The Elbe Flood in August 2002—Organic Contaminants in Sediment Samples Taken After the Flood Event*

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In the course of this study 37 sediment samples were analyzed. They were taken after the flooding in September 2002 along the Elbe and at the mouths of its major tributaries. The sampling program covered the entire river stretch that was affected by the floods, from Obrístvi (Czech Republic) to the Elbe estuary (North Sea) on the German coast. Analyses were performed for dioxins, nonylphenols, nonylphenol ethoxylates, bisphenol A, DEHP, musk fragrances, polybrominated diphenylethers, chloroalkylphosphates, organochlorine compounds, PAH, and organotin compounds. The results show that only a few weeks after the flood, contaminant concentrations in solid matter were comparable to those prevailing beforehand. Significant sources of contaminant input proved to be the tributaries Vltava (Moldau), Bilina (both in the Czech Republic), and the Mulde (Germany), as well as industrial and municipal sewage treatment works (STW) located along the Elbe. Further point sources are to be found in still water zones such as harbors and abandoned channels. These sources are activated when erosive action stirs up older

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sediments. Statistical analyses of the congener distribution of the dioxins provided evidence on the sources of these contaminants and freight levels in different river sections. The chemical analyses were complemented by results of ecotoxicological investigations with two sediment organisms (*Chironomus riparius* and *Potamopyrgus antipodarum*).  

**Key Words:** Elbe flood; Sediments; Dioxins; Xenoestrogenic plasticizers and detergents; Musk fragrances; PBDE; Chloralkylphosphates; Organochlorine compounds; PAH; Organotin compounds; Ecotoxicological investigations.

**INTRODUCTION**

The river Elbe is one of the major rivers in Central Europe. From its source in the Riesengebirge (Czech Republic) to its mouth at the North Sea near Cuxhaven (Federal Republic of Germany) it flows over a distance of 1091 km and has a catchment area of 148,268 km², of which about one-third is located in the Czech Republic and two-thirds in Germany. In the limnic part of the Elbe the water discharges are characterized by the snow melt in springtime and heavy rainfalls in the summer, which normally lead to floods in the catchment areas. The affected regions are the areas between the dikes as well as polder areas. Flow conditions in the estuary are governed both by the river’s discharge and by the tides.

Extreme and widespread precipitation over the Czech Republic and Eastern Germany led to a disastrous flood in the catchment areas of the upper course of the Elbe, the tributaries Vltava (Moldau) and Mulde in August 2002. The Spolana factory, a chemical plant in the Czech Republic (Neratovice) that deals with particularly problematical substances, was flooded as well as a large number of STW on the Vltava and in the upper and middle course of the Elbe in Germany. The area of Bitterfeld-Wolfen (former GDR) on the river Mulde achieved notoriety for excessive contaminant emission until 1990. Substances from industrial and municipal STW and contaminated areas entered the Elbe and gave rise to a serious pollution situation of which, however, it is very difficult to assess the extent.

The basis of this investigation constituted sediment samples taken about one month after the event from the section of the river affected by flooding. This was between Obristvi (Czech Republic) and the Wadden Sea (North Sea, Trischendamm) on the German coast. A large number of organic contaminants was investigated. The aim was to document the sediment contamination throughout the Elbe in respect of mainly persistent contaminants directly following the flood. The choice of the analyzed compounds was governed by experience in the light of long-standing data sources; additionally, some substances were analyzed for the first time in the Elbe. The possibility of dioxin (PCDD/F) contamination was of particular interest, as there was reason to expect that the floods had caused contaminants to be washed out from the site of the Spolana chemical plant and from the Mulde into the Elbe. The sources
of PCDD/F contamination can be traced by means of statistical analysis of the congener distribution, which also allows for estimating PCDD/F freight loads above and below certain river stretches. The chemical analyses were completed by ecotoxicological investigations involving the sediment samples and two different test organisms. The direct comparison of biological responses at identical sites revealed significant differences for samples taken before and immediately after the flood.

MATERIALS AND METHODS

Sampling
Sediment samples were taken from 37 sampling sites along the Elbe and the mouths of relevant tributaries. Eleven sites are in the Czech Republic, 26 sites in the German section of the river. Collection of fine-grained, aerobic sediments from the upper sediment layers was performed using a Van Veen bottom grab or a spatula. The sampling was carried out between September 8 and 16, 2002, after the flood had subsided in parts of the river where there is little flow activity, such as between breakwaters, in abandoned channels, or in harbors. In some cases the sampling was performed from boats. Figure 1 shows the sampling...
sites with their respective location along the river course between Obristvi (downstream of the Spolana chemical plant) and Trischendamm (Wadden Sea zone of the North Sea). By convention the kilometer marking of the Elbe is given using negative numbers between the source and the Czech-German border and positive numbers between the border and the mouth.

