,45	269,26	259,18
Total PCDFs	289,65	188,48	124,55	416,29	317,82
Total PCDD/Fs	503,47	348,94	184,00	685,54	576,99

Lab. Code:	DP-08-247-070409-7	DP-08-248-120509-3	DP-08-258-200409-1	DP-08-255-200409-13	DP-08-257-240409-1
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Zehren, km 89,7 (links)	Domnitzsch, km 173 (links)	Spittelwasser	Mulde, Dessau, km 7,6	Bode, Neugattersleben
Sampling	03.09.-01.10.08	03.09.-29.09.08	03.09.-01.10.08	27.08.-01.10.08	01.10.2008
Type of sample:	FDS	FDS	FDS	FDS	SPM
Mass Analysed:	5,07	5,06	5,17	5,07	5,18
Data analysed:	25.04.2009	22.05.2009	30.04.2009	01.05.2009	09.05.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
2,3,7,8 - substituted PCDD/Fs					
2378-TCDD	1,98	1,56	9,65	2,16	2,20
12378-PeCDD	1,48	0,79	16,88	3,58	5,44
123478-HxCDD	0,83	1,16	14,48	2,73	7,52
123678-HxCDD	1,61	1,78	40,53	9,44	14,75
123789-HxCDD	1,82	2,36	30,99	7,15	13,27
1234678-HpCDD	22,40	30,26	327,83	85,42	133,91
OCDD	158,27	386,60	2800,94	604,54	587,07
2378-TCDF	11,08	20,56	563,79	23,73	57,44
12378-PeCDF	6,50	10,33	1408,63	49,81	84,24
23478-PeCDF	6,53	11,80	740,44	21,17	50,27
123478-HxCDF	10,74	12,48	5829,23	139,17	228,46
123678-HxCDF	3,81	3,93	1479,86	76,28	157,28
234678-HxCDF	3,50	4,17	408,36	30,55	84,35
123789-HxCDF	1,76	2,68	570,07	30,53	68,10
1234678-HpCDF	13,59	15,70	4379,99	354,02	777,76
1234789-HpCDF	2,38	2,67	2048,51	142,54	352,81
OCDF	34,63	46,82	12028,97	1315,44	2567,04
WHO-TEQ-2005	9,58	11,73	1256,66	51,94	101,96
Homol. ΣPCDD/Fs					
TCDD	11,84	12,99	622,29	84,34	94,33
PeCDD	9,69	14,15	322,81	48,71	103,78
HxCDD	22,89	32,27	460,51	99,18	141,46
HpCDD	47,51	67,77	669,75	163,48	232,27
OCDD	158,27	386,60	2800,94	604,54	587,07
TCDF	94,42	119,68	4366,08	503,88	1239,81
PeCDF	84,71	109,06	5862,21	492,66	1174,81
HxCDF	41,61	49,51	11068,53	545,14	1286,76
HpCDF	24,84	27,09	8372,83	673,80	1552,76
OCDF	34,63	46,82	12028,97	1315,44	2567,04
Total PCDDs	250,20	513,77	4876,30	1000,24	1158,92
Total PCDFs	280,19	352,16	41698,62	3530,91	7821,18
Total PCDD/Fs	530,40	865,93	46574,92	4531,16	8980,10

Lab. Code:	DP-08-256-200409-14	DP-08-242-070409-4	DP-08-241-070409-3	DP-08-240-070409-2	DP-08-244-070409-5
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Saale, Rosenberg, km 3,8	Magdeburg, km 318	Cumlosen, km 470	Schnackenburg, km 474	Geesthacht, km 586
Sampling	27.08.-01.10.08	08.09.-29.09.08	08.09.-30.09.08	28.08.-02.10.08	01.09.-30.09.08
Type of sample:	FDS	FDS	FDS	FDS	FDS
Mass Analysed:	5,16	5,02	5,06	4,99	5,02
Data analysed:	01.05.2009	25.04.2009	25.04.2009	24.04.2009	25.04.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
2,3,7,8 - substituted PCDD/Fs					
2378-TCDD	1,30	3,18	1,70	2,13	1,10
12378-PeCDD	2,95	4,67	3,00	3,47	2,78
123478-HxCDD	3,20	3,93	2,15	2,97	1,98
123678-HxCDD	7,34	12,56	4,99	7,61	4,54
123789-HxCDD	5,44	10,27	4,06	6,28	3,61
1234678-HpCDD	92,33	115,68	57,32	72,28	40,64
OCDD	745,49	777,13	382,63	467,58	246,66
2378-TCDF	20,64	43,23	23,42	28,90	15,60
12378-PeCDF	28,15	51,32	28,54	39,99	21,97
23478-PeCDF	21,00	48,33	24,64	23,67	13,13
123478-HxCDF	64,78	122,17	64,62	100,47	53,72
123678-HxCDF	43,71	86,49	44,24	74,06	37,80
234678-HxCDF	25,17	43,51	24,05	36,38	17,32
123789-HxCDF	20,70	40,16	20,05	30,82	17,32
1234678-HpCDF	212,50	402,83	208,77	346,74	170,49
1234789-HpCDF	84,09	181,43	85,48	146,40	72,37
OCDF	668,73	1340,25	656,31	1080,65	549,11
WHO-TEQ-2005	34,80	67,75	35,53	48,77	26,74
Homol. ΣPCDD/Fs					
TCDD	42,20	90,28	45,76	55,32	33,47
PeCDD	41,77	72,78	37,02	47,70	27,94
HxCDD	76,47	121,55	55,05	72,97	42,74
HpCDD	167,31	213,72	113,30	142,39	76,66
OCDD	745,49	777,13	382,63	467,58	246,66
TCDF	375,63	887,04	356,29	520,19	304,85
PeCDF	421,83	771,99	398,02	529,67	276,87
HxCDF	364,48	730,03	372,35	582,41	315,80
HpCDF	447,86	840,05	424,94	674,27	348,14
OCDF	668,73	1340,25	656,31	1080,65	549,11
Total PCDDs	1073,24	1275,46	633,77	785,95	427,48
Total PCDFs	2278,53	4569,36	2207,90	3387,20	1794,77
Total PCDD/Fs	3351,78	5844,82	2841,68	4173,15	2222,25

Lab. Code:	DP-08-259-120509-6	DP-08-238-200409-11	DP-08-260-200409-3	DP-08-261-120509-7	DP-08-239-200409-12B
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Buhnenfeld, Bullenhausen, km 599	Bunthaus, km 609	Süderelbe, km 619,5	Köhlbrand, km 623	Seemannshöft, km 629
Sampling	26.06.2008	01.09.-01.10.08	24.06.2008	24.09.2008	01.09.-01.10.08
Type of sample:	Sediment, EP	FDS	Sediment, EP	Sediment, EP	FDS
Mass Analysed:	5,05	5,08	5,12	5,08	5,08
Data analysed:	22.05.2009	01.05.2009	08.05.2009	23.05.2009	26.05.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
2,3,7,8 - substituted PCDD/Fs					
2378-TCDD	1,45	1,30	1,29	0,67	1,45
12378-PeCDD	2,26	1,63	1,89	0,85	1,13
123478-HxCDD	2,82	1,34	2,04	1,37	1,48
123678-HxCDD	6,03	3,88	4,70	2,89	3,60
123789-HxCDD	5,57	3,82	4,46	3,27	2,79
1234678-HpCDD	64,86	40,30	54,94	29,19	38,06
OCDD	434,94	253,40	362,93	208,57	243,18
2378-TCDF	21,05	16,37	14,12	8,04	10,23
12378-PeCDF	31,53	22,15	22,65	11,03	15,27
23478-PeCDF	14,45	16,20	12,82	7,47	8,67
123478-HxCDF	75,03	50,27	55,63	29,45	32,51
123678-HxCDF	55,47	35,60	39,77	20,41	21,22
234678-HxCDF	27,60	18,63	19,99	10,89	13,63
123789-HxCDF	25,27	15,24	17,78	9,04	9,56
1234678-HpCDF	270,98	169,68	212,01	107,48	122,26
1234789-HpCDF	107,83	63,84	81,78	38,33	38,70
OCDF	822,99	487,23	647,76	323,08	358,77
WHO-TEQ-2005	35,69	25,92	27,34	14,54	17,31
Homol. ΣPCDD/Fs					
TCDD	47,25	31,08	39,21	22,43	33,21
PeCDD	41,87	27,47	29,87	18,86	16,03
HxCDD	87,03	55,73	61,47	39,17	48,75
HpCDD	124,07	76,20	116,25	62,21	87,28
OCDD	434,94	253,40	362,93	208,57	243,18
TCDF	405,00	281,20	231,61	157,82	266,27
PeCDF	373,96	287,80	282,38	146,36	213,17
HxCDF	450,99	411,70	306,02	172,40	196,21
HpCDF	515,33	330,96	407,48	200,04	230,30
OCDF	822,99	487,23	647,76	323,08	358,77
Total PCDDs	735,16	443,87	609,73	351,24	428,45
Total PCDFs	2568,27	1798,89	1875,24	999,70	1264,72
Total PCDD/Fs	3303,43	2242,77	2484,97	1350,94	1693,17

