Evaluation of PCDD/PCDF Data in a River System in South Mississippi - Part 1

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Abstract

Using cluster analysis and Multivariate Data Analysis (MDA), sediment and soil samples from the State of Mississippi were compared with the effluents of a pulp mill, a potential point source. Additionally data of many known sources of PCDD/PCDF from the scientific literature were included in the evaluation. Both methods were shown to be able to distinguish between different matrices with known PCDD/PCDF contamination (e.g. PCP, PCB, kraft pulp mill effluents). In some instances, a specific PCDD/PCDF source could be correlated to an environmental sample. Neither the cluster analysis nor the MDA identified the pulp mill as a source of PCDD/PCDF found in the river drainage.

1. Introduction

Emissions of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) into water are not as well investigated and have not been analyzed with the same intensity as air emissions of these substances. Well known sources of dioxins and furans to receiving waters are point sources such as discharges from industrial facilities, e.g. effluents from pulp and paper mills and wood treating facilities, sewer plants, as well as diffuse inputs, e.g. leachates from landfills or run-offs from streets. As PCDD/PCDF are very poorly soluble in water and have high log K_{OC} values they do not stay in the aqueous phase but strongly adsorb to particles; thus, sediments of rivers, lakes, and oceans are the ultimate sinks for water-borne dioxins and furans (Rappe et al. 1987, Fiedler et al. 1990).

2. Methods

All data from the State of Mississippi, soil, sediment samples from Leaf and Pascagoula Rivers and their tributaries, and mill effluent data were obtained as authentic analysis reports from sources given under "References" in Table 1. Additional PCDD/PCDF data were taken from the literature. These data were selected according the following criteria:

- Samples should be representative for the matrix,
- A broad spectrum of homologue and congener patterns should be considered,
- Samples which might be considered as a possible source of contamination for soils and sediments in the Leaf River area should be included.

Using the criteria mentioned above, we selected 37 external data for comparison with 22 sediment data from the Leaf/Pascagoula River, 12 soil data from locations that have been flooded repeatedly in the past, 7 targeted sediment data from tributaries (with known history of dioxin contamination, e.g. wood industry), 6 effluent data from a pulp mill located at the

Leaf River, and finally, 17 sewage sludges from EPA Region 4 analyzed within the US National Sewage Sludge Survey. Thus, a total of 101 full-congener PCDD/PCDF analyses have been evaluated (Table 1) and the results will be given below. In a second publication (Rappe et al. 1994) we concentrated on a smaller data set where only 38 soil and sediment samples within the river system and the floodplain, respectively, have been considered.

The external samples included industrial chemicals with known PCDD/PCDF-contamination such as PCB, TCB, PCP, and Na-PCP. Samples from the kraft pulp and paper industry were included as well as samples of typical urban origin, e.g. waste water effluents from family homes and municipal sewage sludges from the city of Bayreuth/Germany and septic tanks in Sweden.

Table 1: List of samples used for statistical evaluation

ID-No.	Sample Description	References
1-6	Pulp mill Effluent, Mississippi	Internal data from mill
7-14	Sediments above the pulp mill (- - - - -)	DEQ 1992
15-28	Sediments below the pulp mill (+++++)	DEQ1992
29+30	Water, sewer, inflow + outflow, Bayreuth, Germany	Horstmann 1994
31+32	Sewage sludge, Bayreuth, Germany	Horstmann 1994
33-35	Water, household effluents, wash water, Germany	Horstmann 1994
36-38	Gully sediments, Germany	Horstmann 1994
39-40	Septic tank, Sweden	Swedish EPA
41-44	Soil at Leaf River (above - - - -, below +++++ the pulp mill)	Eco Logic 1994
45+51	Sediments from tributaries to Leaf River	DEQ
52-55	Soils at Leaf River & Bogue Homo	Eco Logic 1994
56-59	Soils at Pascagoula River	Eco Logic 1993
60-69	Kraft pulp mill effluents & pulp samples, Sweden	Swansson 1988
70-73	PCB, Polychlorinated biphenyls (Clophen A30-A60)	Hagenmaier 1990
74+75	PCP, Pentachlorophenol (European brands)	Hagenmaier & Brunner 1987
76+77	Sodium pentachlorophenate, Na-PCP (European and U.S. brands)	Hagenmaier & Brunner 1987
78	TCB, Trichlorobenzene	Hagenmaier 1987
79-95	Sewage Sludge--EPA, US National Sewage Sludge Survey	EPA 1989
96-101	Compost, Germany	Schäfer 1993