**Analyzed Compounds and Test Organisms**

The samples were analyzed for (i) polychlorinated-p-dibenzodioxins and polychlorinated dibenzofurans (PCDD/F, 17 WHO congeners); (ii) xenoestrogenic plasticizers and detergents: bisphenol A (2,2'-bis(4-hydroxyphenyl)propane, BPA), branched nonylphenols (NP), and branched nonylphenol ethoxylates (NP:nEO, n = 1–3), di(2-ethylhexyl)phthalate (DEHP); (iii) synthetic polycyclic musk fragrances (MFR): Galaxolide® (CAS name: 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyran, HHCB) and Tonalide® (CAS name: 1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl)-ethanone, AHTN); (iv) polybrominated diphenylethers (PBDE, BDE 209); (v) chloroalkylphosphates: tributylphosphate (TBP), tris(2-chloroethyl)phosphate (TCEP), tris(1-chloro-2-propyl)phosphate (TCP), tris(1,3-dichloro-2-propyl)phosphate (TDPP), tris(2-butoxyethyl)phosphate (TBEP); (vi) organochlorine compounds (OCC): hexachlorocyclohexane isomers (α- and β-HCH), sum of DDT+metabolites (sum DDT); dichlorodiphenyldichloroethylene (p,p'-DDE), 2,2-bis(p-chlorophenyl)-1,1-dichloroethane (o,p'-DDD and p,p'-DDD), dichloro-diphenyl-trichloroethane (o,p'-DDT and p,p'-DDT), sum of PCB: polychlorinated biphenyls: PCB congeners No. 28, 52, 101, 138, 153, 180, and hexachlorobenzene (HCB); (vii) polycyclic aromatic hydrocarbons (PAH): fluoranthene (FLU), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(g,h,i)perylene (BghiP), indeno(1,2,3-cd)pyrene (I123P); (viii) organotin compounds: monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), and tetrabutyltin (TeBT); and (ix) ecotoxicological studies with *Chironomus riparius* (Insecta) and *Potamopyrgus antipodarum* (Gastropoda).

FDS = freshly deposed sediments.

**Methods**

The analytical methods are published or described as follows: (i) PCDD/F;[1] (ii) xenoestrogenic plasticizers and detergents;[2] (iii) polycyclic musk fragrances: microwave extraction with toluene, GC-MSD; (iv) PBDE;[3] (v) chloroalkylphosphates: extraction with acetone, GC-FPD; (vi) organochlorine compounds: microwave extraction with toluene, GC-MSD; (vii) PAH: microwave extraction with toluene, GC-MSD; and (viii) organotin compounds,[4] and (ix) 28 d-sediment toxicity test[5,6] according to OECD 218.[7]

“< value” = concentration below the limit of quantification (LOQ).
RESULTS AND DISCUSSION

Thirty-seven sediment samples yielded results for 53 individual substances belonging to eight different substance groups. The abbreviations for the substance descriptors are listed in the section “Analyzed Compounds and Test Organisms.” The substances involved belong to the so-called POPs, Persistent Organic Pollutants. On account of their chemical properties these substances are also readily adsorbed by sediments and suspended particulate matter and frequently lipophile, so that they accumulate in aquatic organisms. For the sake of clarity the concentration patterns throughout the Elbe and at the mouths of tributaries are presented graphically, whereby in a few cases individual results are summed and shown together. Table 1 provides an overview, showing the minimum, maximum, and median values per individual substance. The table shows clearly that the highest concentrations (based on dry mass) were detected for the substances DEHP, NP, PAH, and for the summed DDT compounds. The dioxins are given according to the standard WHO-TEQ convention and therefore do not reflect the concentration levels for individual congeners.

Dioxins (PCDD/F)