Lab. Code:	DP-08-262-200409-4	DP-08-249	DP-08-235-070409-1	DP-08-237-200409-10	DP-08-250-120509-4
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Wedel, km 643	Grauerort, km 661	Stör, Heiligenstedten	Brunsbüttel, Elbehafen, km 693	Cuxhaven, km 725
Sampling	01.09.-30.09.08	05.09.-02.10.08	11.09.2008	11.09.2008	15.09.-16.09.08
Type of sample:	FDS	FDS	Sediment, EP	Sediment, EP	SPM
Mass Analysed:	5,13	5,02	5.0	5,17	5,04
Data analysed:	01.05.2009	25.04.2009	24.04.2009	01.05.2009	22.05.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
2,3,7,8 - substituted PCDD/Fs					
2378-TCDD	0,93	0,56	1,21	2,71	1,47
12378-PeCDD	1,34	1,13	1,90	2,35	1,81
123478-HxCDD	1,54	1,25	1,75	2,25	2,23
123678-HxCDD	3,28	1,85	3,68	5,32	5,21
123789-HxCDD	3,04	1,81	3,70	4,49	5,40
1234678-HpCDD	36,52	23,55	42,03	57,86	54,64
OCDD	226,95	145,13	271,95	402,93	352,59
2378-TCDF	7,70	7,76	8,66	11,78	9,68
12378-PeCDF	15,07	8,45	13,11	21,10	17,57
23478-PeCDF	10,83	6,09	8,67	13,64	10,05
123478-HxCDF	33,73	18,57	28,68	48,54	38,62
123678-HxCDF	23,88	12,10	19,93	32,86	27,52
234678-HxCDF	13,41	7,27	11,07	17,72	15,02
123789-HxCDF	10,38	5,32	7,90	14,08	10,97
1234678-HpCDF	141,63	69,22	115,44	217,38	172,19
1234789-HpCDF	43,61	20,43	32,68	57,58	44,28
OCDF	415,51	183,00	326,50	698,64	435,60
WHO-TEQ-2005	18,08	10,60	16,73	27,15	21,23
Homol. ΣPCDD/Fs					
TCDD	25,46	21,78	27,71	38,58	28,51
PeCDD	20,74	17,07	24,77	28,66	38,13
HxCDD	49,60	43,70	54,91	63,14	82,28
HpCDD	78,21	57,58	88,79	185,00	133,42
OCDD	226,95	145,13	271,95	402,93	352,59
TCDF	163,31	153,07	149,44	244,18	157,50
PeCDF	188,58	141,11	152,00	264,59	203,31
HxCDF	214,76	145,52	164,84	286,12	294,52
HpCDF	255,41	128,27	199,80	350,58	289,79
OCDF	415,51	183,00	326,50	698,64	435,60
Total PCDDs	400,95	285,25	468,13	718,31	634,93
Total PCDFs	1237,58	750,96	992,58	1844,11	1380,73
Total PCDD/Fs	1638,52	1036,22	1460,71	2562,41	2015,66

Lab. Code:	DP-08-267-270409-7	DP-08-263-270409-3	DP-08-265-270409-5	DP-08-266-120509-8	DP-08-264-270409-4
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Nordsee, KS8	Nordsee, KS11	Nordsee Messstelle 21; 2 km von Verklappstelle	Nordsee Messstelle 69; 12 km von Verklappstelle	Nordsee Messstelle 90; Referenzgebiet
Sampling	15.08.2008	15.08.2008	16.08.2008	19.08.2008	18.08.2008
Type of sample:	Sediment, EP	Sediment, EP	Sediment, EP	Sediment, EP	Sediment, EP
Mass Analysed:	5,07	5,1	5.0	5,03	5,02
Data analysed:	09.05.2009	09.05.2009	09.05.2009	23.05.2009	09.05.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
2,3,7,8 – substituted PCDD/Fs					
2378-TCDD	3,67	8,10	0,53	0,34	0,55
12378-PeCDD	1,55	1,36	0,55	0,19	0,59
123478-HxCDD	1,53	1,47	0,54	0,44	1,04
123678-HxCDD	4,17	3,09	1,20	0,86	1,68
123789-HxCDD	3,49	3,11	1,15	0,86	1,51
1234678-HpCDD	44,11	32,03	15,15	11,43	18,42
OCDD	296,81	192,89	90,69	75,13	112,99
2378-TCDF	6,45	6,88	1,56	1,48	1,78
12378-PeCDF	6,45	11,60	1,94	1,26	2,19
23478-PeCDF	5,54	7,16	2,08	1,51	2,05
123478-HxCDF	16,10	28,54	5,15	3,34	6,30
123678-HxCDF	10,78	18,98	2,81	1,74	4,03
234678-HxCDF	7,83	11,02	2,19	1,71	2,72
123789-HxCDF	3,48	6,59	1,03	0,72	1,28
1234678-HpCDF	93,27	123,97	25,52	17,62	32,97
1234789-HpCDF	15,80	29,95	4,33	2,72	5,67
OCDF	216,06	272,09	52,49	44,46	65,94
WHO-TEQ-2005	14,14	21,92	3,82	2,48	4,48
Homol. ΣPCDD/Fs					
TCDD	26,19	27,08	8,64	5,21	11,51
PeCDD	24,17	22,37	10,37	6,62	10,99
HxCDD	56,99	46,57	22,00	17,44	30,65
HpCDD	100,50	72,42	36,38	29,04	45,53
OCDD	296,81	192,89	90,69	75,13	112,99
TCDF	92,06	116,77	21,08	18,05	31,05
PeCDF	96,43	138,03	27,76	20,24	33,63
HxCDF	104,45	169,31	31,39	20,39	40,79
HpCDF	151,33	196,90	40,21	30,38	53,45
OCDF	216,06	272,09	52,49	44,46	65,94
Total PCDDs	504,65	361,34	168,08	133,44	211,67
Total PCDFs	660,34	893,11	172,93	133,51	224,86
Total PCDD/Fs	1164,99	1254,45	341,01	266,95	436,54

Lab. Code:	DP-09-114-101109-5	DP-09-115-101109-6	DP-09-116-101109-7	DP-09-117-101109-8	DP-09-118-101109-9
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	North Sea KS8/1	North Sea KS8/2	North Sea KS8/3	North Sea KS8/4	North Sea KS11/1
Sampling	30.09.2009	30.09.2009	30.09.2009	30.09.2009	30.09.2009
Type of sample:	Sediment, EP	Sediment, EP	Sediment, EP	Sediment, EP	Sediment, EP
Mass Analysed:	5.0	5.0	5.0	5.0	5.0
Data analysed:	22.01.2010	22.01.2010	22.01.2010	22.01.2010	22.01.2010
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
2,3,7,8 - substituted PCDD/Fs					
2378-TCDD	0,70	0,48	0,29	0,31	0,69
12378-PeCDD	0,36	0,21	0,26	0,29	0,94
123478-HxCDD	0,50	0,42	0,40	0,29	1,25
123678-HxCDD	0,88	1,03	0,73	0,47	2,51
123789-HxCDD	1,17	0,70	0,62	0,85	2,14
1234678-HpCDD	13,85	12,94	9,83	8,41	27,12
OCDD	88,39	89,38	65,75	48,20	108,39
2378-TCDF	1,93	1,67	1,27	1,06	5,97
12378-PeCDF	2,34	1,88	1,60	1,22	15,96
23478-PeCDF	1,73	1,93	1,49	1,32	8,36
123478-HxCDF	6,30	4,57	4,12	3,27	35,43
123678-HxCDF	3,56	3,01	2,31	1,85	24,57
234678-HxCDF	2,28	2,30	1,96	1,71	16,55
123789-HxCDF	0,83	1,06	0,87	0,64	7,98
1234678-HpCDF	25,84	22,21	17,43	13,61	146,85
1234789-HpCDF	4,86	4,01	3,37	2,42	38,16
OCDF	66,18	58,35	43,21	34,72	368,83
WHO-TEQ-2005	3,88	3,24	2,62	2,32	16,52
Homol. ΣPCDD/Fs					
TCDD	7,62	7,21	3,95	3,36	18,97
PeCDD	6,07	7,48	4,81	4,47	22,41
HxCDD	21,96	19,74	15,40	11,92	40,61
HpCDD	43,00	36,82	25,58	22,24	62,82
OCDD	88,39	89,38	65,75	48,20	108,39
TCDF	29,88	24,31	21,00	23,66	143,56
PeCDF	36,14	30,52	23,39	16,78	177,89
HxCDF	35,73	29,79	24,43	20,03	217,63
HpCDF	42,72	35,28	27,55	21,86	242,70
OCDF	66,18	58,35	43,21	34,72	368,83
Total PCDDs	167,03	160,63	115,49	90,20	253,20
Total PCDFs	210,64	178,24	139,58	117,04	1150,62
Total PCDD/Fs	377,68	338,87	255,07	207,24	1403,82

