The Elbe flood in August 2002 – occurrence of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/F) and dioxin-like PCB in suspended particulate matter (SPM), sediment and fish


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Abstract As a result of extreme precipitation in August 2002 major flooding occurred in the catchment area of the rivers Elbe, Vltava (Moldau) and Mulde. Pollutants from industrial sites and from municipal sewage treatment works (STW) entered the Elbe and led to a serious pollution problem in the river. PCDD/F concentrations (in pg WHO-TEQ/g dw) in SPM ranged from 7–150, in sediments from 3–140; the “safe sediment value” of 20 was exceeded in 46% of the samples. 24 eels showed a wide concentration variation for these contaminants. The WHO-PCDD/F+PCB-TEQ values lay in the range from 11–56 pg/g ww, whereby the WHO-PCB-TEQ values were several times higher than the WHO-PCDD/F-TEQ values. The maximum permitted value of 4 pg WHO-PCDD/F/g ww (EU Directive No. 2375/2001) was reached or exceeded in 54% of the individuals. A statistical analysis using data from SPM and sediment samples showed that in the Czech river section the flooding activated a contamination source in the vicinity of the Spolana works. The influence of the tributary Mulde could be clearly demonstrated. Only a major clean-up of the contaminated sites in Bitterfeld can lead to a mid to long term improvement in respect of PCDD/F and dioxin-like PCB input into the Elbe.

Keywords Dioxins; Elbe flood; fish; sediments; SPM

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 (Germany) it flows over a distance of 1,091 km and has a catchment area of 148,268 km² – with about one third located in the Czech Republic and two thirds located in the Federal Republic of Germany. The upper course of the river Elbe is exemplified by about 65 weirs and countless
chemical plants located along the river Elbe as well as along the tributaries. The middle course of the river Elbe runs downstream to the weir of Geesthacht (the only weir in the German section of the river), for the most part traversing the territory of the former German Democratic Republic (GDR). There are a number of chemical plants and large industrial areas in this section of the river, of which the area of Bitterfeld on the river Mulde achieved the most notoriety for excessive contaminant emission. The lower course of the river Elbe comprises the stretch from the weir at Geesthacht to the river’s mouth at Cuxhaven. Running through the international port of Hamburg the river receives a significant load of contaminants and nutrients originating from municipal and industrial sewage, especially in the harbor area (e.g. ship yards). Flow conditions in the estuary are governed both by the river’s discharge and by the tides.

Extreme and widespread precipitation over Austria, the Czech Republic, Slovakia and Eastern Germany led to a disastrous flood in the catchment areas of the Vltava (Moldau), Elbe, Mulde and Danube in August 2002. A particularly sensitive plant, the Spolana chemicals factory in the Czech Republic, was flooded as well as a large number of municipal STW on the Vltava and in the upper and middle courses of the Elbe in Germany. Substances from contaminated areas, industrial and municipal STW entered the Elbe and gave rise to a serious pollution situation of which, however, it is very difficult to assess the extent.

At the center of public attention was the possibility that PCDD/F and dioxin-like PCB were released into the environment from the Spolana site and from contaminated industrial sites from the area of Bitterfeld. There was concern that these highly toxic substances may be introduced directly (Spolana) or indirectly (Bitterfeld) via the Mulde into the Elbe (Hochwasserbericht, 2003). SPM samples were taken from flooded river stretches during the flooding; immediately after the event sediment samples were taken and fish were caught and analysed. Further aspects covered by these investigations were the question as to whether pollution emitters can be determined on the basis of a statistical analysis of congeners patterns in SPM and sediments as well as the accumulation of PCDD/F and dioxin-like PCB in fish – together with an assessment for PCDD/F from the food legislation point of view.

**Methods**

**Sampling**

*SPM.* The water samples were collected during the flooding using various methods: by helicopter (Spolana works, Obristvi, Schmilka and Mulde; ARGE ELBE report 2000), by means of continuous flow centrifugation (Magdeburg, Bunthaus/Zollenspieker and Seemannshöft) or directly from the Elbe (Wittenberg, Magdeburg) and Mulde using a sampling bottle.

*Sediment.* Collection of mainly fine grained, aerobic sediments from upper sediment layers using a Van Veen bottom grab or a spoon spatula. The sampling was done between 09/08/02 and 09/16/02 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.