At the center of public attention was the possibility that PCDD/F had been released into the environment during the flood from the Spolana site and from contaminated industrial sites in the region of Bitterfeld-Wolfen. There was concern that these highly toxic substances may be introduced directly (Spolana) or indirectly (Bitterfeld-Wolfen) via the river Mulde into the Elbe.[8] The analysis was performed for the 17 WHO congeners; the results are shown in Figure 2.
### Table 1: Statistical calculations with the results of organic contaminant analyses in sediment samples of the river Elbe and the mouths of five tributaries after the flood event in August 2002;∗ = ethoxylate units n = 1–3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>Unit</th>
<th>Min</th>
<th>Med</th>
<th>Max</th>
</tr>
</thead>
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<tr>
<td>PCDD/F</td>
<td>37</td>
<td>pg WHO-TEQ/g dm</td>
<td>3</td>
<td>16</td>
<td>140</td>
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<tr>
<td>DEHP</td>
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<td>1030</td>
<td>4390</td>
<td>90480</td>
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<tr>
<td>BPA</td>
<td>37</td>
<td>µg/kg dm</td>
<td>&lt;5</td>
<td>30</td>
<td>1630</td>
</tr>
<tr>
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<td>µg/kg dm</td>
<td>31</td>
<td>124</td>
<td>15200</td>
</tr>
<tr>
<td>NPnEO+</td>
<td>37</td>
<td>µg/kg dm</td>
<td>&lt;50</td>
<td>132</td>
<td>990</td>
</tr>
<tr>
<td>MFR</td>
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<td>µg/kg dm</td>
<td>&lt;1</td>
<td>20</td>
<td>161</td>
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<td>&lt;1</td>
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<tr>
<td>CAP</td>
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<td>4.2</td>
<td>17</td>
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<tr>
<td>OCC</td>
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<td>&lt;5</td>
<td>162</td>
</tr>
<tr>
<td>α-HCH</td>
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<td>&lt;5</td>
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<tr>
<td>β-HCH</td>
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<td>µg/kg dm</td>
<td>&lt;5</td>
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<td>119</td>
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<tr>
<td>p,p′-DDE</td>
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<td>p,p′-DDD</td>
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<td>521</td>
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<tr>
<td>p,p′-DDT</td>
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<td>µg/kg dm</td>
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<td>&lt;5</td>
<td>58</td>
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<tr>
<td>p,p′-DDE</td>
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<td>µg/kg dm</td>
<td>&lt;5</td>
<td>16</td>
<td>235</td>
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<tr>
<td>Sum DDT</td>
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<td>&lt;5</td>
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<td>1100</td>
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<tr>
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<td>58</td>
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<tr>
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<td>&lt;5</td>
<td>13</td>
<td>76</td>
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<tr>
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<td>&lt;5</td>
<td>51</td>
<td>272</td>
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<td>134</td>
<td>991</td>
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<td>PAH</td>
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<td>119</td>
<td>2690</td>
<td>45100</td>
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<tr>
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<td>752</td>
<td>14000</td>
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<td>19</td>
<td>281</td>
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<tr>
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<td>µg/kg dm</td>
<td>24</td>
<td>562</td>
<td>9800</td>
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<tr>
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<td>µg/kg dm</td>
<td>37</td>
<td>324</td>
<td>3690</td>
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<tr>
<td>BghiP</td>
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<td>µg/kg dm</td>
<td>28</td>
<td>284</td>
<td>2790</td>
</tr>
<tr>
<td>OTC</td>
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<td>µg cation/kg dm</td>
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<td>43</td>
<td>946</td>
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<td>576</td>
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<td>2560</td>
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<tr>
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<td>µg cation/kg dm</td>
<td>&lt;1</td>
<td>1.2</td>
<td>417</td>
</tr>
</tbody>
</table>

For abbreviations see "Analyzed Compounds and Test Organisms."

The PCDD/F concentrations in the Czech river section and in Germany upstream of the Mulde were relatively low: between 3 and 11 pg WHO-TEQ/g dm. At the mouth of the Mulde at Dessau and a short way downstream at Breitenhagen an abrupt increase by a factor of eight to nine was recorded,
with values of 121 and 140 pg WHO-TEQ/g dm respectively. After this the values show an almost continuous decline in the direction of the North Sea (Fig. 2).

In order to assess whether fish whose nourishment directly or indirectly originates from aquatic sediments may be adversely affected, the “safe sediment value” of 20 pg I-TEQ/g dm\(^9\) provides a basis for consideration. Using this value as a yardstick, this level was equaled or exceeded in 17 of 37 samples (46%); this indicates the likelihood of an unacceptable tissue residue in fish and birds.\(^9\) With the exception of the mouth of the Bilina, the samples from the Czech river section returned values below this level. In contrast, all the sediment samples from the mouth of the Mulde to the tidal reaches (the harbor at Wedel) must be considered to be significantly contaminated. Only in the estuarine section of the river do the values go below the level of the “safe sediment value” (sampling sites Brunsbüttel and Trischendamm) on account of the combination of the highly contaminated sediments with less polluted sediments (Fig. 2).

A statistical analysis using data of 73 samples from suspended particulate matter and sediment showed in 13 cases that congener patterns for neighboring sampling sites along the Elbe differed significantly from one another. For this analysis a model was developed that characterizes the contaminant levels within the relevant limits of statistical certainty. In the Czech river section the flooding activated an additional contamination source in the vicinity of the Spolana chemical plant. A significant contribution to the PCDD/F can be attributed to the Dresden region, and the dominating influence of the Mulde could be clearly demonstrated. Over a third of the PCDD/F contamination of the Elbe downstream of Dresden can be traced to input from the area around Dresden. The catchment area of the Mulde contains the severely contaminated region around Bitterfeld with numerous chemical plants and waste sites. Results of several multivariate statistical methods indicate that the dioxin contamination was caused partly by metallurgy processes and not only by chemical production.\(^10\) From here PCDD/F are transported via smaller waterways into the Mulde and then into the Elbe. Comparing the data of Magdeburg and Hamburg it could also be deduced that there are further emission points downstream of Magdeburg. The calculations show that more than one-third of the PCDD/F contamination in the Elbe at Hamburg is not due to input from the Mulde or other sources upstream of Magdeburg, but arises further downstream.

Eels (Anguilla anguilla) accumulate strongly lipophile substances such as PCDD/F on account of the large proportion of fats in their physical constitution. This renders them very suitable as indicators for environmental monitoring.