Lab. Code:	DP-09-119-101109-10	DP-09-120-101109-11	DP-09-121-101109-12
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	North Sea KS11/2	North Sea KS11/3	North Sea KS11/4
Sampling	30.09.2009	30.09.2009	30.09.2009
Type of sample:	Sediment, EP	Sediment, EP	Sediment, EP
Mass Analysed:	5.0	5.0	5.0
Data analysed:	22.01.2010	22.01.2010	22.01.2010
Concentration:	pg/g	pg/g	pg/g
2,3,7,8 - substituted PCDD/Fs			
2378-TCDD	1,64	0,52	1,13
12378-PeCDD	1,36	0,61	1,26
123478-HxCDD	1,29	0,61	1,55
123678-HxCDD	2,82	1,54	2,97
123789-HxCDD	2,63	1,53	3,26
1234678-HpCDD	31,66	15,60	30,49
OCDD	176,76	82,15	149,80
2378-TCDF	5,69	3,22	6,65
12378-PeCDF	10,77	6,88	16,96
23478-PeCDF	7,53	3,41	7,70
123478-HxCDF	25,69	15,31	39,00
123678-HxCDF	16,58	10,66	27,95
234678-HxCDF	10,32	6,34	15,17
123789-HxCDF	6,57	3,72	9,54
1234678-HpCDF	114,60	67,31	162,74
1234789-HpCDF	28,10	16,86	45,24
OCDF	269,21	165,13	393,70
WHO-TEQ-2005	14,62	7,73	18,37
Homol. ΣPCDD/Fs			
TCDD	22,92	12,28	28,40
PeCDD	23,64	11,64	27,93
HxCDD	51,31	25,42	51,17
HpCDD	76,21	39,15	71,39
OCDD	176,76	82,15	149,80
TCDF	107,04	63,54	146,28
PeCDF	136,58	81,83	202,81
HxCDF	160,34	97,11	237,89
HpCDF	191,44	112,39	274,19
OCDF	269,21	165,13	393,70
Total PCDDs	350,84	170,64	328,68
Total PCDFs	864,61	520,00	1254,87
Total PCDD/Fs	1215,46	690,64	1583,56

EP = single sample

SPM = suspended particulate matter (centrifuge)

FDS = freshly deposited sediment (composite sample)

Appendix III

Analysis results: DL-PCB

Lab. Code:	DP-08-251-070409-11	DP-08-271-200409-8	DP-08-253-120509-5B	DP-08-272-200409-9	DP-08-252-070409-12
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Pardubice-Semtin, km -237	Valy, km -228	Klavary, km -186	Lysa nad Labem, km -151	Cerinovsko, km -115
Sampling	30.09.2008	28.08.-02.10.08	30.09.2008	28.09.-01.10.08	30.09.2008
Type of sample:	Sediment, EP	FDS	Sediment, EP	FDS	Sediment, EP
Mass Analysed:	5,02	5,04	5,01	5,05	5,05
Data analysed:	25.04.2009	01.05.2009	26.05.2009	01.05.2009	25.04.2009
Concentration:					
DL-PCBs	pg/g	pg/g	pg/g	pg/g	pg/g
PCB-81	275,06	68,16	19,98	42,48	22,90
PCB-77	2664,32	1378,61	587,70	1245,01	367,58
PCB-126	178,60	30,84	11,70	39,09	64,28
PCB-169	39,54	4,61	2,05	5,45	8,14
PeCB-105	1784,22	1074,09	287,68	1196,01	791,27
PeCB-114	452,21	141,21	39,68	165,99	124,71
PeCB-118	4043,81	2539,84	900,37	3995,10	3870,49
PeCB-123	253,53	50,60	13,64	46,15	25,85
HxCB-156	1864,23	736,18	244,22	1742,86	1890,19
HxCB-157	188,44	75,87	24,38	136,17	181,28
HxCB-167	598,07	326,05	111,25	694,56	892,42
HpCB-189	444,81	146,17	47,14	384,71	338,56
Total DL-PCBs	12786,831	6572,220	2289,800	9693,586	8577,695
WHO-TEQ-2005	19,68	3,53	1,35	4,46	6,96
WHO-TEQ-1998	20,46	4,14	1,53	5,68	8,16

Lab. Code:	DP-08-270-120509-9	DP-08-268-200409-5	DP-08-254-070409-14	DP-08-269-200409-6	DP-08-246-070409-6
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Obristvy, km -114	Vitava, Zelcin, km -110	Zernoseky, km -52	Decin, km -14	Schmilka, km 4
Sampling	26.08.-23.09.08	26.08.-30.09.08	30.09.2008	28.08.-02.10.08	01.09.-29.09.08
Type of sample:	FDS	FDS	Sediment, EP	FDS	FDS
Mass Analysed:	5.0	5.0	5.0	5.02	5.0
Data analysed:	23.05.2009	01.05.2009	25.04.2009	01.05.2009	25.04.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
DL-PCBs					
PCB-81	26,40	21,12	16,66	33,20	23,87
PCB-77	781,59	508,89	435,18	826,17	628,69
PCB-126	32,68	50,02	41,91	50,81	47,23
PCB-169	5,11	6,94	6,19	7,11	6,72
PeCB-105	902,98	689,94	nd	1326,24	1051,59
PeCB-114	151,78	111,87	nd	306,51	207,11
PeCB-118	3356,68	3071,29	nd	5922,48	4659,24
PeCB-123	32,72	19,82	nd	39,92	28,87
HxCB-156	1735,90	1832,55	nd	3375,74	2684,29
HxCB-157	130,37	152,15	nd	248,36	209,58
HxCB-167	714,89	773,65	nd	1316,83	1175,46
HxCB-189	358,13	398,49	nd	645,67	535,19
Total DL-PCBs	8229,238	7636,741	(499,938)	14099,045	11257,850
WHO-TEQ-2005	3,73	5,48	(4,43)	5,78	5,31
WHO-TEQ-1998	4,88	6,60	(4,30)	8,01	7,05

Lab. Code:	DP-08-247-070409-7	DP-08-248-120509-3	DP-08-258-200409-1	DP-08-255-200409-13	DP-08-257-240409-1
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Zehren, km 89,7 (links)	Domnitzsch, km 173 (links)	Spittelwasser	Mulde, Dessau, km 7,6	Bode, Neugattersleben
Sampling	03.09.-01.10.08	03.09.-29.09.08	03.09.-01.10.08	27.08.-01.10.08	01.10.2008
Type of sample:	FDS	FDS	FDS	FDS	SPM
Mass Analysed:	5,07	5,06	5,17	5,07	5,18
Data analysed:	25.04.2009	22.05.2009	30.04.2009	01.05.2009	09.05.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
DL-PCBs					
PCB-81	14,39	14,91	226,69	6,54	11,88
PCB-77	380,32	384,15	3418,44	133,32	225,65
PCB-126	30,09	31,12	300,21	14,51	26,31
PCB-169	4,69	4,87	61,97	3,94	5,47
PeCB-105	715,33	719,64	2245,51	366,12	1138,63
PeCB-114	99,58	83,52	411,40	48,75	113,44
PeCB-118	2738,96	2601,01	7086,31	1172,82	4049,65
PeCB-123	21,78	22,68	175,92	13,33	47,35
HxCB-156	1399,22	1248,69	2351,18	400,51	750,58
HxCB-157	132,03	122,65	420,78	72,84	164,12
HxCB-167	622,30	560,46	983,04	183,92	332,84
HxCB-189	269,58	266,60	519,43	84,76	111,92
Total DL-PCBs	6428,259	6060,320	18200,883	2501,362	6977,847
WHO-TEQ-2005	3,37	3,47	32,72	1,66	3,02
WHO-TEQ-1998	4,29	4,29	33,61	1,93	3,76

