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Dioxin in the river Elbe

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HIGHLIGHTS

- In the 1940s the Elbe was probably contaminated with dioxin from a magnesium plant.
- Nowadays the Elbe is contaminated from dioxin emissions from its floodplains.
- The dioxin patterns of the magnesium production and the Elbe are similar.
- Extreme floods do not contribute significantly to the dioxin level in the Elbe.
- It seems practically impossible to perform a dioxin remediation in the Elbe.

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ABSTRACT

This paper provides a macro-analysis of the dioxin contamination in the river Elbe from the 1940s to the present. Based on different data sets, the historic dioxin concentration in the Elbe has been reconstructed. For the section between the tributary Mulde and Hamburg, during the 1940s, we find a concentration of about 1500 pg WHO-TEQ g^{-1}. We argue that this dioxin contamination was caused mainly by emissions from a magnesium plant in Bitterfeld-Wolfen, whose effluents were discharged into a tributary of the river Mulde which flows into the Elbe. Dioxin pattern recognition with neural networks (Kohonen) confirms this. A model simulation shows that a hypothetical dioxin concentration of 10,000 pg WHO-TEQ g^{-1} in the tributary Mulde could have caused the reconstructed dioxin concentration of 1500 pg WHO-TEQ g^{-1} in the Elbe. The recent dioxin concentration (about 25–100 pg WHO-TEQ g^{-1}) in the river Elbe, downstream the tributary Mulde, originates, according to our hypothesis, from emissions of the banks and the highly contaminated flood plains (transport of the particle bound dioxin). As other possible dioxin sources, the following could be excluded: the dioxin concentration in the Mulde, groynes, small ports, sport boat harbours, and extreme floods. Our hypothesis is supported by the results of pattern recognition techniques and a model simulation. According to these findings, we argue that remediation efforts to reduce the dioxin concentration in the river Elbe are unlikely to be successful.

1. Introduction

The river Elbe (Fig. 1a, Fig. 2a and Fig. 3a) is one of the major rivers in Central Europe. It originates in the Krkonoše Mountains of north-western Czech Republic before traversing Bohemia (Czech Republic), then Germany and flowing into the North Sea at Cuxhaven, 110 km northwest of Hamburg (total length: 1094 km, catchment area: 148,268 km^2, 25 million people) (FGG Elbe).

For the most part, its dioxin concentration in the section between the mouth of the tributary Mulde and Hamburg is higher than the concentration in the river Rhine (Umweltbundesamt, 2007) and in the river Danube (Umlauf et al., 2011).

Several publications have discussed the dioxin contamination of the river Elbe basin (Wilken et al., 1994; Götz et al., 1996, 1998; Götz and Lauer, 2003; Umlauf et al., 2005; Stachel et al., 2006; Götz et al., 2007; Lechner, 2007; Bunge et al., 2007; Umlauf et al., 2010, 2011; FGG Elbe, 2011, LHW Sachsen-Anhalt, 2007, 2012, Tauw, 2013; Baborowski and Heininger, 2013; Förstner et al., 2016).

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In 1994, Wilken et al. reported that it could not be excluded that the high dioxin contamination in the floodplains of the Elbe results from dioxin transport throughout the river. The authors addressed chloralkali electrolysis processes at the chemical production plant in Bitterfeld as a possible dioxin source. An evaluation with the cluster method neural networks (Kohonen) led to the hypothesis that the source of a considerable part of the dioxin pollution of the Elbe and its floodplains had been thermic processes in the metallurgical industry like magnesium and copper production at Bitterfeld. (Götz and Lauer, 2003).

In this study we reconstructed the historical dioxin contamination in the river Elbe, its tributaries and its floodplains at the Elbe section between the mouth of the Mulde and Hamburg (about 350 stream km) and gave a hypothesis of its cause. We believe this will help us to get a better understanding of the cause of the recent Elbe dioxin contamination. In the above mentioned literature, there are some suggestions to explain the recent dioxin concentrations in this Elbe section: elevated dioxin concentrations in the tributary Mulde, contaminated sediments in side structures of the river Elbe like groynes and small ports and extreme floods. In this study, we critically examine these proposals and investigate if they can be falsified. Our methodological approach is first to collect all the available significant measured dioxin data, then to arrange and classify them in tables and figures, and evaluate them by simple statistical methods. At a second stage of evaluation, we apply a simple mass balance model and extended cluster analysis with neural networks (Kohonen). Based on our results, we briefly address the question of whether it is possible to perform a remediation to reduce the dioxin concentration in the river Elbe.

2. Methods

2.1. Dioxins

For simplicity, the two groups of substances polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are referred as dioxins in this paper.

