PCDD/Fs and Dioxin-like PCBs in Soils after the Flooding of River Elbe and Mulde in 2002

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Introduction

On account of the Elbe and Mulde flooding in 2002 the UFZ Centre for Environmental Research Leipzig/Halle co-ordinated an ad hoc project entitled 'Pollutant studies following the flooding in August 2002 - determining the potential hazards in the Elbe and the Mulde' (BMBF ad-hoc-Verbundprojekt Elbe Hochwasser 2002). In the frame of this project, the Institute of Environment and Sustainability of the Joint Research Centre of the European Commission addressed the issue of the contamination of PCDD/Fs and dioxin-like PCBs in flooded soils. The objective of this survey was to assess the contamination of urban and agricultural soils in relation to current land use, to estimate the specific impact of the flooding in 2002 and to link the contamination data to possible sources.

Methods and Materials

51 top soil samples from flooded areas and 3 sediment samples were sampled along the river Elbe between Dresden and Lauenburg (Elbe km 90 – km 568) and the river Mulde between Nossen and the inlet into river Elbe at Dessau**.** Samples from behind broken dams were from flooded agricultural areas, playgrounds, private gardens, sport areas etc, whereas the samples from the riverbanks were pasture areas. All soil samples were taken according to the procedures laid down in the German Soil Protection Ordinance[1] (0-10 cm in playgrounds and pasture soils, 0-30 cm in private gardens and agricultural soils). The soil and sediment samples were freeze dried, disaggregated and sieved to a grain size <2mm. Analysis of PCDD/Fs and DL-PCBs was based on isotope dilution using HRGC-HRMS for quantification. The applied methodology follows a combination of USEPA method 1613 for PCDD/Fs (where 13-C labelled OCDF was added to the proposed 13-C surrogate mixture) and USEPA method 1668A for the DL-PCBs. A mixture of all C13-labelled WHO-TEQ relevant dioxin and PCB congeners was added to 30 g dry weight sample prior to extraction. Extraction was done in 300 ml n-hexane/acetone (220/30; vol/vol) using Soxhlet extractors for 48 h. Extract purification was executed with an automated clean-up system (Power-Prep P6, from Fluid Management Systems (FMS) Inc., Watertown, MA, USA). The chromatographic principle is based on the method proposed by Smith, Stalling and Johnson [2]. A detailed description of the Power-Prep method and its performance is given by Abad et al. [3]. The GC system was a HP-6890 (Hewlett Packard, Waldbronn, Germany), using a split/splitless-injector with borosilicate liner (4 mm i.d.) (Zwingen, Switzerland). The samples were analysed on two capillary columns with different polarities to detect possible co-elution of TEQ-relevant congeners

with non-toxic congeners present in the extract. (DB-5MS, J&W Scientific, Folsam, CA, USA and RTX-2330, Restek, Belleforte PA, USA). The GC was coupled with a VG Autospec Ultima mass spectrometer (Micromass, Manchester, UK) operating in EI-mode at 34 eV with a resolution of >10000. Two masses in the M+ isotope cluster were monitored for each analyte and each internal standard. Whenever interferences were encountered, more masses were monitored.

Results and Discussion

In the following, the results are discussed on a dry weight base in TEQ. The congener specific data set as well as information on other kinds of pollutants can be obtained from the final report of the BMBF project [4].

PCDD/Fs (I-TEQ) in soils in relation to German guidelines for land use [5]: In the investigated pasture areas (green signature) almost all soils exceed the corresponding guideline value of 5 pg/g I-TEQ (Figure 1).