Lab. Code:	DP-08-256-200409-14	DP-08-242-070409-4	DP-08-241-070409-3	DP-08-240-070409-2	DP-08-244-070409-5
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Saale, Rosenberg, km 3,8	Magdeburg, km 318	Cumlosen, km 470	Schnackenburg, km 474	Geesthacht, km 586
Sampling	27.08.-01.10.08	08.09.-29.09.08	08.09.-30.09.08	28.08.-02.10.08	01.09.-30.09.08
Type of sample:	FDS	FDS	FDS	FDS	FDS
Mass Analysed:	5,16	5,02	5,06	4,99	5,02
Data analysed:	01.05.2009	25.04.2009	25.04.2009	24.04.2009	25.04.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
DL-PCBs					
PCB-81	6,75	9,68	8,85	6,19	3,89
PCB-77	156,77	240,71	241,83	161,68	100,99
PCB-126	16,54	24,99	19,72	16,43	10,33
PCB-169	2,94	5,37	3,76	3,45	2,17
PeCB-105	1055,87	930,94	897,54	468,06	294,12
PeCB-114	91,71	100,94	85,80	54,08	33,70
PeCB-118	3541,16	3731,08	3377,78	1820,01	1134,54
PeCB-123	33,10	31,73	27,98	16,40	12,26
HxCB-156	718,26	1226,82	1114,56	581,40	315,06
HxCB-157	131,83	157,08	138,73	78,17	47,43
HxCB-167	327,48	523,22	465,17	263,28	142,98
HxCB-189	101,53	237,82	192,90	123,34	59,81
Total DL-PCBs	6183,958	7220,384	6574,610	3592,491	2157,270
WHO-TEQ-2005	1,94	2,90	2,30	1,87	1,17
WHO-TEQ-1998	2,65	3,82	3,16	2,30	1,42

Lab. Code:	DP-08-259-120509-6	DP-08-238-200409-11	DP-08-260-200409-3	DP-08-261-120509-7	DP-08-239-200409-12B
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Buhnenfeld, Bullenhausen, km 599	Bunthaus, km 609	Stiderelbe, km 619,5	Köhlbrand, km 623	Seemannshöft, km 629
Sampling	26.06.2008	01.09.-01.10.08	24.06.2008	24.09.2008	01.09.-01.10.08
Type of sample:	Sediment, EP	FDS	Sediment, EP	Sediment, EP	FDS
Mass Analysed:	5,05	5,08	5,12	5,08	5,08
Data analysed:	22.05.2009	01.05.2009	08.05.2009	23.05.2009	26.05.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
DL-PCBs					
PCB-81	6,43	4,18	4,71	2,98	8,28
PCB-77	170,56	110,48	134,16	76,42	199,03
PCB-126	20,02	10,29	12,92	7,04	15,31
PCB-169	3,64	2,36	2,61	1,26	2,89
PeCB-105	568,86	301,34	379,43	269,21	406,80
PeCB-114	60,40	30,19	42,22	35,17	67,88
PeCB-118	1855,34	1098,27	1367,86	942,99	1556,69
PeCB-123	16,81	10,22	12,77	8,37	16,77
HxCB-156	629,53	310,63	412,64	291,15	729,27
HxCB-157	78,81	48,51	60,31	40,25	91,01
HxCB-167	282,77	147,79	197,58	139,85	316,44
HxCB-189	121,52	63,17	77,36	56,76	191,47
Total DL-PCBs	3814,705	2137,425	2704,544	1871,454	3601,844
WHO-TEQ-2005	2,24	1,17	1,46	0,80	1,74
WHO-TEQ-1998	2,70	1,41	1,78	1,04	2,25

Lab. Code:	DP-08-262-200409-4	DP-08-249	DP-08-235-070409-1	DP-08-237-200409-10	DP-08-250-120509-4
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Wedel, km 643	Grauerort, km 661	Stör, Heiligenstedten	Brunsbüttel, Elbehafen, km 693	Cuxhaven, km 725
Sampling	01.09.-30.09.08	05.09.-02.10.08	11.09.2008	11.09.2008	15.09.-16.09.08
Type of sample:	FDS	FDS	Sediment, EP	Sediment, EP	SPM
Mass Analysed:	5,13	5,02	5,0	5,17	5,04
Data analysed:	01.05.2009	25.04.2009	24.04.2009	01.05.2009	22.05.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
DL-PCBs					
PCB-81	3,24	3,79	3,01	4,99	3,26
PCB-77	82,08	111,56	92,40	196,31	114,61
PCB-126	8,51	9,19	13,81	15,76	11,02
PCB-169	2,49	2,02	2,92	3,88	2,07
PeCB-105	207,75	242,68	245,37	437,91	220,05
PeCB-114	24,28	30,87	32,03	69,05	23,29
PeCB-118	733,97	911,96	927,28	1927,99	818,58
PeCB-123	7,20	9,74	10,45	23,01	9,15
HxCB-156	225,61	348,40	329,67	630,19	216,58
HxCB-157	34,31	43,38	48,51	103,62	35,21
HxCB-167	112,95	162,48	164,92	336,04	118,09
HxCB-189	47,50	72,15	71,94	130,43	50,82
Total DL-PCBs	1489,894	1948,228	1942,316	3879,175	1622,752
WHO-TEQ-2005	0,98	1,05	1,53	1,82	1,22
WHO-TEQ-1998	1,13	1,29	1,75	2,29	1,38

Lab. Code:	DP-08-267-270409-7	DP-08-263-270409-3	DP-08-265-270409-5	DP-08-266-120509-8	DP-08-264-270409-4
Project:	ELBE RIVER North Sea KS8	ELBE RIVER North Sea KS11	ELBE RIVER North Sea 21; 2 km from dumping site	ELBE RIVER North Sea 69; 12 km from dumping site	ELBE RIVER North Sea 90; reference area
Sampling Location:	15.08.2008 Sediment, EP	15.08.2008 Sediment, EP	16.08.2008 Sediment, EP	19.08.2008 Sediment, EP	18.08.2008 Sediment, EP
Mass Analysed:	5,07	5,1	5,0	5,03	5,02
Data analysed:	09.05.2009	09.05.2009	09.05.2009	23.05.2009	09.05.2009
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
DL-PCBs					
PCB-81	6,82	2,27	1,43	0,90	1,58
PCB-77	204,83	83,73	43,86	30,04	53,70
PCB-126	15,49	8,33	3,62	2,76	5,11
PCB-169	3,08	1,61	0,65	0,48	1,11
PeCB-105	295,45	167,55	77,09	81,46	97,16
PeCB-114	35,15	23,56	6,74	7,84	9,27
PeCB-118	1218,21	745,02	265,10	269,35	338,81
PeCB-123	13,42	8,71	2,55	3,45	3,68
HxCB-156	170,20	116,76	42,40	58,12	52,08
HxCB-157	35,01	22,62	8,56	8,72	10,52
HxCB-167	111,91	78,75	25,50	28,65	31,47
HxCB-189	39,15	26,32	7,69	11,12	9,38
Total DL-PCBs	2148,724	1285,232	485,188	502,884	613,879
WHO-TEQ-2005	1,72	0,93	0,40	0,31	0,57
WHO-TEQ-1998	1,88	1,03	0,44	0,36	0,61