After the flooding, 24 eels of marketable size were caught in the middle course of the Elbe near Gorleben (km 493, Federal State of Lower Saxony) in September 2002. The muscle tissue was analyzed for PCDD/F and dioxin-like
PCB. The WHO-PCDD/F+PCB-TEQ values were in the range of 11 to 56 pg/g ww, with a median value of 29 pg/g ww.\textsuperscript{[11]} Generally, the contamination of eels with PCDD/F is not a new phenomenon and appears typical for the Elbe. A further point to bear in mind is that eels are nomadic by nature, so that the contaminants found may have accumulated in the eels under investigation at a location different from the one where they were caught. This possibility was confirmed by statistical analyses of the PCDD/F congener patterns for eels caught at various points in the Elbe in the years 1996, 1998, 2002, and 2003.

**Xenoestrogenic Plasticizers and Detergents**

Analyses were conducted in sediment samples for branched nonylphenols (NP), nonylphenol ethoxylates (NPnEO, \(n = 1–3\)), bisphenol A (BPA), and di(2-ethylhexyl)phthalate (DEHP).

Branched nonylphenols consist of a mixture of various isomers. Most NP are used in the production of nonylphenol ethoxylates with 1 to 40 ethoxy units. NPnEO have been applied in many industrial sectors, for example as non-ionic surfactants. Microbiological degradation of NPnEO in the aquatic system leads to the presence of NP via short ethoxy units. NP and NPnEO have estrogenic effects on the reproductive system of fish,\textsuperscript{[12]} whereby NP appear in the List of Priority Substances (Annex X) as “priority hazardous substances” and DEHP as “possible hazardous substances” in the EC-Directive Decision No. 2455/2001/EC.

BPA is used in many different technical applications, mainly as an intermediate in the production of polycarbonate and epoxy resin. Other applications include its use as a stabilizing agent in plastics or as an antioxidant in tire production. Exposure experiments with prosobranch snails indicate that BPA in low concentrations might affect wild populations.\textsuperscript{[13]} DEHP is used, as are other phthalates, as plasticizers for plastics such as PVC. They are suspected of having an estrogenic effect on aquatic organisms.\textsuperscript{[14]}

Figure 3 shows the results of these analyses. The concentrations of NP dominate with a maximum value of 15,200 \(\mu g/kg\ dm\) in the sample from the Elbe at Lostau. The cause of these high NP-concentrations is likely to be the discharge of treated wastewater from the STW at Gerwisch (Magdeburg). Upstream from Lostau the NP-concentrations in both the Czech and the German river sections are about two orders of magnitude lower. In the Czech section the values for the NP-concentrations range between 30 and 1020 \(\mu g/kg\ dm\) (mouth of the Ohre and the Elbe at Vanov/Strekov respectively), whereas the German section below Lostau returned values between 110 und 1950 \(\mu g/kg\ dm\) (Wedel and Sandfurth respectively). The concentration values for NPnEO range from 75 \(\mu g/kg\ dm\) (Wedel) to 990 \(\mu g/kg\ dm\) (mouth of the Vltava).

The BPA-concentrations proved to be lower than for the substances already mentioned, with a range of positive findings between 7 \(\mu g/kg\ dm\) (Roudnice)
and 1630 µg/kg dm at the mouth of the Bilina (Usti nad Labem). The Bilina receives the wastewater of the Czech chemical plant Spolana, a manufacturer and user of BPA, which probably accounts for the high BPA concentrations in sediment samples (Fig. 3).

Investigations on freshly deposed sediments (FDS, four weeks mixed samples)\(^{[15]}\) between 1998 and 2000 returned comparable results for NP, NPnEO, and BPA.\(^{[2,16]}\)

This is the first measurement program on this scale in which DEHP was investigated in sediment samples taken throughout the Elbe. The results in Figure 3 return a concentration range from 1030 µg/kg dm (Trischendamm) to 90,500 µg/kg dm (mouth of the Mulde), showing that DEHP is ubiquitous in the Elbe and certain tributaries. Significant peak values in excess of 10,000 µg/kg dm were measured in the Czech section upstream of Prague and in the Vltava (Libice, Dolni Berkovice), at the mouth of the Bilina (Spolana, Usti nad Labem), and at the Czech-German border near Hrensko (Fig. 3). Subsequently the concentration levels sink below 10,000 µg/kg dm until the mouth of the Mulde, where there is a drastic increase to a peak of 90,500 µg/kg dm. A further instance of a high DEHP concentration was found at Lostau (26,000 µg/kg dm). Downstream of this sampling site the concentration levels recede steadily, reaching a minimum value of 1030 µg/kg dm in sediments from the Wadden Sea at Trischendamm. In many cases the DEHP concentrations are one to two orders of magnitude above those for NP, NPnEO, and BPA.
Synthetic Polycyclic Musk Fragrances (MFR)

The sediment samples were also analyzed for traces of the MFR Galaxolide® (HHCB) and Tonalide® (AHTN).

MFR are industrial scents used in cleansing agents and cosmetics. They are transported into rivers almost exclusively via household wastewater and municipal STW. MFR are persistent and show a relatively high accumulation potential. Previous studies indicated that HHCB and AHTN do not represent a chronic toxic risk for aquatic organisms.[17]

Figure 4 shows that the concentration levels of HHCB are higher than for AHTN, the respective ranges being <1 to 160 µg/kg dm and <1 to 85 µg/kg dm. The sampling sites Libcice (Vltava), mouth of the Bilina, and Lostau all returned high peaks.