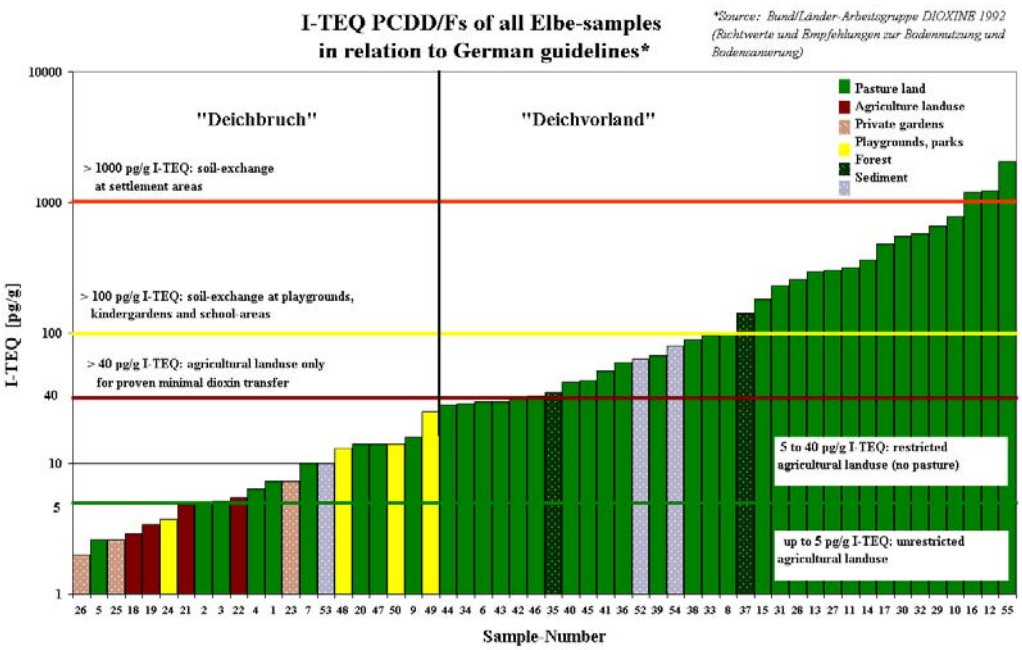

Figure 1: Overview on the I-TEQ from PCDD/Fs for all samples in relation to land use and the German guideline values for soil

The maximum I-TEQ was around 2100 pg/g in sample No.55 (Elbe-km 477), which means an excess of the guideline by more than a factor 400. In agricultural soils (brown signature) no excess of the guideline value of 40 pg/g was observed, maximum I-TEQs were around 5 pg/g. In children's playgrounds, parks, and sports fields (yellow signature) no excess of the guideline value was observed. The maximum I-TEQ of 25 pg/g at a playground (sample No. 49) is well below the guideline value of 100 pg/g.

The significance of the flood in 2002 –areas behind broken dams compared to riverside soils:

Figure 1 shows that high contaminant levels of PCDD/Fs were detected exclusively in regularly flooded areas riverside from the dam (labelled as 'Deichvorland'). At all the urban and agricultural sites behind the dam, which were affected only once in 2002 (labelled as 'Deichbruch'), the detected levels are in a range, which is typical for this type of land use. This indicates that the 2002 flooding had only a minor impact on the soil contamination with PCDD/Fs. The different history of contamination becomes also visible when comparing the PCDD/F congener distributions in urban soils flooded only once in 2002 to the congener profiles present in the river banks: In Figure 6 an exemplary comparison is made for sample No. 7, a pasture area at km 325, flooded only in 2001 and the river banks close by, at km 301. The congener distribution at the 325 km site flooded only in 2002 has a considerable TEQ contribution from PCDDs whereas the riverbank at km 301 shows a significantly different profile, which is dominated by PCDFs instead.

Contribution of PCBs to the combined WHO TEQ for PCDD/Fs and DL-PCBs: Figure 2 displays the relative TEQ contribution from DL-PCBs. The samples are plotted in the same order as in Figure 1 and the vertical read lines indicate the concentration range of the combined WHO-TEQ from PCDD/Fs and DL-PCBs. In most cases and especially at higher contamination levels, the TEQ contribution from DL-PCBs is negligible. In the group below 10 pg/g WHO-TEQ the median contribution of PCBs is 13 %. The 3 higher contaminated samples were soils of urban character such as a kindergarten, a sports ground, and a private garden. In the group between 10 and 100 pg/g WHO-TEQ the median contribution of PCBs is 10 %. The 4 higher polluted samples were one sediment and 3 soils from pasture areas.