*Fish.* 24 eels were caught using a fish basket at Gorleben (km 493) in September 2002 after the flooding. All the eels were fit and large enough to be marketable.

**Analytical methods.** Freeze dried samples were soxhlet extracted with toluene after spiking the material with internal standards (17 $^{13}$C$_{12}$ PCDD/F and 12 $^{13}$C$_{12}$ PCB). Measurement
Results and discussion

SPM

Figure 2 shows the occurrence of PCDD/F in SPM from the Elbe and the tributary Mulde during the flooding; the locations of the sampling sites for SPM are shown in Figure 1. Figure 2 records the varying daily contamination situation during the flooding. In addition, the water level on the respective sampling days is shown as a guide. It can be seen that the contamination levels in the area of the Spolana works and a short distance downstream at Obriství, 11 and 7 pg WHO-TEQ/g dw respectively, were not very high, although the works premises were completely flooded. It can be assumed that PCDD/F did emanate from the site, but not as much as was feared.

The analysed WHO-TEQ values at the sampling site Wittenberg, which lies about 40 km upstream of the point of entry of the Mulde into the Elbe, ranged between 4 and 15 pg/g dw and can be regarded as representative of the situation immediately before the influence of the Mulde took effect. In Figure 2 a sharp rise in the concentration can be observed at the mouth of the Mulde near Dessau. The values range from 10 to 160 pg WHO-TEQ/g dw, whereby the values in excess of 100 pg WHO-TEQ/g dw were recorded on 08/17/02,

Figure 2 Concentrations of WHO-PCDD/F in SPM samples from the river Elbe and the Mulde (flood in August 2002)
08/20/02 and from 08/23–08/26/02. These were the days on which the largest material loads were introduced from the catchment area of the Mulde. The most likely source of the flood induced contamination with PCDD/F are the industrial sites in the area around Bitterfeld. By comparison, in August and December 1999 the Hamburg environment administration obtained WHO-TEQ values in 30-day mixed samples (freshly deposed sediments, FDS, Stachel et al., 1995) of 95 pg/g dw and 111 pg/g dw respectively. This indicates that during the flooding the Mulde caused a marked increase in the concentration. It was not possible to calculate freight loads on the basis of water level recordings because the gauges were destroyed by the flood. However, it is clear that the quantities of PCDD/F on SPM transported during the flood must have represented a high level of contamination in the Elbe over a short period.

The influence of the Mulde could be observed at Magdeburg, about 65 km downstream from the mouth of the Mulde, in the form of an abrupt increase in the PCDD/F concentration (Figure 2). The values range from 41 to 87 pg WHO-TEQ/g dw. Peaks of 87, 86 and 82 pg WHO-TEQ/g dw were analysed in the samples from 08/19/02, 08/20/02 and 08/21/02, which corresponds to the period when the water level reached its maximum at Magdeburg (Figure 2). By comparison, in August 1998 a 30-day mixed FDS-sample obtained at Magdeburg returned a value of 51 pg WHO-TEQ/g dw (Hamburger Umweltberichte 57/99).

Figure 2 also shows the PCDD/F values recorded at the two sampling sites in Hamburg, Bunthaus/Zollenspieker and Seemannshöft. It can be seen that the maximum values at Bunthaus/Zollenspieker are higher than those recorded further upstream at Magdeburg, a result which was also revealed in investigations which took place in 1994 (Götz et al., 1998). The range of WHO-TEQ values for this sampling site was 56 to 118 pg/g dw, whereby the values in excess of 100 pg/g dw were recorded on the 08/24/02 and the 08/28/02. These peaks correspond to the highest water levels at Neu Darchau (Figure 2). The sampling site Seemannshöft returned rather lower WHO-TEQ values in the range of 52 to 87 pg/g dw.

Values of 73 and 66 pg WHO-TEQ/g dw (30-day mixed samples, FDS) were recorded in single samples at the site Bunthaus in 1998; in 1999 the values were 33 and 31 pg/g dw. At Seemannshöft the corresponding WHO-TEQ values were 12 and 22 pg/g dw in 1998 and 16 and 18 pg/g dw in 1999 (Environmental and Health Authority, Hamburg, unpublished results). Thus both sampling sites returned significantly lower values in previous years. The high WHO-TEQ values occurring during the flood are probably mainly due to the remobilization of PCDD/F of older, previously laid down sediments from river zones which are normally not subject to strong currents; the unusual flow conditions led to a partial resuspension of the sediments.