HHCB, AHTN, and the nitro musk compounds musk xylene and musk ketone have been included in routine investigations on the Elbe and its tributaries since 1998 in FDS (eight weeks mixed samples).[18] These studies have shown that, whereas the two nitro musk fragrances occur in concentrations either below or around the limit of determination of 0.5 µg/kg dm, the data for HHCB and AHTN reveal concentration levels similar to those measured for the sediment samples in September 2002. Thus the concentration levels for the two polycyclic musk fragrances returned to the pre-flood levels within a relatively short space of time.

Studies on eels (Anguilla anguilla), bream (Abramis brama), and pike-perch (Stizostedion lucioperca) that were caught in various parts of the Elbe over a period of years underline the accumulative tendencies of HHCB and AHTN in biota.[18,19]

![Figure 4: Musk fragrances in sediment samples from the river Elbe and the mouths of its tributaries (September 2002). For abbreviations see “Analyzed Compounds and Test Organisms.”](image-url)
Polybrominated Diphenylethers (PBDE)

PBDE are used as reactive flame retardants in polymers. PentaBDE are specified in the List of Priority Substances (Annex X) of the EC-Directive (Decision No. 2455/2001/EC) as “priority hazardous substances.” PBDE 99 (2,2′,4,4′,5-pentabromoDE) exhibits features of endocrine disrupters in vivo, at the organ level, and at the molecular level.[20]

PBDEs were determined in 27 sediment samples from the Elbe and its tributaries. Figure 5 documents the occurrence of decabromodiphenyl ether (BDE 209). BDE patterns in most sediment samples were dominated by BDE 209, which in the German part of the river Elbe contributes on average 78% ± 6% of the total PBDE content of the sediment samples. In the Czech Republic three samples showed the same congener pattern, while in the other samples higher percentages of tetra- to hexabrominated congeners (up to 70%) were determined. This indicates input of technical penta-formulation from local point sources. Besides decaBDE the congeners BDE 47, BDE 85, BDE 99, BDE 100, BDE 153, BDE 154, and BDE 183 (indicator of technical octa-formulation) were detected at low concentrations in most samples. BDE 209 concentrations are shown in Figure 5 and ranged from 0.5 to 17.4 µg/kg dm. In general, concentrations in the German section of the river Elbe were higher than those in the Czech Republic and increased up to the weir at Geesthacht near Hamburg (sampling site 30). Downstream of this site a decline in BDE 209 concentrations was observed. Probably, tidal influence causes mixing of contaminated particles from the river Elbe and uncontaminated material from the North Sea resulting in decreasing BDE concentrations toward the mouth of the river Elbe. Moreover, in the river section upstream the weir at Geesthacht (site 30) the flow velocity of the river is low, and hence sedimentation of suspended particulate
matter increases. Discharges of BDE 209 from the river Mulde running through industrialized regions of Saxony and Saxony-Anhalt into the river Elbe were observed only after normalizing results to organic carbon content (data not shown). The highest BDE 209 levels in the Czech section of the river Elbe were found in the two tributaries Vltava (site 3) and Ohre (site 6) and at Obristvi two kilometers downstream of the chemical plant Spolana. Much higher BDE 209 levels than those observed in this study were reported from the Western Scheldt (up to 510 µg/kg dm\textsuperscript{[21]}), the river Rhine at Lobith near the German-Dutch border (84 µg/kg dm\textsuperscript{[21]}), the river Tees in the UK, (up to 1400 µg/kg dm\textsuperscript{[22]}), and from other Dutch (470 to 990 µg/kg OC), Irish, and British rivers (up to 104,700 µg/kg OC\textsuperscript{[23]}). Low BDE 209 concentrations were found in freshwater sediments from the river Danube,\textsuperscript{[24]} which corresponds with the results reported here.

**Chloroalkylphosphates**

Tris(1-chloro-2-propyl)phosphate (TCPP) and tris(2-chloroethyl)phosphate (TCEP) are used in technical products as softening agents and as flame retardants. These substances exhibit long-term toxic characteristics,\textsuperscript{[25]} and TCEP is suspected of having mutagenic effects,\textsuperscript{[26]} for which reason it is increasingly being replaced by TCPP. This trend is confirmed by the results of the present study (Fig. 6).

The sediment samples were analyzed for the chloroalkylphosphates tributylphosphate (TBP), TCPP, TCEP, tris(1,3-dichloro-2-propyl)phosphate (TDPP), and tris(butoxyethyl)phosphate (TBEP). The results documented in Figure 6 show that the highest concentrations were determined for TCPP.

![Figure 6: Decabromo diphenylether (BDE 209) in sediment samples from the river Elbe and the mouths of its tributaries (September 2002).](image-url)
The values ranged from 5.9 to 311 \( \mu g/kg \) dm, whereby the highest values around 300 \( \mu g/kg \) dm were measured at the sampling sites Libcice (Vltava) and Tangermünde. Concentrations in excess of 100 \( \mu g/kg \) dm were found at the sampling sites Libcice (Vltava), mouth of the Bilina, Hrensko (border), Coswig, Tangermünde, Damnatz, Geesthacht, Bunthaus (the Elbe divides at this point), and Trischendamm. The sample from the Wadden Sea (Trischendamm) returned comparatively high chloroalkylphosphate concentrations. However, data from the ARGE ELBE\(^{[27]}\) from estuarine FDS (eight weeks mixed samples) in previous years does not indicate that the flood caused a significant increase altogether, so the values measured at Trischendamm probably represent a local exception.