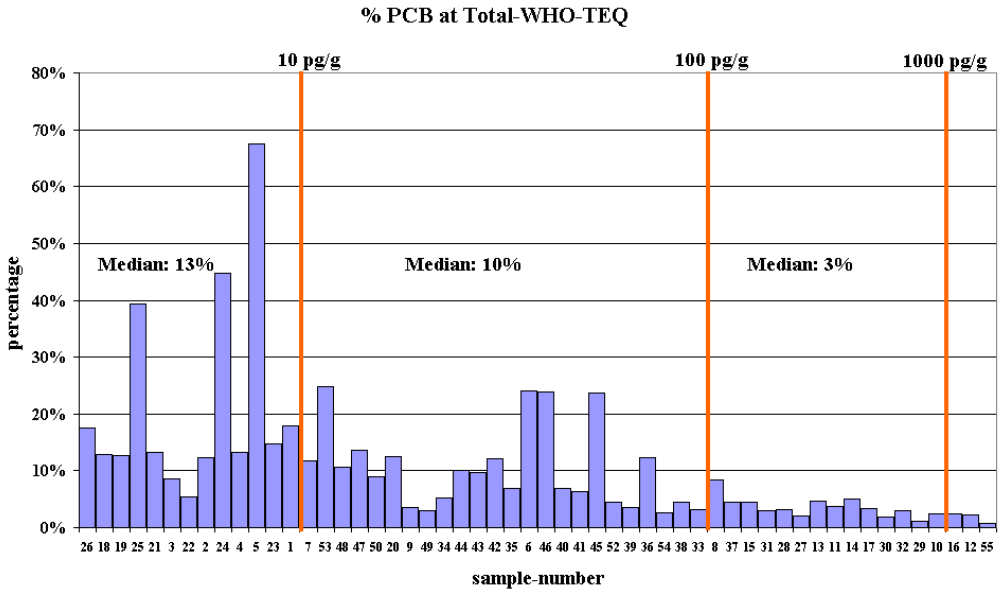

Figure 2: Contribution of dioxin-like PCBs to the WHO-TEQ (PCDD/Fs and DL-PCBs)

In the group above of 100 pg/g WHO-TEQ the median contribution of PCBs is only 3 % with no sample exceeding a contribution of more than 7%. The maximum concentration of DL-PCBs was 28 pg/g WHO-TEQ in a playground soil. Obviously the contamination with DL-PCBs is of minor importance in the catchments of Elbe and Mulde. The declining contribution of DL-PCBs to the WHO TEQ at higher concentrations suggests that the PCB contamination in soil originates from different sources than PCDD/Fs.

Elbe downstream profile of PCDD/Fs in riverbank soils: Downstream contaminant profiles are a useful tool for identifying sources along the riverside and to estimate whether the tributary rivers play a significant role or not. Although the number as well as the spatial distribution of the samples taken in 2002 is far from being sufficient to answer this question consistently, some hypotheses may be proposed. The following discussion is limited to sampling sites Elbe downstream of km 114 (No. 20) and the Mulde downstream of Mulde-km 128. All upstream samples were taken behind the dams and are therefore not comparable with those riverbank soils affected regularly by floods. In Figure 3 the WHO-TEQs of PCDD/Fs along river Elbe are plotted in a downstream order together with an indication of the inlets of the main tributaries Mulde, Saale and Havel. The congener distributions of PCDD/Fs plotted in Figure 4 can serve as an additional source of information to identify sources. The Elbe soils prior to the inlet of river Mulde show moderate contamination with PCDD/Fs. The WHO-TEQ found at km 114 (right-hand side) was 15 pg/g, which doubles up along with the next 127 km downstream: At Elbe-km 241 (left-hand side) an Ø of 30 pg/g (median of 31 pg/g, n=5) was detected. Further Elbe downstream, at km 285 (right-hand side), the WHO-TEQ doubles again (Ø of 75 pg/g, median of 64 pg/g, n=7).

