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Dioxin (PCDD/F) in the River Elbe - investigations of their origin by multivariate statistical methods

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1. Introduction

The aim of this investigation is to find out the sources of the dioxin contamination in the solids (sediments and suspended particulate matter, SPM) of the River Elbe as well as in soils of the flooding areas of the Elbe using multivariate statistical methods.

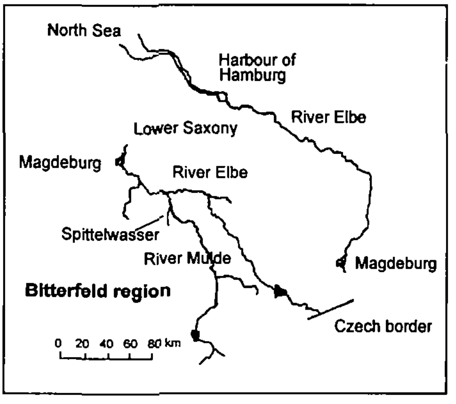

Figure 1: Map of the River Elbe from the Czech border to the North Sea

The I-TEQ (international toxic equivalents) concentrations in the solids of the River Elbe between the Czech border and the tributary Mulde are very low (10.-.15 ng /kg d.w.) [1]. The River Mulde flows through the region Bitterfeld, an industrial center of the former German Democratic Republic. In sediments of the River Mulde and in those of the River Spittelwasser - which ends in the River Mulde- dioxin concentrations up to 600 ng I-TEQ/ kg d.w. and up to 3000 ng I-TEQ/ kg d.w. respectively were found. In soil samples of the flooding areas of the River Spittelwasser up to 180 000 ng I-TEQ/ kg d.w. were detected [2,3]. Downstream of the highly polluted River Mulde, the I-TEQ concentrations in the Elbe increase. There is a further increase until the river meets the area of Hamburg (ca. 100 ng I-TEQ/kg d.w.). Downstream of Hamburg up to the North Sea the concentrations are much lower (2-22 ng I-TEQ/kg d.w.). A possible explanation for this decrease could be the dilution of more contaminated limnic SPM with less contaminated marine SPM [1,4]. Beside that, high concentrations of dioxin were measured in soil samples of the flooding areas of the River Elbe in Lower Saxony (up to 2300 ng I-TEQ/ kg d.w.) [5].

2. Data base description

For the statistical investigation, the dioxin data of the following samples were taken into account: 21 sediment and SPM samples of the River Elbe (from the Czech border up to the North Sea, excluding the harbour of Hamburg), 17 sediment samples of the harbour of Hamburg [1,4], 21 soil samples of the flooding areas of the River Elbe in Lower Saxony [5] and 34 sediment and soil samples of the Bitterfeld region [2,3]. Additionally, we used 6 sediment samples of surface waters in Hamburg [4], which do not communicate with the River Elbe. Dioxin values of samples of the following dioxin sources were also used: Mg-production [6], „Kieselrot“ [7,8], sintering plants [9], PCP [10], PCB [11,12], chloralkali process [13], a herbicide plant (Hamburg, now closed) [14], municipal waste incinerators (MWI) [15,16], urban air (Hamburg) [17], deposition (Hamburg) [18] and sewage sludge (Hamburg) [19]. Finally the whole data pool consists of 137 samples.