**Organochlorine Compounds (OCC)**

The OCC that were investigated are persistent, lipophile, and readily accumulated pesticides, pesticide metabolites, and industrial chemicals. They were produced in large quantities in the former GDR and in the Czech Republic in the past, and due to insufficiently treated effluents significant amounts of OCC, together with by-products such as \( \alpha\)- and \( \beta\)-HCH, were introduced into the Elbe and the Mulde. HCH isomers and hexachlorobenzene (HCB) are specified in the List of Priority Substances (Annex X) of the EC-Directive (Decision No. 2455/2001/EC) as “priority hazardous substances.” The sediment samples were analyzed for HCH-isomers, DDT compounds including metabolites, HCB, and PCB. The individual substances investigated are listed in the section “Analyzed Compounds and Test Organisms.”

Figure 7 contains the concentration profiles for all the OCC analyzed. For the sake of clarity the compounds from the DDT group and the six PCB...
congeners are summed. The figure shows that HCB concentrations attained a high level in the Elbe, whereby the Bilina can be identified as the most significant source (HCB concentration 990 µg/kg dm); this river receives the wastewater of the Spolana chemical works. Further peaks in the German section were registered at the sampling sites Coswig (600 µg/kg dm) and Sandfurth (480 µg/kg dm) (Fig. 7).

The summed curve for the DDT compounds including metabolites shows high peaks at the sampling sites Decin (550 µg/kg dm), Coswig (390 µg/kg dm), and Meißen (410 µg/kg dm), followed by a drastic increase at the mouth of the Mulde, where a concentration of 1100 µg/kg dm was recorded (Fig. 7). The Mulde also represents the most significant source for input of HCH isomers α- and β-HCH into the Elbe, whereby the freight levels for β-HCH are distinctly higher than for α-HCH. Upstream of the Mulde the concentrations of both HCH isomers are below the LOQ of 5 µg/kg dm; then there is sharp increase—comparable to the DDT compounds—at the mouth of the Mulde. Downstream of the Mulde the values for both isomers settle down to a much lower level, which does not exceed 40 µg/kg dm (β-HCH) (Fig. 7).

The sum of the six PCB congeners shows high peaks at the sampling sites Litomerice (270 µg/kg dm), Decin (150 µg/kg dm), and Hrensko (200 µg/kg dm) and shows that PCB are introduced into the Elbe mainly in the Czech section and in the border region (Fig. 7). A comparison of OCC concentrations measured in this study with earlier long-term measurement programs for FDS (four weeks mixed samples) from the Elbe and its tributaries shows that the values recorded are of the same order of magnitude.⁸⁻²⁸

The OCC under investigation are persistent, extremely lipophile, and accumulate readily in aquatic organisms. In consequence some fish species in the Elbe are not fit for human consumption. This is particularly true for eels in respect of HCB. In some cases eels were also found to be contaminated with β-HCH and DDT (summed compounds) to a degree exceeding the maximum tolerable amounts specified in German foodstuffs legislation.⁹⁻²⁹

Polycyclic Aromatic Hydrocarbons (PAH)

PAH are engendered mainly through incomplete combustion of fossil fuels; they are introduced into rivers through deposition from the atmosphere. Local point sources also originate from industrial sites, e.g., from the oil and coal industries. For these sources old sites need to be taken into consideration as well. The main toxic effects of individual PAH are their carcinogenic properties with respect to aquatic organisms.⁹⁻³⁰

The sediment samples were analyzed for the six PAH specified in the “Trinkwasserverordnung”³¹ (Drinking Water Regulations). These are benzo(a)pyrene (BaP), benzo(b)fluoranthen (BbF), benzo(k)fluoranthene (BkF), benzo(g,h,i)perylene (BghiP), fluoranthene (FLU), and indeno(1,2,3-cd)pyrene
(I123P), which are also specified in the List of Priority Substances (Annex X) of the EC Directive (Decision No. 2455/2001/EC). The results of the longitudinal profile are shown in Figure 8.

All the PAH were recorded in very high concentrations at the sampling site Lostau, with extreme values for the substances FLU (45,100 \(\mu g/kg \ dm\)), BbF (14,000 \(\mu g/kg \ dm\)), and BaP (9800 \(\mu g/kg \ dm\)). It is possible that the sample from Lostau contained material from deeper strata than the others, so that the values do not reflect the present contamination situation. Up till the early nineties effluent from a coke works was introduced into the Elbe on the left bank upstream of the STW Gerwisch (Magdeburg), which probably explains these extreme PAH concentrations in the sediment.