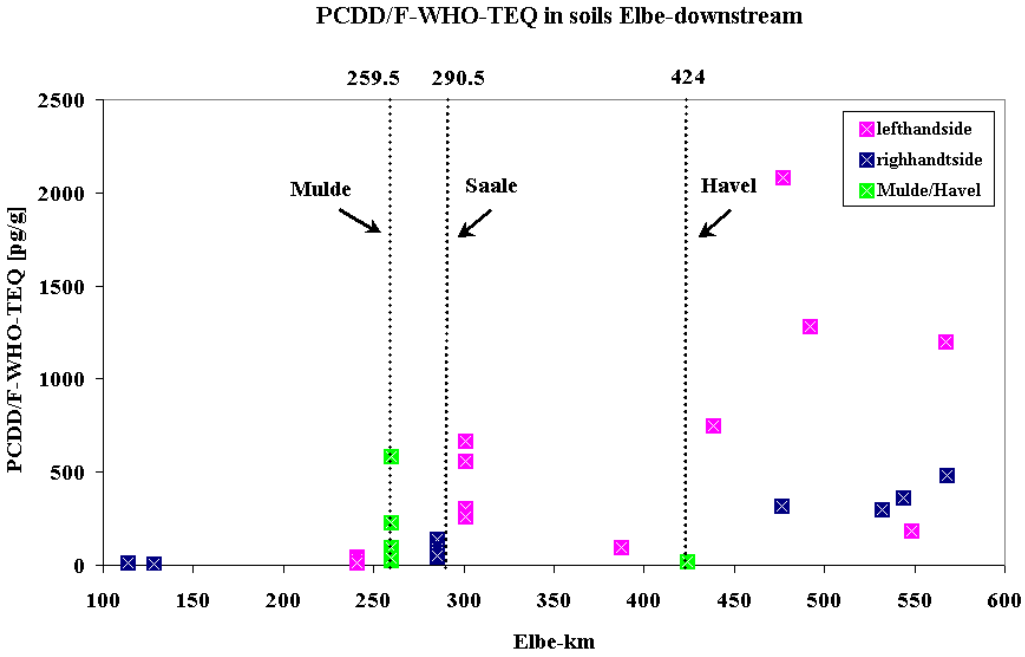

Figure 3: Elbe-downstream profile of PCDD/F contamination in soils riverside of the dams

The rise in the contamination levels 25.5 km after the inlet of river Mulde apparently results from the higher contamination present in the Mulde catchments. These findings are supported by the results from the samples (No. 31-35) at Mulde-km 128 shortly before the inlet of river Mulde into river Elbe (Elbe-km 259.5), where an Ø of 194 pg/g WHO-TEQ (median of 96 pg/g, n=5) were found. The influence of the Mulde on the PCDD/F content in the river Elbe is furthermore confirmed by a shift within the congener distribution in river Elbe downstream of the Mulde inlet (Figure 4). A considerable rise in PCDD/F contamination was observed only 11 km downstream the Saale inlet: At Elbe-km 301 (left-hand side), an Ø WHO-TEQ of 446 pg/g (median of 432 pg/g, n=4) was observed. Again the congener distribution of PCDD/Fs shifts after the inlet of river Saale. Both observations indicate an additional contribution from contaminants present in the river Saale catchments, although no confirming soil data from the Saale catchments have been available in this project. Interestingly, the congener profiles found in the Mulde soils are very similar to those detected in the Elbe soils after the Saale. Apparently, both Elbe tributaries are impacted from similar kinds of industrial sources. The dominance of the penta- and hexachlorinated furans in the TEQ, together with the appearance of octachlorodibenzofuran indicates that metallurgic processes (especially along Mulde and Saale) are an important source of PCDD/Fs [6].