Lab. Code:	P-09-114-101109-5	P-09-115-101109-6	P-09-116-101109-7	P-09-117-101109-8	P-09-118-101109-9
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	North Sea KS8/1	North Sea KS8/2	North Sea KS8/3	North Sea KS8/4	North Sea KS11/1
Sampling	30.09.2009	30.09.2009	30.09.2009	30.09.2009	30.09.2009
Type of sample:	Sediment, EP	Sediment, EP	Sediment, EP	Sediment, EP	Sediment, EP
Mass Analysed:	5.0	5.0	5.0	5.0	5.0
Data analysed:	22.01.2010	22.01.2010	22.01.2010	22.01.2010	22.01.2010
Concentration:	pg/g	pg/g	pg/g	pg/g	pg/g
DL-PCBs					
PCB-81	1,1773	1,5249	0,9258	1,0188	1,0398
PCB-77	37,1331	35,0200	72,2574	26,3667	27,0221
PCB-126	3,0234	3,2156	2,9783	2,2777	5,7083
PCB-169	0,7017	0,5323	0,3205	0,3084	1,5961
PeCB-105	99,784	98,889	80,671	84,753	180,684
PeCB-114	8,302	9,787	5,944	7,446	25,088
PeCB-118	361,565	347,339	253,627	244,589	803,925
PeCB-123	3,6342	3,9849	2,9208	2,8119	9,1112
HxCB-156	50,114	42,762	39,840	33,756	99,959
HxCB-157	10,066	10,524	6,635	5,968	19,819
HxCB-167	32,202	29,781	19,155	20,085	74,778
HpCB-189	8,8432	8,8589	7,1569	5,6037	22,3351
Total DL-PCBs	574,510	551,925	415,949	405,011	1235,699
WHO-TEQ-2005	0,39513	0,40828	0,36919	0,29116	0,76438
WHO-TEQ-1998	0,34469	0,35804	0,32743	0,25212	0,65880

Lab. Code:	P-09-119-101109-10	P-09-120-101109-11	P-09-121-101109-12
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	North Sea KS11/2	North Sea KS11/3	North Sea KS11/4
Sampling	30.09.2009	30.09.2009	30.09.2009
Type of sample:	Sediment, EP	Sediment, EP	Sediment, EP
Mass Analysed:	5.0	5.0	5.0
Data analysed:	22.01.2010	22.01.2010	22.01.2010
Concentration:	pg/g	pg/g	pg/g
DL-PCBs			
PCB-81	2,1329	0,9981	1,3332
PCB-77	76,5537	30,5231	46,8089
PCB-126	8,6083	3,7097	6,6362
PCB-169	1,7262	0,9036	1,7043
PeCB-105	303,901	107,019	154,820
PeCB-114	37,550	16,247	30,689
PeCB-118	1202,739	451,379	925,907
PeCB-123	11,7514	5,9284	9,5655
HxCB-156	199,325	65,172	115,808
HxCB-157	36,965	12,831	20,731
HxCB-167	115,309	45,768	81,149
HxCB-189		13,7364	29,1302
Total DL-PCBs	1907,540	718,080	1367,799
WHO-TEQ-2005	1,17987	0,48855	0,88185
WHO-TEQ-1998	0,97934	0,42297	0,76086

EP = single sample, SPM = suspended particulate matter (continuous centrifuge), FDS = freshly deposited sediment (composite sample), nd = not determined

Appendix IV

Analysis results: indicator-PCB

Lab. Code:	DP-08-251-070409-11	DP-08-271-200409-8	DP-08-253-120509-5B	DP-08-272-200409-9	DP-08-252-070409-12
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Pardubice-Semtin, km -237	Valy, km -228	Klavary, km -186	Lysa nad Labem, km -151	Cerinovsko, km -115
Sampling	30.09.2008	28.08.-02.10.08	30.09.2008	28.09.-01.10.08	30.09.2008
Type of sample:	Sediment, EP	FDS	Sediment, EP	FDS	Sediment, EP
Mass Analysed:	5,02	5,04	5,01	5,05	5,05
Data analysed:	25.04.2009	01.05.2009	26.05.2009	01.05.2009	25.04.2009
Concentration:	ng/g	ng/g	ng/g	ng/g	ng/g
Indicator PCBs					
TriCB-28	22,931	21,472	8,292	18,480	7,353
TeCB-52	12,948	45,930	5,976	19,781	5,258
PeCB-101	9,370	11,832	2,651	11,900	10,259
PeCB-118	4,044	2,540	0,900	3,995	3,870
HxCB-138	15,772	9,223	2,990	23,325	22,638
HxCB-153	19,387	12,595	4,549	35,690	33,022
HpCB-180	14,994	9,874	3,423	29,399	22,826
Total Indicator PCBs	99,446	113,465	28,782	142,571	105,227

Lab. Code:	DP-08-270-120509-9	DP-08-268-200409-5	DP-08-254-070409-14	DP-08-269-200409-6	DP-08-246-070409-6
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Obristwy, km-114	Vitava, Zelcin, km-110	Zernoseky, km-52	Decin, km-14	Schmilka, km 4
Sampling	26.08.-23.09.08	26.08.-30.09.08	30.09.2008	28.08.-02.10.08	01.09.-29.09.08
Type of sample:	FDS	FDS	Sediment, IP	FDS	FDS
Mass Analysed:	5,00	5,00	5,00	5,02	5,00
Data analysed:	23.05.2009	01.05.2009	25.04.2009	01.05.2009	25.04.2009
Concentration:	ng/g	ng/g	ng/g	ng/g	ng/g
Indicator PCBs					
TriCB-28	11,474	4,405	nd	7,771	6,276
TeCB-52	13,094	1,905	nd	7,163	6,204
PeCB-101	10,175	7,827	nd	16,822	13,455
PeCB-118	3,357	3,071	nd	5,922	4,659
HxCB-138	20,329	23,158	nd	42,090	34,924
HxCB-153	28,142	32,864	nd	53,577	50,318
HpCB-180	23,659	29,546	nd	46,902	39,801
Total Indicator PCBs	110,230	102,776	nd	180,249	155,636

Lab. Code:	DP-08-247-070409-7	DP-08-248-120509-3	DP-08-257-240409-1	DP-08-255-200409-13	DP-08-258-200409-1
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Zehren, km 89,7 (links)	Dommitzsch, km 173 (links)	Spittelwasser	Mulde, Dessau, km 7,6	Bode, Neugattersleben
Sampling	03.09.-01.10.08	03.09.-29.09.08	03.09.-01.10.08	27.08.-01.10.08	01.10.2008
Type of sample:	FDS	FDS	FDS	FDS	SPM
Mass Analysed:	5,07	5,06	5,18	5,07	5,17
Data analysed:	25.04.2009	22.05.2009	09.05.2009	01.05.2009	30.04.2009
Concentration:	ng/g	ng/g	ng/g	ng/g	ng/g
Indicator PCBs					
TriCB-28	3,493	3,174	7,941	0,932	3,852
TeCB-52	3,900	3,642	8,617	1,278	6,558
PeCB-101	7,355	6,263	9,926	1,960	6,795
PeCB-118	2,739	2,601	7,086	1,173	4,050
HxCB-138	18,053	15,678	17,760	3,781	6,796
HxCB-153	24,033	21,594	19,530	4,382	7,346
HpCB-180	20,001	17,454	13,179	3,218	2,935
Total Indicator PCBs	79,574	70,406	84,038	16,722	38,331

Lab. Code:	DP-08-256-200409-14	DP-08-242-070409-4	DP-08-241-070409-3	DP-08-240-070409-2	DP-08-244-070409-5
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Saale, Rosenberg, km 3,8	Magdeburg, km 318	Cumlosen, km 470	Schnackenburg, km 474	Geesthacht, km 586
Sampling	27.08.-01.10.08	08.09.-29.09.08	08.09.-30.09.08	28.08.-02.10.08	01.09.-30.09.08
Type of sample:	FDS	FDS	FDS	FDS	FDS
Mass Analysed:	5,16	5,02	5,06	4,99	5,02
Data analysed:	01.05.2009	25.04.2009	25.04.2009	24.04.2009	25.04.2009
Concentration:	ng/g	ng/g	ng/g	ng/g	ng/g
Indicator PCBs					
TriCB-28	2,337	2,857	2,376	1,553	1,106
TeCB-52	3,386	4,425	2,855	1,954	1,250
PeCB-101	5,126	7,103	5,865	3,343	2,024
PeCB-118	3,541	3,731	3,378	1,820	1,135
HxCB-138	6,609	12,803	11,876	6,418	3,527
HxCB-153	6,969	16,859	15,534	8,529	4,514
HpCB-180	3,745	13,730	10,896	6,087	3,076
Total Indicator PCBs	31,714	61,508	52,780	29,704	16,632