The FLU concentrations remain comparatively high further downstream until below Hamburg Harbor, with values approximately between 1000 and 4500 \(\mu g/kg \ dm\). Various maxima were recorded at the sampling sites Liblice (influence of the Vltava, 4500 \(\mu g/kg \ dm\)), Vanov/Strekov (4300 \(\mu g/kg \ dm\)), Tangermünde (4100 \(\mu g/kg \ dm\)), and Geesthacht (3300 \(\mu g/kg \ dm\)). The concentration levels for the compounds BbF, BkF, BaP, BghiP, and I123P are lower than for FLU and are in many cases below 1000 \(\mu g/kg \ dm\). The maxima for these five PAH are generally to be found at the same sampling sites as for the FLU maxima (Fig. 8).

A comparison with results for FDS (four weeks mixed samples) from previous years shows PAH concentrations of the same order of magnitude. As is the case with the present data, the previous data also reveals FLU as being most prevalent.\[28,32\]
Organotin Compounds

One of the analyzed organotin compounds, tributyltin (TBT), is used as an antifouling agent on ships’ hulls because of its biocidal properties, which prevent the growth of marine and freshwater organisms. TBT also produces androgenic effects, and its presence can lead to the extinction of local snail populations.[33] The sale and use of TBT for antifouling paint was banned at European level on the basis of the Directive 2002/62/EC. However, the substance will continue to present a problem in the Elbe and other rivers for some time to come because it is remobilized when sediments are disturbed for any reason. TBT compounds are specified in the List of Priority Substances (Annex X) of the EC-Directive (Decision No. 2455/2001/EC) as “priority hazardous substances.” Monobutyltin (MBT) and dibutyltin (DBT) belong to the degradation products of TBT, while tetrabutyltin (TeBT) is used in the production of TBT. The results of the analysis are shown in Figure 9.

As is the case for other contaminants, the organotin concentrations show a remarkable increase at the mouth of the Mulde, followed initially by a steady decline. The high TeBT concentration at the mouth of the Mulde is most notable. This value may be traced to discharges from a former manufacturer of antifouling constituents. In this plant TBT was produced from TeBT, and the wastewater was treated in STW, after which it found its way via smaller rivers into the Mulde and then into the Elbe. TeBT is considered to be a typical “marker” for the Elbe, and it can be found as far as the estuarine section.[34] An extremely high TBT concentration—2560 µg TBT/kg dm—was analyzed in the sediment sample from Hamburg Docks (Reiherstieg). In this case the causal agent is

![Figure 9](image-url)
likely to be a local shipyard. Upstream of the mouth of the Mulde (sampling sites Obristvi to Kurzer Wurf) and in the estuarine section (Brunsbüttel and Trischendamm) the organotin concentrations are relatively low, with the exception of MBT at the mouth of the Bilina (Fig. 9).

Ecotoxicological Investigations

For toxicity testing of the sediments the midge *Chironomus riparius* (Insecta, Chironomidae) and the freshwater mudsnail *Potamopyrgus antipodarum* (Gastropoda, Hydrobiidae) were exposed to aliquots of the 37 sediment samples for 28 days. At the end of the test the end points emergence (*C. riparius*) and reproduction (*P. antipodarum*) were monitored. For a subset of 19 sampling sites (12, 15, 19, 21–36), the contamination level and the biological response of both species were also recorded before the flood of August 2002. The direct comparison of biological responses at identical sites revealed significant differences for samples taken before (in 2000) and immediately after the flood.

The total emergence of *C. riparius* ranged from 50% (site 19) to 100% (site 36), as demonstrated in Figure 10b. Compared to the control (95% emergence), there are no significant differences for any of the field sediments (one-way-ANOVA, Tukey HSD test) even at those few sampling sites (19, 26, 30, and 31) with a comparably low emergence, due to high standard deviations. The emergence of *C. riparius*, exposed in pre-flood sediments, was more reduced compared to the findings of the present study (Fig. 10a). The average number of embryos in snails exposed to native sediments ranged from 14 (control) to 25 (site 23) (Fig. 10d). In contrast to these findings, the embryo numbers in the brood pouch of *P. antipodarum* decreased significantly when the snails were exposed to sediments (sites 15, 19, 23, 24, 26, 28, 30–35) taken before the flood (Fig. 10c). As shown in Figure 10d, the field sediments turned out to have a promoting effect on the embryo production per female compared to the control sediment. Despite the fact that the xenoestrogens BPA and octylphenol caused a stimulation of embryo production in *P. antipodarum* in a 28 d-sediment test, no significant correlation between the embryo production and the concentrations of estrogenic compounds (e.g., BPA, NP) in the field sediments was found. Other factors (e.g., mixture effects of contaminants or abiotic sediment properties such as content of organic carbon, TOC) may also have contributed to the increase of embryo numbers beside the measured xenoestrogens.