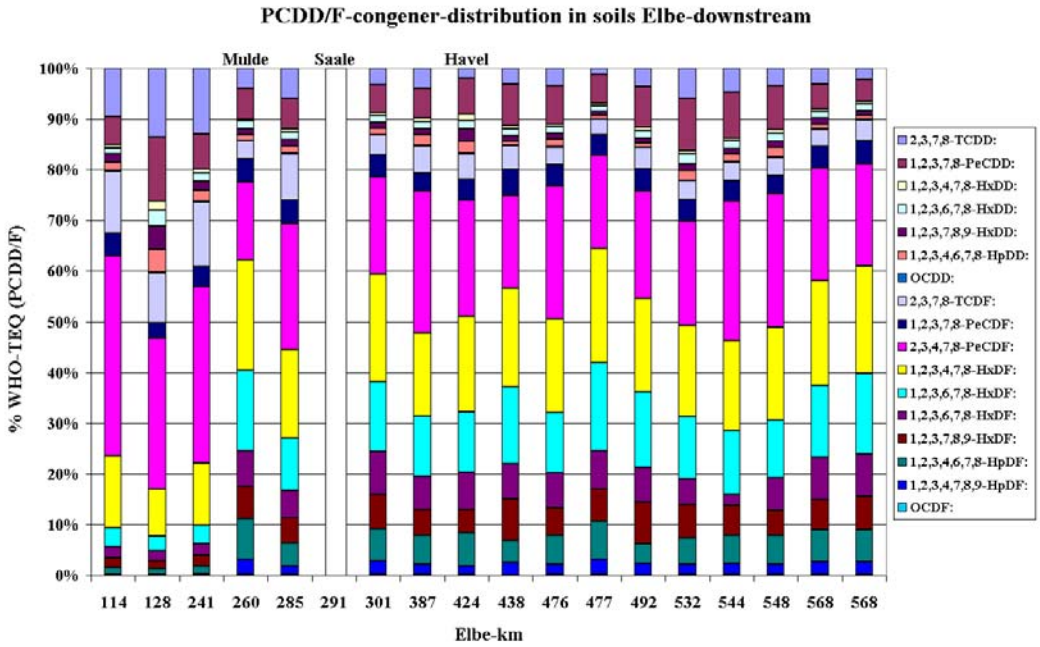

Figure 4: Elbe–downstream profile of PCDD/F-congener-distribution in soils riverside of the dams

The congener distributions at all investigated riverbank soils downstream the Mulde and Saale inlets show similar patterns indicating that metallurgic processes play a major role in PCDD/F contamination along the whole Elbe downstream of km 260. At Elbe km 438, 14 km after the inlet of river Havel, the WHO-TEQ in soil raised to 774 pg/g left-hand side of river. However, this time the increase cannot be related to inputs from river Havel, since the WHO-TEQ measured in the

Havel-associated soils was only 17 pg/g. Further downstream the Elbe, at km 477, another contamination peak was found on the left-hand side of the river. These riverbank soils contained more than 2000 pg/g WHO-TEQ. Close by, but on the right-hand side of the river at km 476 the WHO-TEQ was only 320 pg/g. Fifteen km further downstream at km 492 (left-hand side), 1300 pg/g WHO-TEQ were measured in the riverbanks. Further downstream the WHO-TEQs stabilize in the range between 180 and 430 pg/g until sample No 16 at km 567.5, where another remarkable rise up to a concentration of 1200 p/g WHO-TEQ in the riverbanks left-hand side can be observed. The sample from the close-by riverbanks right-hand side at km 568 (No. 17) shows a lower PCDD/F contamination of 480 pg/g WHO-TEQ. It is notable that the downstream concentration development of PCDD/Fs on a carbon weight base shows the same tendency as discussed above for the concentrations calculated on a dry weight base. This indicates that the observed gradients in PCDD/F concentrations on a dry weight base did not result from spatial variations in the sedimentation rate of suspended organic material and the associated PCDD/Fs. The spatial variations measured in 2002 are most probably due to different intensity of emissions in the past.

Conclusions

From the available data it can be concluded that no action needs to be taken regarding the PCDD/Fs present in the investigated urban and agricultural areas flooded only in 2002. In contrast, grazing as well as animal feedstuff cultivation on all pasture areas riverside from the dams should be avoided due to the significant excesses of the existing guideline values for PCDD/Fs. The high PCDD/F levels that are present at the riverside of the dams, represent a cumulative memory from past floods rather than a recent contamination from 2002. The downstream profile of PCDD/Fs in the riverbank soils upstream the Havel inlet indicate a strong influence of the rivers Mulde and Saale on the contamination of the Elbe with PCDD/Fs. From the congener distributions of PCDD/Fs it seems the metallurgic processes were the dominating sources. In contrast, the river Havel does not seem to be notably polluted. Downstream the Havel inlet, where the highest pollutant levels of PCDD/Fs were observed the situation is less clear. The existence of additional sources is obvious. This area needs more detailed exploration regarding these sources. It should be noted that the WHO-TEQ in the riverbanks left-hand side of River Elbe tends to be higher (180 – 2100 pg/g) than at the right-hand side (300 – 480 pg/g). Congener profiles in the riverbanks downstream of Elbe-km 290 show comparable patterns similar to the patterns detected in the riverbanks of river Mulde.

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