Lab. Code:	DP-08-259-120509-6	DP-08-238-200409-11	DP-08-260-200409-3	DP-08-261-120509-7	DP-08-239-200409-12B
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Buhnenfeld, Bullenhausen, km 599	Bunthaus, km 609	Süderelbe, km 619,5	Köhlbrand, km 623	Seemannshöft, km 629
Sampling	26.06.2008	01.09.-01.10.08	24.06.2008	24.09.2008	01.09.-01.10.08
Type of sample:	Sediment, IP	FDS	Sediment, IP	Sediment, IP	FDS
Mass Analysed:	5,05	5,08	5,12	5,08	5,08
Data analysed:	22.05.2009	01.05.2009	08.05.2009	23.05.2009	26.05.2009
Concentration:	ng/g	ng/g	ng/g	ng/g	ng/g
Indicator PCBs					
TriCB-28	1,756	1,023	1,209	0,930	2,091
TeCB-52	2,001	1,328	1,382	1,057	2,004
PeCB-101	3,544	1,991	2,406	1,993	3,256
PeCB-118	1,855	1,098	1,368	0,943	1,557
HxCB-138	6,788	3,405	4,584	3,262	6,713
HxCB-153	9,013	4,254	5,594	4,246	8,540
HpCB-180	6,467	2,809	3,805	2,747	8,714
Total Indicator PCBs	31,423	15,908	20,348	15,177	32,874

Lab. Code:	DP-08-262-200409-4	DP-08-249	DP-08-235-070409-1	DP-08-237-200409-10	DP-08-250-120509-4
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	Wedel, km 643	Grauerort, km 661	Stör, Heiligenstedten	Brunsbüttel, Elbehafen, km 693	Cuxhaven, km 725,5
Sampling	01.09.-30.09.08	05.09.-02.10.08	11.09.2008	11.09.2008	15.09.-16.09.08
Type of sample:	FDS	FDS	Sediment, IP	Sediment, IP	SPM
Mass Analysed:	5,13	5,02	5.0	5,17	5,04
Data analysed:	01.05.2009	25.04.2009	24.04.2009	01.05.2009	22.05.2009
Concentration:	ng/g	ng/g	ng/g	ng/g	ng/g
Indicator PCBs					
TriCB-28	0,552	0,949	0,637	1,253	0,716
TeCB-52	0,660	1,072	0,614	2,244	0,599
PeCB-101	1,480	2,047	1,735	4,937	1,329
PeCB-118	0,734	0,912	0,927	1,928	0,819
HxCB-138	2,590	4,292	3,551	7,462	2,579
HxCB-153	3,366	5,905	4,615	9,935	3,588
HpCB-180	2,137	4,400	3,151	5,932	2,228
Total Indicator PCBs	11,518	19,578	15,230	33,691	11,858

Lab. Code:	DP-08-267-270409-7	DP-08-263-270409-3	DP-08-265-270409-5	DP-08-266-120509-8	DP-08-264-270409-4
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	North Sea KS8	North Sea KS11	North Sea 21, 2 km from dumping site	North Sea 69, 12 km from dumping site	North Sea 90, reference area
Sampling	15.08.2008	15.08.2008	16.08.2008	19.08.2008	18.08.2008
Type of sample:	Sediment, IP	Sediment, IP	Sediment, IP	Sediment, IP	Sediment, IP
Mass Analysed:	5,07	5,10	5,00	5,03	5,02
Data analysed:	09.05.2009	09.05.2009	09.05.2009	23.05.2009	09.05.2009
Concentration:	ng/g	ng/g	ng/g	ng/g	ng/g
Indicator PCBs					
TriCB-28	1,235	0,449	0,258	0,388	0,303
TeCB-52	1,012	0,710	0,163	0,309	0,187
PeCB-101	1,806	1,153	0,336	0,398	0,423
PeCB-118	1,218	0,745	0,265	0,269	0,339
HxCB-138	1,993	1,294	0,511	0,647	0,627
HxCB-153	3,416	2,414	0,691	0,811	0,863
HpCB-180	1,383	0,954	0,268	0,447	0,328
Total Indicator PCBs	12,063	7,719	2,492	3,270	3,070

Lab. Code:	P-09-114-101109-5	P-09-115-101109-6	P-09-116-101109-7	P-09-117-101109-8	P-09-118-101109-9
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	North Sea KS8/1	North Sea KS8/2	North Sea KS8/3	North Sea KS8/4	North Sea KS11/1
Sampling	30.09.2009	30.09.2009	30.09.2009	30.09.2009	30.09.2009
Type of sample:	Sediment, EP	Sediment, EP	Sediment, EP	Sediment, EP	Sediment, EP
Mass Analysed:	5.0	5.0	5.0	5.0	5.0
Data analysed:	22.01.2010	22.01.2010	22.01.2010	22.01.2010	22.01.2010
Concentration:					
Indicator PCBs	ng/g	ng/g	ng/g	ng/g	ng/g
TriCB-28	0,259	0,250	0,205	0,225	0,154
TeCB-52	0,265	0,266	0,200	0,218	0,872
PeCB-101	0,443	0,416	0,327	0,285	1,273
PeCB-118	0,362	0,347	0,254	0,245	0,804
HxCB-138	0,588	0,530	0,419	0,398	1,112
HxCB-153	0,881	0,768	0,613	0,502	2,462
HpCB-180	0,337	0,273	0,267	0,202	0,690
Total Indicator PCBs	3,135	2,851	2,284	2,074	7,366

Lab. Code:	P-09-119-101109-10	P-09-120-101109-11	P-09-121-101109-12
Project:	ELBE RIVER	ELBE RIVER	ELBE RIVER
Sampling Location:	North Sea KS11/2	North Sea KS11/3	North Sea KS11/4
Sampling	30.09.2009	30.09.2009	30.09.2009
Type of sample:	Sediment, EP	Sediment, EP	Sediment, EP
Mass Analysed:	5.0	5.0	5.0
Data analysed:	22.01.2010	22.01.2010	22.01.2010
Concentration:	ng/g	ng/g	ng/g
Indicator PCBs			
TriCB-28	0,457	0,215	0,310
TeCB-52	1,036	0,490	1,158
PeCB-101	1,710	0,696	1,543
PeCB-118	1,203	0,451	0,926
HxCB-138	2,166	0,776	1,528
HxCB-153	3,583	1,321	3,059
HpCB-180	1,779	0,449	1,027
Total Indicator PCBs	11,933	4,399	9,551

EP = single sample, SPM = suspended particulate matter (centrifuge), FDS = freshly deposited sediment (composite sample)

Appendix V

Quality control

Lab. Code:	DP-QC-070409-15	DP-QC-200409-15	DP-QC-270409-8	DP-QC-120509-2		
Project:	QC	QC	QC	QC	QC	QC
Sampling Location:						
Type of sample:	SEDIMENT BVB	SEDIMENT BVB	SEDIMENT BVB	SEDIMENT BVB		
Mass Analysed:	5.0	5.0	5.0	5.0		
Data analysed:	25.04.2009	09.05.2009	09.05.2009	23.05.2009		
Concentration:	ng/g	ng/g	ng/g	ng/g	Average	%RSD
2,3,7,8 - substituted PCDD/Fs						
2378-TCDD	0,0060	0,0078	0,0066	0,0081	0,0071	13,79
12378-PeCDD	0,0022	0,0024	0,0021	0,0024	0,0023	7,54
123478-HxCDD	0,0027	0,0030	0,0027	0,0032	0,0029	9,99
123678-HxCDD	0,0060	0,0067	0,0058	0,0066	0,0063	6,84
123789-HxCDD	0,0036	0,0042	0,0036	0,0042	0,0039	7,98
1234678-HpCDD	0,069	0,077	0,071	0,081	0,0743	7,20
OCDD	0,727	0,844	0,777	0,901	0,8124	9,39
2378-TCDF	0,012	0,011	0,010	0,013	0,0115	7,96
12378-PeCDF	0,013	0,013	0,013	0,014	0,0132	5,90
23478-PeCDF	0,014	0,014	0,013	0,016	0,0141	7,98
123478-HxCDF	0,044	0,050	0,047	0,062	0,0507	15,66
123678-HxCDF	0,022	0,025	0,024	0,030	0,0251	13,77
234678-HxCDF	0,016	0,018	0,017	0,019	0,0176	8,58
123789-HxCDF	0,009	0,010	0,010	0,011	0,0098	8,89
1234678-HpCDF	0,149	0,186	0,171	0,278	0,1959	29,06
1234789-HpCDF	0,025	0,030	0,029	0,043	0,0317	25,39
OCDF	0,641	0,758	0,722	1,010	0,7828	20,37
Upper-bound						
I-TEQ	0,030	0,034	0,031	0,039	0,0334	11,70
1998 WHO-TEQ	0,030	0,034	0,031	0,038	0,0331	11,37
2005 WHO-TEQ	0,027	0,031	0,028	0,035	0,0303	11,86
Middle-bound						
I-TEQ	0,03	0,03	0,03	0,04	0,0334	11,70
1998 WHO-TEQ	0,03	0,03	0,03	0,04	0,0331	11,37
2005 WHO-TEQ	0,03	0,03	0,03	0,04	0,0303	11,86
Lower-bound						
I-TEQ	0,03	0,03	0,03	0,04	0,0334	11,70
1998 WHO-TEQ	0,03	0,03	0,03	0,04	0,0331	11,37
2005 WHO-TEQ	0,03	0,03	0,03	0,04	0,0303	11,86
Total PCDD/Fs						
TCDD	0,08	0,10	0,08	0,11	0,0918	12,55
PeCDD	0,07	0,07	0,07	0,09	0,0752	10,48
HxCDD	0,11	0,12	0,11	0,13	0,1157	8,40
HpCDD	0,14	0,15	0,15	0,16	0,1500	7,62
OCDD	0,73	0,84	0,78	0,90	0,8124	9,39
TCDF	0,21	0,21	0,20	0,24	0,2158	7,52
PeCDF	0,20	0,21	0,20	0,22	0,2088	4,22
HxCDF	0,21	0,24	0,23	0,27	0,2368	11,24
HpCDF	0,24	0,30	0,28	0,41	0,3083	23,64
OCDF	0,64	0,76	0,72	1,01	0,7828	20,37
Total PCDDs	1,13	1,29	1,18	1,38	1,2451	9,21
Total PCDFs	1,50	1,73	1,63	2,15	1,7524	15,91
Total PCDD/Fs	2,62	3,02	2,82	3,53	2,9975	13,01