**Sediment**

In September 2002 aerobic sediment samples from the upper sediment layers were taken from 37 sampling sites along the Elbe and the mouths of relevant tributaries between Obristvi (Czech Republic) and Trischendamm (Wadden Sea zone of the North Sea), in order to document the PCDD/F situation after the flood. 11 sites are in the Czech Republic, 26 sites on the German section of the river. The large number of sites was chosen with the aim of creating a solid information base with which to evaluate the findings. Figure 1 shows the location of the sites; the results are shown in Figure 3. The picture revealed by Figure 3 generally corresponds with the pollutant distribution during the flooding as shown in Figure 2 (SPM).

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 dw. At the mouth of the
Mulde 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 dw respectively. After this the values show an almost continuous decline in the direction of the North Sea on account of mixing with less polluted particles. Thus at the weir at Geesthacht the level reduced to 45 pg WHO-TEQ/g dw and in the tidal reaches a further reduction to approximately 40 pg WHO-TEQ/g dw (Bunthaus) and 7 pg WHO-TEQ/g dw (Trischendamm) was recorded.

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 dw (Evers et al., 1996) provides a basis for consideration. This value is exceeded in 17 of 37 samples (46%). With the exception of the mouth of the Bílina 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” on account of the combination of the highly contaminated sediments with other less polluted sediments.

Fish

Eels (Anguilla anguilla) accumulate strongly lipophile substances such as PCDD/F and PCB on account of the large proportion of fats in their physical constitution. This renders them very suitable as indicators for environmental monitoring. In addition, they constitute a part of the human diet and can therefore represent a danger to human health if they contain excessive amounts of toxic substances.

After the flooding 24 eels of marketable size were caught in the middle course of the Elbe near Gorleben (km 493) in September 2002. The muscle tissue was analysed for PCDD/F and dioxin-like PCB. The results are presented in Figure 4. The distribution of the WHO-PCDD/F+PCB-TEQ values amongst the individual specimens is remarkably wide. The WHO-PCB-TEQ values are several times higher than the WHO-PCDD/F-TEQ values. The WHO-PCDD/F+PCB-TEQ values lie in the range of 11 to 56 pg/g ww, with a median value of 29 pg/g ww.

The EC Directive No. 2375/2001 provides the basis for an evaluation in respect of food-stuff legislation aspects. The maximum permitted value of 4 pg WHO-PCDD/F-TEQ/g ww was found or exceeded in 13 eels (54%). In view of the EC’s planned inclusion of dioxin-like PCB and alteration of the maximum permitted values, it may be assumed that many more of the samples would exceed the limits which are to be expected in future.
By comparison the data involves muscle tissue samples from eels caught in 1996, 1998 and 1999. Thus an eel pool-sample from the Elbe dating from 1996 consisting of five individuals caught between Zollenspieker and Geesthacht yielded a level of 19 pg WHO-PCDD/F-TEQ/g ww and 24 pg WHO-PCB-TEQ/g ww (three non-ortho PCB: No. 77, 126 and 169). In 1998 eel pool-samples were taken from areas around Geesthacht (10 individuals), Bunthaus (20 individuals) and Mühlenberger Loch (km 635, 10 individuals) which returned the following results: for WHO-PCDD/F-TEQ 5.8 pg/g ww, 22 pg/g ww and 7.3 pg/g ww respectively; for WHO-PCB-TEQ the figures were 28 pg/g ww, 59 pg/g ww and 37 pg/g ww respectively. The sampling sites are all located in the Hamburg area. In a further investigation of 6 individual eels caught in 1999 in Hamburg Harbor WHO-PCDD/F-TEQ/g ww levels between 2.0 and 6.9 were recorded. Generally, it may be observed in view of these results that the contamination of eels with PCDD/F and dioxin-like PCB is not a new phenomenon and appears to be 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 to the one where they were caught.