The TOC content in the sediments increased significantly after the flood (6.1%) compared to a TOC of 2.6% before the flood. An increase of the TOC was also observed shortly after the extreme flood event in the river Odra. In case of the Elbe sediments the enhanced food supply for detrivorous organisms such as *C. riparius* and *P. antipodarum* may have masked toxic effects of sediment contaminants.
Another explanation for the significantly different biological response of both test organisms before and after the flood is an alteration in bioavailability of pollutants. Bioavailability may have been reduced by adhesion on the organic fraction. For example, a negative correlation of the emergence of *C. riparius* and the sediment toxicity of triphenyltin in fine-grained sediment was found. The post-flood sediments mainly consisted of a major fine grit fraction constituting a major difference to sediments taken before the flood. The median grain size of 19 sampling sites was 115 µm before the flood instead of 22 µm after the flood, resulting in a decrease of bioavailability of toxic substances.

Comparison with data from previous years indicates that concentration levels for substances in sediments returned to pre-flood levels within just a few weeks of the event. This assessment is based on a comparison with data.
from long-term measurement programs. The oldest data were recorded in 1984 using samples taken between Schnackenburg (kilometer 474, on the border between the former East and West Germanys) and Cuxhaven (kilometer 725, Elbe estuary). Further data were gathered immediately after the reunification of the two states, covering the entire course of the Elbe from its source to its mouth. The contaminants under investigation are represented by specific compounds in the List of Priority Substances (Annex X) of the EC Directive (Decision No. 2455/2001/EC). The directive requires EU member states to monitor these compounds. On the basis of these measurement programs, the tributaries Vltava, Bilina, and Mulde, together with industrial and municipal sources, have been identified as significant point sources for individual contaminants or for summed parameters. The region Bitterfeld-Wolfen in the former GDR is very widely polluted, causing a high degree of contamination in the Elbe with dioxins and other organochlorine compounds.

The harbor at Lostau demonstrates the toxic hazard potential emanating from still water zones at times of flooding. Erosion caused during floods exposes deeper sediment layers, thus causing pollutants to be released back into the river system. For this reason the measurement results from this sampling site need careful interpretation. Further input of contaminants is caused by marine transport in the tidal section of the river and activities in Hamburg Harbor (TBT). In the tidal reaches contaminated suspended particulate matter mixes with less contaminated material from the North Sea, leading to a general reduction in contaminant concentrations in estuarine sediments.

The findings of the ecotoxicological studies point up that post-flood sediments of the river Elbe caused both higher emergence rates in the midge and higher numbers of embryos in the mudsnail. Contrary to expectations the toxicity of the sediments decreased after the flood, probably because of a reduction in bioavailability of pollutants as a result of increasing TOC values after the flood.[5]

The floodwater transported a large amount of contaminated material toward the North Sea, but this additional freight appears to have caused only a temporary increase in contaminant concentrations in sediments. This means that the critical situation in respect of many different substances that had already been documented before the flood has neither improved nor become significantly worse. After the main flood had passed, water continued to drain from flooded areas, many of them contaminated, so that contaminants were washed into the rivers. Here, too, no permanent increase in contaminant concentrations in sediments was observed. Potential contamination sources of this kind include older sediments in still water zones.

Chemical analyses were performed on samples taken shortly before and during the main flood wave. The results show that the highest contaminant freights were transported immediately before the peak of the wave because the extremely large volume of water caused massive displacement of material.
As a result an increase in contaminant concentrations occurred in the particulate and aqueous phases.[8] This phenomenon deserves closer attention in planning monitoring programs to document future flood events so that the contamination situation in the Elbe and its tributaries can be determined more comprehensively.

CONCLUSIONS

Analyses of sediment samples taken in September after the flood of August 2002 have provided evidence of a large number of organic contaminants, some in very high concentrations. The substances investigated were dioxins, industrial chemicals displaying endocrine effects, musk fragrances, polybrominated diphenylethers, chloralkylphosphates, organochlorine compounds, polycyclic aromatic hydrocarbons, and organotin compounds, whereby some representatives of these substances are listed in Annex X of the List of Priority Substances of the Decision No. 2455/2001/EC. The tributaries Vltava, Bilina, and Mulde, Hamburg Harbor, and the tidal reaches were identified as significant point sources for contamination. Some substances such as the musk fragrances are introduced into the Elbe via municipal STW; other sources contributing to serious contamination problems in the Elbe and its tributaries are industrial plants (Spolana) and abandoned sites (e.g., the former industrial complex Bitterfeld-Wolfen). In 46% of the samples dioxin TEQ exceeding the “safe sediment value” of 20 pg I-TEQ/g dm were recorded, which may be expected to lead to sustained detriment for fish and water birds.[9] However, the sediment toxicity tests have shown no significant effects on benthic invertebrates such as Chironomus riparius (Insecta) and Potamopyrgus antipodarum (Mollusca) within the exception of increasing embryo numbers in the snail species constituting an effect, which is typically observed under estrogenic exposure.[6] Moreover, using pre-flood sediments, the effects were more obvious.

Finally, it may be concluded that it will not be possible to achieve a significant medium to long-term improvement of the pollution situation in the Elbe and its tributaries without addressing the question of input from sources in the Czech section (e.g., Spolana) and from the contaminated sites around Bitterfeld-Wolfen. Contamination levels from these sources need to be greatly reduced. Appropriate measures should be adopted in the foreseeable future, both to promote a positive and sustainable development in the limnic Elbe and the ecologically labile Wadden Sea zone and also in respect of commercial exploitation of Elbe fish.

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