Project:	QC	QC	used for the 13th Intercalibration Study Final Results 13th Round International Intercalibration 2008 about Sediment A Participants n.: 86					
	Bias % calculated Vs Average	Bias % calculated Vs Median	ng/g Average	ng/g Median	ng/g Min	ng/g Max	SD	%RSD
2,3,7,8 - substituted PCDD/Fs								
2378-TCDD	80,52	82,70	0,0089	0,0086	0,0003	0,0296	0,0037	42%
12378-PeCDD	59,99	85,21	0,0038	0,0027	0,0003	0,0440	0,0062	163%
123478-HxCDD	63,54	87,57	0,0046	0,0033	0,0002	0,0653	0,0078	172%
123678-HxCDD	75,10	93,29	0,0084	0,0067	0,0003	0,1352	0,0151	181%
123789-HxCDD	57,59	77,84	0,0068	0,0050	0,0002	0,0800	0,0100	148%
1234678-HpCDD	78,50	81,48	0,095	0,091	0,001	0,820	0,091	96%
OCDD	94,98	91,59	0,855	0,887	0,000	1,529	0,281	33%
2378-TCDF	73,90	76,28	0,016	0,015	0,001	0,068	0,008	52%
12378-PeCDF	81,59	87,76	0,016	0,015	0,001	0,098	0,011	69%
23478-PeCDF	78,04	81,04	0,018	0,017	0,001	0,080	0,010	56%
123478-HxCDF	102,18	98,42	0,050	0,052	0,001	0,111	0,019	39%
123678-HxCDF	96,19	94,56	0,026	0,027	0,001	0,073	0,010	40%
234678-HxCDF	92,00	97,77	0,019	0,018	0,001	0,170	0,019	101%
123789-HxCDF	114,86	175,39	0,009	0,006	0,000	0,029	0,007	83%
1234678-HpCDF	110,03	109,78	0,178	0,178	0,001	0,531	0,075	42%
1234789-HpCDF	80,92	102,20	0,039	0,031	0,000	0,640	0,071	181%
OCDF	100,56	101,66	0,778	0,770	0,000	2,025	0,261	34%
Upper-bound								
1998 WHO-TEQ	84,17	87,10	0,039	0,038	0,006	0,174	0,020	50%

Bias % calculated Vs Average=average "round robin" dev. average analysis Elbe samples

Appendix VI

Analysis method

Overview

A multi residual sample preparation method for determination of PCDD/Fs, indicator-PCBs, DL-PCBs. The analysis of all compounds was done using isotope dilution and HRGC/HRMS techniques starting from one extract.

Standards and Chemicals

68-CVS and 68-LCS were native and ¹³C-labelled internal standards for 12 congeners DL-PCBs (Wellington Laboratories Guelph, Ontario, Canada). EC-4058 was native for indicator-PCBs (CIL, Andover, Massachusetts, USA). ¹³C-labelled PCB-111 and PCB-170 were used as recovery standards (Wellington Laboratories Guelph, Ontario, Canada).

EPA-1613CVS, EPA1613LCS and EPA-1613ISS were native, ¹³C-labelled internal and recovery standards respectively for 17 PCDDs/Fs. The standards were obtained from Wellington Laboratories (Guelph, Ontario, Canada).

All organic solvents used were Dioxin analysis grade (Sigma-Aldrich, Buchs SG, Switzerland). Sulphuric acid was 98% extra pure (VWR International s.r.l., Milan, Italy). Cleanup of PCDD/F, PCBs and PBDEs was conducted on ready to use multi-layer (acidic silica, basic alumina and carbon) columns (Fluid Management Systems (FMS) Inc., Watertown, MA, USA).

Extraction

The samples were lyophilized, disaggregated and homogenised in a mortar, and finally sieved < 2 mm. 5g of dry sample was extracted with a mixture of n-hexane/acetone (v/v, 220/30) by Soxhlet for 24 h after spiking with isotope-labelled surrogate standards. Copper powder was added to the solvent during the extraction to remove Sulphur.

Clean up

After treatment of the raw extract with conc. H₂SO₄ extract purification was executed with an automated clean-up system (Power-Prep P6, Fluid Management Systems (FMS) Inc., Watertown, MA, USA). This system was previously described (Abad et al., 2000; Covaci et al, 2003; Pirard et al., 2003; Thomsen et al., 2004) uses a multi-layer silica column (acid/neutral), basic alumina and carbon column combination. Two fractions were collected, one containing Mono-ortho PCBs, Indicator-PCBs and one for Non-ortho PCBs and PCDD/Fs. After evaporation of the solvents to near dryness, the syringe standards were added and a final volume of 30 µl was adjusted.

Instrumental

All instrumental analysis of PCDD/Fs and PCBs were based on isotope dilution using HRGC-HRMS (high resolution gas chromatography – high resolution mass spectrometry) for quantification on the basis of EPA1613, EPA 1668 and EPA 1614 methods.

Non-ortho PCBs, PCDD/Fs were analyzed on double HRGC (Thermo Trace GC Ultra, Thermo Electron, Bremen, Germany), coupled with a DFS high resolution mass spectrometer HRMS (Thermo Electron, Bremen, Germany) operating in the EI-mode at 45 eV with a resolution of >10000. For Non-ortho PCBs, PCDD/Fs the two most abundant ions of the isotopic molecular cluster were recorded for both native and labelled congeners.

The Non-ortho PCBs, PCDD/Fs were separated on a BP-DXN 60 m long with 0.25 mm i.d. (inner diameter) and 0.25 μm film (SGE, Victoria, Australia). The following gas-chromatographic conditions were applied for non-ortho PCBs, PCDD/Fs: split/splitless injector at 280 °C, constant flow at 1.0 ml min^{-1} of He, GC-MS interface at 300 °C and a GC program rate: 160 °C with a 1 min. hold, then 2.5 °C min^{-1} to 300 °C and a final hold at 300 °C for 8 min.

Gas chromatographic conditions for OCPs were: Split/splitless injector at 250 °C, constant flow at 1.0 ml min^{-1} of He, GC-MS interface at 270 °C and a GC program rate: 100 °C with a 1 min. hold, then 10 °C min^{-1} to 300 °C and a final hold at 300 °C for 9 min.

were analyzed on a Sol-Gel-1ms, 15 m with 0.25 mm i.d. and 0.1 μm film GC column (SGE, Victoria, Australia). The following gas-chromatographic conditions were applied: PTV injector with temperature program from 110 to 300 °C at 14.5 °C sec^{-1} , constant flow at 1.0 ml min^{-1} of He, GC-MS interface at 300 °C and a GC program rate: 110 °C with a 1 min. hold, then 20 °C min^{-1} to 300 °C and a final hold at 300 °C for 6 min. The selection of the chromatographic conditions was optimized following the literature indications (Sjödin et al., 1998; Covaci et al., 2003; Björklund et al., 2004; Korytár et al., 2005).