The dioxin concentrations are reported as toxicity equivalents by the World Health Organization: WHO-TEQ (Van den Berg et al., 2006). In some few cases where we couldn't transform the former I-TEQs (NATO/CCMS , 1988) into WHO-TEQs the original I-TEQs are reported here.

Dioxins in the rivers were measured in the solid phase (sediment, SPM (suspended particulate matter) and FDS (freshly deposited sediments, four-week composite samples)) because in the water phase the concentrations are too low, only a few fg/L were measured in the river Elbe (Götz et al., 1994).

2.2. Data sources of the dioxin samples

2.2.1. Data sources of the 388 dioxin samples used for cluster analyses with neural networks (Kohonen)

To perform pattern recognition with neural networks (Kohonen) we could only take dioxin data sets which include the concentrations of the 17 dioxin toxic congeners together with the 8 Cl_4 to Cl_7 dioxin homologues (see chapter 2.3). We took two kinds of sample groups: dioxin exposition samples taken in the Elbe catchment, and second external sample groups from potential dioxin sources. If there were similarities between the sources and the expositions in the Elbe catchment, we analysed if there could be a causal relationship. In comparison to a former cluster analyses (Götz and Lauer (2003) in this study we used for the sample group of the Elbe and its tributaries recent samples from the year 1998–2008. New is the sample group “dated sediment core samples from the Elbe” which may allow distinguishing between the historic and recent dioxin contamination of the Elbe. The sample groups “floodplains of the Spittelwasser”, “river Mulde (tributary of the Elbe)” were completed by more recent samples.

In the dioxin source data set the sample groups “PCP (pentachlorophenol)” and “magnesium production (Norway)” were supplemented by 5 - respectively 16 samples, thus putting the cluster analyses on a broader foundation. The detailed justification that the magnesium samples of the Norwegian plant are representative for the dioxin emissions of the magnesium plant in Bitterfeld is described in Table SM.1 as Supplementary material. The other dioxin source samples were the sample groups “HCH production”, “sinter plants” and “chloralkali process”. We also collected dioxin patterns of the dioxin sources “PCB” and “pulp industry”, but these dioxin patterns were not stable, that means by test cluster analysis these patterns didn't stay in one cluster, they were distributed over different clusters. Therefore these sample groups were not suitable for cluster analyses.

The sources of the 388 samples are listed in Table 1 together with the sampling location, the matrix of the sample, the unit, the year of sampling, the number of samples in each group and the references in which the data were published, and the study design and the analytical methods are described. Additionally all measured dioxin concentrations of each of the 388 samples - the 17 toxic congeners and the 8 Cl_4 to Cl_7 homologues - together with the calculated WHO-TEQs are given in Table SM.2 as Supplementary material.

2.2.2. Data sources of the other dioxin samples

In this paper we also evaluated dioxin concentrations of lots of other dioxin samples. But for these samples data of the 8 Cl_4 to Cl_7 dioxin homologues were not available. For this reason, these samples could not be added to the data set of the 388 samples for the cluster analyses. The sources of these samples are described in the references given when these dioxin samples were mentioned first.

2.3. Cluster analyses with neural networks (Kohonen)

We conducted cluster analyses with neural networks (Kohonen) with dioxin concentrations of 388 dioxin samples in order to examine the similarity of dioxin patterns between different sample groups. First a transformation of the measured concentrations of the 17 highly toxic (2,3,7,8-substituted) dioxin and furan congeners for each sample of the 388 samples was performed (Hagenmaier et al., 1994). The concentrations of the individual congeners were divided by the corresponding Cl_4 to Cl_7 dioxin homologues. As 18th variable, the quotient of PCDD concentration and the total concentration of PCDD plus PCDF was added. A 388 (rows) x 18 (columns) matrix was obtained. Mathematical, each row is a vector with 18 components, which are the 18 transformed dioxin concentrations.

Two levels of data reduction were performed. At the first level the 388 $\times$ 18 data matrix was clustered with a 7 $\times$ 7 Kohonen network (49 neurons). As output a 49 $\times$ 18 matrix (49 codebook vectors, 18 weighting variables) was obtained. At the second level a clustering of the 49 codebook vectors was conducted with the method of the hierarchical cluster analysis (measure of similarity: cosine; clustering method: linkage between the groups) in order to generate cluster solutions. The applied SPSS computation program produced a table in which the 388 dioxin samples together with their cluster membership were listed.

In summary, the dioxin patterns that are the 18 transformed dioxin concentrations of each of the 388 samples were aggregated into clusters in such a way that the patterns in any cluster are as