3. Multivariate statistical methods

The statistical methods have been performed in order to find out the differences and similarities in dioxin profiles between samples of different origin.
The statistical calculations were based on the profiles of the relative congener concentrations: the ratio of the concentration of the 2,3,7,8-substituted congeners to the concentration of the corresponding homologue groups, the concentrations of OCDD and OCDF divided by the concentrations of PCDD and PCDF and the quotient PCDD/(PCDD + PCDF) - in total 18 variables.
The following statistical methods have been applied: factor analysis, hierarchical cluster analysis and K-means cluster analysis and the combinations factor analysis/hierarchical cluster analysis and factor analysis/ K-means cluster analysis [20,21].
With the factor analysis, the 18 dioxin variables were reduced by a mathematic transformation to 3 to 5 factor variables. The factor score plot of the first two factors displays similarities and differences in the dioxin congener profiles. The factor analysis (principal components) was applied either with or without rotation (varimax). With the results of the hierarchical cluster analysis (either with or without standardisation of the values of the variables with a mean 0 and a standard deviation of 1, squared Euclidean distance, Ward's method) dendrograms were plotted and cluster memberships for a range of cluster solutions were calculated. The K-means cluster analysis is based on nearest centroid sorting and produces only one solution for the number of clusters requested. The different statistical methods do not always result in the same cluster membership. The number of clusters has not been determined by use of statistical methods: First calculations were performed with different numbers of clusters. The final number of clusters was then determined by plausibility.
The calculations were made with a SPSS program package for windows version 6.1.

4. Results and Discussion

Only a few results of the numerous calculations by means of various statistical methods are presented in this paper (Figure 2 and Table 1).
The dioxin congener profiles of the samples of the River Elbe (downstream of the River Mulde), the samples of the harbour of Hamburg and the samples of the flooding areas of the Elbe are very similar to the dioxin congener profiles samples of Bitterfeld. (For reasons of clearness the samples of the flooding areas are not presented in Figure 2). It seems that the Bitterfeld contamination may partly have caused the dioxin contamination in the River Elbe, mainly by transport of SPM.
The samples of the dioxin sources „Kieselrot“ und the Mg-production are in the same group as the samples of Bitterfeld. It is remarkable, that the samples of the dioxin sources PCP, PCB, chloralkali