Mono-ortho PCBs and Indicator PCBs were analyzed on a GC (HP-6890, Hewlett Packard, Waldbronn, Germany) coupled with a VG Autospec Ultima high resolution mass spectrometer (Micromass, Manchester, UK) operating in EI-mode at 34 eV with a resolution of >10000.

Mono-ortho PCBs were separated on HT-8 capillary columns, both columns types were 60 m long with 0.25 mm i.d. (inner diameter) and 0.25 μm film (SGE, Victoria, Australia).

Gas chromatographic conditions for Mono-ortho PCBs were: Split/splitless injector at 280 °C, constant flow at 1.5 ml min^{-1} of He, GC-MS interface at 280 °C and a GC program rate: Starting from 120 °C with 20 °C min^{-1} to 180 °C, 2 °C min^{-1} to 260 °C, and 5 °C min^{-1} to 300 °C isotherm for 4 min.

Quality Assurance and Quality Control

The quantified compounds were identified through retention time comparison of the corresponding standard and the isotopic ratios between two ions was recorded for all halogenated compounds analyzed (see Appendix V).

Reference materials (RM) were analyzed in parallel with sediments and SPM samples for PCDD/Fs and DL-PCBs. The concentrations detected were in accordance with the reference values.

Levels of analytical blanks obtained during the sample preparation were at least 10 times lower of the reported concentrations for all compounds studied. The blank level was not subtracted. The reported detection limits were calculated on the bases of a signal to noise ratio of 3/1.

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Appendix VII:
Sampling devices



Van-Veen grab for sampling surface sediment samples (Hamburg Port Authority 2011)



Muddy surface sediment sample from the North Sea (Hamburg Port Authority 2011)



Continuous centrifuge for sampling SPM (LHW, Labor Wittenberg 2010)



Sedimentation chamber in a monitoring station for collecting freshly deposited sediment "FDS" (composite sample, FGG Elbe 2008)

Abstract

The most recent longitudinal sampling profile, taken in 2008 from the river Elbe and its tributaries Vltava (Moldau), Mulde, Spittelwasser, Saale, Bode the Stör and the North Sea near Helgoland, shows contaminations of solid matter with polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (dioxins, PCDD/Fs) and polychlorinated biphenyls (PCBs). While the dioxin contamination is mainly located along the German part of the catchment, PCBs are more abundant in the Czech section. In some of the 43 solid samples investigated high levels of contamination were detected. Selected orientation benchmarks for dioxins and PCBs in sediments and fish are exceeded, suggesting potential hazards for organisms in the contaminated rivers and for human consumption.

Elevated dioxin concentrations in the Spittelwasser-Mulde system and the Saale catchment, together with consistent dioxin congener patterns Elbe downstream of the confluence, indicate that the region of Bitterfeld-Wolfen is the predominant source of the dioxin pollution, which can be traced until far off shore in the sediments of the North Sea near Helgoland. This hypothesis, suggested by the spatial distribution of dioxins, was confirmed through statistical analysis (neural networks), showing that the historic dioxins sources were in the region Bitterfeld-Wolfen in the Mulde catchment as well as in the Saale catchment. Thermal metal, presumably Magnesium production via fused salt electrolysis during the 2nd world war is the most probable primary, historic source of the dioxin contamination.

In particular the German Mulde tributary *Spittelwasser* exhibited a maximum dioxin concentration of 1260 pg WHO₂₀₀₅-TEQ/g. The river Bode, a tributary of the river Saale, showed a value of 102 pg WHO₂₀₀₅-TEQ/g. In the longitudinal profile of the River Elbe, a significant increase in the concentrations was registered after the Mulde confluence near Magdeburg. Concentrations increased from 12 pg WHO₂₀₀₅-TEQ/g (Dommitzsch, km 173, upstream Mulde) to 68 pg WHO₂₀₀₅-TEQ/g (Magdeburg, km 318, downstream Mulde). Further downstream of Magdeburg the concentrations then decreased until the Elbe estuary.

The spatial distribution of dioxins as seen in 2008 matched well with earlier campaigns in 2002, both for aquatic solids and alluvial soils, suggesting minor change of the situation since then.

The main factors contributing currently to the dioxin pollution of the Elbe arise from the sinks of the historic primary releases, which are under hydraulic redistribution since then. In particular the remobilisation of contaminated sediments from the Mulde and Saale catchments and from the slack water zones of the Elbe, as well as soil erosion from contaminated floodplains in the course of high water events, are continuing to introduce dioxins into the river. This can be seen from the comparison of time series of dioxins in suspended solid matter from the Elbe and the tributaries concerned, demonstrating contaminated suspended solid matter from Mulde and Saale being still introduced into the Elbe.

Also the samples from the North Sea revealed elevated levels of dioxins of up to 16 WHO₂₀₀₅-TEQ/g (KS11) that display the congener pattern from the Bitterfeld-Wolfen Region. The observations suggest that suspended solids originating from Bitterfeld-Wolfen have been transported into in the North Sea South of Helgoland.

The spatial information obtained on the occurrence of PCDD/Fs, as well as the fingerprint based source apportionments suggest the need to inhibit further remobilization from the Spittelwasser catchment and the adjacent historic production sites and, in second line, from contaminated alluvial soils and slack water zones downstream of the Spittelwasser.

In contrast to the PCDD/Fs, PCBs are mainly present in the in the Upper Elbe in the Czech Republic. After the German border PCBs display an overall decrease.

Dioxin-like PCBs (DL-PCBs) in the Elbe had a maximum value of 20 pg WHO₂₀₀₅-TEQ/g at Pardubice-Semtin (CZ, km -237). The overall maximum of 37 pg WHO₂₀₀₅-TEQ/g was detected in the *Spittelwasser*, the latter not impacting the catchment significantly due to its low discharge.

The maximum concentration of the 7 indicator PCBs in the river Elbe was 180 ng/g at Decin (CZ, km -14). Downstream of Decin and along the whole German stretch a decline in the PCB concentrations was registered.

Higher values for the 7 indicator PCBs found in the former sewage sludge dumping zones in the North Sea were 4.5 ng/g (average KS8) and 8.2 ng/g (average KS11) respectively. In comparison, the indicator PCBs from the sampling site 69 and the reference area (site 90) yielded about 3 ng/g, which could be indicative of the influence of the dumping.

Other than PCDD/Fs, PCB emissions into the Elbe cannot be attributed to a dominant source or region. Indicator PCBs did rise more or less constantly in concentration until the German border, suggesting a variety of cumulative emission sources along the whole Czech stretch.

Thus, no specific recommendation on how to decrease the PCB pressure on the River Elbe can be given on the basis of the data acquired in this study. Detailed regional scale monitoring in the Czech stretch, together with the evaluation of production statistics regarding potential PCB sources are needed here. After all the PCB toxicity in eel is exceeding that of PCDD/F up to an order of magnitude (investigations of eels taken after the flood event in August 2002).

As an amendment to the chemical analyses, two Ah-receptor based bioassays (DR CALUX^R and EROD), which display the dioxin-like activity of all pollutants present, were performed on a subset of the samples (blind study). For The DR CALUX^R the comparison revealed a good agreement between the HRGC/HRMS results on dioxins and dioxin-like PCBs along the German stretch and the bioassay. However, along the Czech section of the Elbe the DR CALUX^R displayed a 10 times higher dioxin-like activity than the chemical analyses. This suggests that the solid material in the Czech section contains additional persistent dioxin-like acting pollutants. In comparison to the DR CALUX^R test, the EROD assay displayed even higher dioxin-like activities, less than 1 % of the observed signal could be explained by the PCDD/Fs and dioxin like PCBs quantified via chemical analyses. The differences can be explained by the fact that the clean up procedure for the DR CALUX^R eliminated the less persistent organic pollutants in the extract, while the EROD procedure remained sensitive to those.

More research is needed to identify the compounds behind the so far unexplained signal of the bioassays and to localize their emission sources.

Regarding the risk for the aquatic food chain and the human diet, the reduction of PCBs in the River Elbe ecosystem appears crucial as indicated by the dominance of the PCB over the PCDD/Fs in toxicity equivalents detected in eel samples.

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