**Statistical analysis**

These analysis results provided the raw data for a structural analysis of the congener patterns and the correlation of SPM and sediment samples (n = 73) to possible emission sources using a newly developed statistical dilution model. The basis of this structural analysis is the assumption that, within certain wide limits of tolerance and despite dilution effects, concentration patterns for different congeners should remain stable from one sampling site to another if no major emission points exist between them. Thus a statistically significant change in the distribution of the concentrations can be taken as an indication that either further emission sources exist between the sampling sites or that a modification in the river morphology occurs (such as a change in sediment grain size distribution and matrix or differing sedimentation rates). A further assumption is that where such modifications occur, the original concentration distribution persists in dilution, so that the resulting congener pattern still provides an image of overlapping or combined pollutant distributions.

The analysis revealed significant changes either upstream or downstream of the following sampling sites: Spolana (km –120, SPM, 08/16/02); Neratovice (km –117 to –118, sediment 05/13/02); Dolni Berkovice (km –104); Vanov/Streckov (km –41); Pillnitz (km 43); Wittenberg (km 220); Breitenhagen (km 290); Lostau (km 336); Sandfurth (km 363); Arneburg (km 409); Hitzacker (km 522); Tespe (km 579) und Köhlfleet (Hamburg Harbor).

**Figure 4** Concentrations of PCDD/F and dioxin-like PCB in 24 eels (muscle tissue) from the river Elbe (sampling site Gorleben, km 493). The eels were caught in September 2002.
Similarly, the samples taken further downstream show significantly different congener patterns: the mean PCDD/F concentrations are somewhat higher than in the preceding samples. These samples display three different congener patterns with varying contributions to the summed TEQ value. In addition, the samples from the sampling sites Pillnitz, Wittenberg, Breitenhagen, Lostau, Sandfurth, Arneburg, Hitzacker, Tespe and Köhlfleet (Hamburg Harbor) each show significant variations in comparison with the concentration distributions of the preceding samples. This is particularly marked in the case of the sample from Breitenhagen: with the exception of OCDD all the congeners are present in concentrations several times higher than in the samples from further upstream. Only at Sandfurth do the OCDD concentrations begin to increase, whereas the other congeners already show a decrease. These variations in behavior can only be explained in terms of further emission sources and extreme dilution effects. The sample from the sampling site at Tespe provides a particularly clear example: changes in the concentration patterns of HpCDD and OCDD imply strong dilution effects – but this is implausible, especially in view of the fact that the congener patterns in Hamburg correlate well with those from Magdeburg. Thus the statistically significant discontinuities could be attributable not so much to additional emission sources, but rather to variations in sedimentation conditions.

Conclusions

PCDD/F and dioxin-like PCB were found in various matrices of the river Elbe. In some SPM samples taken during the flooding in August 2002 very high PCDD/F values in excess of 100 pg WHO-PCDD/F/g dw were measured; the respective pollutants probably originated in the river Mulde or came from resuspended sediments washed out of still water zones. The quantities of PCDD/F transported with the floodwater must have been very considerable. The industrial plants and contaminated sites from the area around Bitterfeld represent an important contaminant source, whereas it appears that the Spolana works, which were completely inundated by the floods, only contributed a relatively small amount to the overall pollutant load.

Sediment samples taken after the flooding from both the Czech and the German sections of the river and the mouths of major tributaries deliver a similar picture: The Mulde and thus the Bitterfeld region were shown to be the main source of these substances. Using the “safe sediment value” of 20 pg I-TEQ-PCDD/F/g dw as a yardstick, it is clear that the Elbe is still seriously polluted with PCDD/F. Therefore it is to be concluded that a noticeable reduction in PCDD/F levels can only be achieved through a major clean-up program for the Bitterfeld problem sites.

In a number of analyses, both recent and older, involving muscle tissue from eels a broad scattering of PCDD/F results was revealed. In 54% of samples from individuals caught in September 2002 from the river near Gorleben the EC maximum permitted value of 4 pg WHO-PCDD/F/g ww was exceeded. The contamination with WHO-PCB-TEQ is markedly higher than with WHO-PCDD/F-TEQ, and for these contaminants no maximum values have yet been established.

The results of the statistical analysis on the basis of congener patterns enabled SPM and sediment samples to be correlated to possible emission sources. The model showed that the flooding activated a new contamination source in the area around the Spolana works and the sampling site Obristvi. In addition the influence of the river Mulde could be clearly shown. In the case of the sampling site at Tespe significantly abrupt changes in congener distribution appear more likely to be due to varying sedimentation conditions than the influence further emission sources.
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References