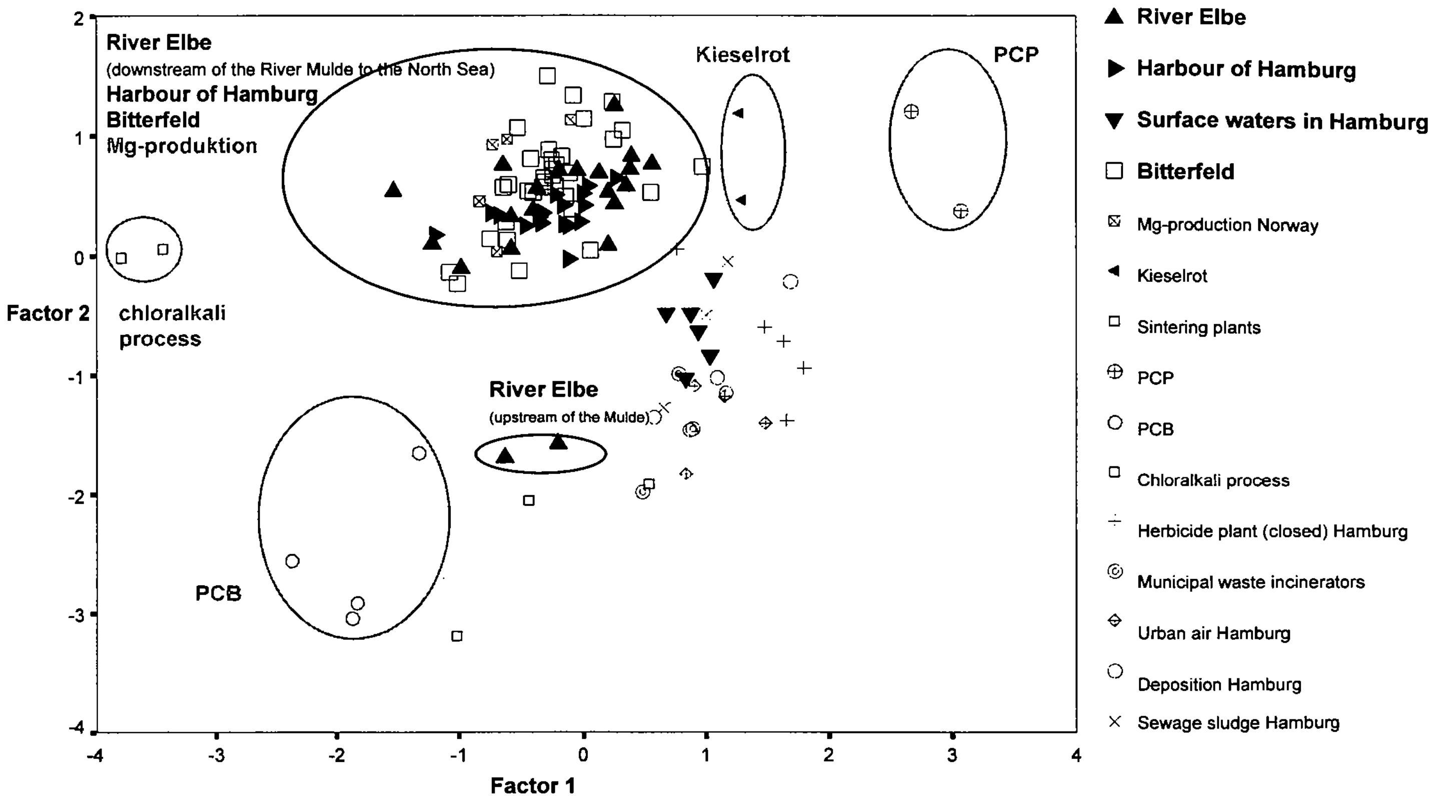

Figure 2: The score plot from the factor analysis with principal components (PCA). The relative PCDD/F-congenere profiles in the new coordinate space defined by the first two factors. Comparision of sediment and SPM-samples of the River Elbe, sediment samples of the harbour of Hamburg, sediment and soil samples from the Bitterfeld region, sediment samples of surface waters in Hamburg and samples of various dioxin sources.

process and herbicide production (all are samples of processes based on chlorine chemistry) show no similarity with the samples of Bitterfeld. This could be an indication, that to a certain extend, Bitterfeld was contaminated not only by chemical production, but also by metallurgy processes.
The samples of the herbicide plant (now closed) in the harbour of Hamburg are not in the same cluster as the samples of the harbour of Hamburg. Thus the herbicide plant could not be identified as a significant point source for the contamination of the harbour. (The area of the former production site is connected with the River Elbe by a canal system.)
The samples of the surface waters in Hamburg and the sewage sludge samples of Hamburg are in one group with the deposition samples. The pollution of these surface waters is affected by rain water overflows belonging to the sewage system in these areas. The PCP samples form a distinct cluster. Therefore we suggest that the main dioxin source responsible for the contamination of the sewage sludge samples and the investigated surface waters is of „thermal" origin.

From these evaluations a general conclusion can be drawn: Only identical results obtained with different statistical methods should be used for interpretation.

Table 1: Results of cluster analysis

Hierarchical cluster analysis		K-means cluster analysis	
Cluster	Samples	Cluster	Samples
1	Bitterfeld	1	PCB
1	Kieselrot	2	Bitterfeld
1	River Elbe (downstream River Mulde)	2	Kieselrot
1	Harbour of Hamburg	2	River Elbe (downstream River Mulde)
1	Flooding areas (Elbe)	2	Harbour of Hamburg
2	Bitterfeld	2	Flooding areas (Elbe)
2	Mg-production	3	Herbicide plant
2	Flooding areas (Elbe)	4	PCP
3	PCP	5	Sintering plants
4	PCB	5	Municipal waste incinerators
5	Chloralkali process	5	Urban air
6	Sintering plants	6	Deposition
6	Municipal waste incinerators	6	Sewage sludge
6	Urban air	6	River Elbe (upstream River Mulde)
7	Deposition	6	Surface waters Hamburg
7	Sewage sludge	7	Bitterfeld
7	River Elbe (upstream River Mulde)	7	Mg-production
7	Surface waters Hamburg	7	Flooding areas (Elbe)
8	Herbicide plant	8	Chloralkali process

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