2.1 Cluster Analysis

The cluster analysis we used is similar to a method developed by Hagenmaier et al. (1993). Here, the WARD method was chosen to form groups (= clusters) of similar size of samples for which the variance (= deviation) is minimised (Backhaus et al. 1989, Crunkilton et al. 1987). All concentration data have to be normalised to be comparable. Concentrations below the detection limit were treated as zero. We used three different normalisations which represent three approaches to the pattern recognition of PCDD/PCDF. The rationale behind is that PCDD/PCDF homologue profiles may undergo various transformation reactions in the environment (e.g. dechlorination) and thus, they can change considerably between source and sample. In contrast, congeners of the same degree of chlorination are affected in the same way; so, the congener pattern is more stable than the homologue profile and should be better preserved in the sample. The three steps included:

a) **Relative concentration of PCDD/PCDF homologues:** The concentration of each of the tetra- through octachlorinated dioxin and furan homologue is divided by the total sum of PCDD/PCDF. Thus. a single sample is characterized by 10 ratios.

b) **Relative concentration of 2,3,7,8-substituted congeners within the corresponding homologue:** The concentration of each 2,3,7,8-substituted congener is divided by the

concentration of the corresponding homologue. For Cl_8DD and Cl_8DF, its concentration is divided by the concentration of either PCCD or PCDF, respectively. A total of 17 ratios will characterize a given sample.

c) **Relative amount of 2,3,7,8-substituted congeners at total TEQ:** The I-TEQ of the individual 2,3,7,8-substituted congeners is divided by the total I-TEQ of the sample. This approach takes into account that the 2,3,7,8-substituted congeners are more persistent in the environment and thus, older samples may have perserved its original composition of the toxic congeners. 17 characteristic ratios per sample are generated.

For visualisation the results obtained from a cluster analysis are plotted as a dendrogram on a scale with relative distances (1-25) wherein a short distance indicates a high degree of similarity between samples whereas long distances occur when samples are different.

2.2 Multivariate Data Analysis (MDA)

In the multivariate data handling each sample is treated as a separate object build up by 2,3,7,8-substituted congener and homologue concentrations which together constitute 25 variables in the calculation. All variables are normalized against the sum of variables and scaled to equal standard deviation within each sample. Levels below the detection limit are treated as missing data (Wold et al. 1984). The multivariate calculation is made with a SIMCA program packet version 3B (UMETRI). To identify the direction in the multivariate space which contains the maximum of data variation between the pulp mill emission samples #1 to #6 from the bulk samples an extra variable (No. 26) as a Y-matrix was introduced in the PLS discriminant analysis against the dependent X-matrix (variables #1 to #25) (for PLS application, see Tysklind et al. 1993).

3. Results

Results of the Cluster Analysis: From the dendrograms obtained by the three-step cluster analysis the first step (= Ratio Homologue/Sum PCDD/PCDF, not shown here) divides the samples in two major groups where group 1 comprises all samples that are characterized by Cl_8DD as the predominant homologue and a second more heterogeneous group which includes samples with dominating amounts of PCDF. The second step (= Ratio 2,3,7,8-substituted congener/Homologue) confirmed these findings in a more heterogenous dendrogram. The dendrogram of the 3rd and most sophisticated step of the cluster analysis (= Contribution of each 2,3,7,8-substituted congener to the I-TEQ) is shown in Figure 1. Four of the six Mississippi pulp mill effluents have been clustered with the highest degree of similarity (samples #1, #4, #5, #6) into one distinct group. One sewage sludge sample from the US National Sewage Sludge Survey is included as well. This group is in the neighbourhood of samples obtained from non-point locations, such as household waters (#29, #34, #39) and composts. Interestingly, two of the pulp mill effluent samples (#2, #3) are found in one group with three old Swedish kraft mill samples. These two Mississippi effluent samples (#2, #3) were taken when the mill utilized some amount of molecular chlorine in its five stage bleaching process.

Results of the MDA: The results from the MDA are plotted in Figure 2 which explains 30 (x-axis), 20 (y-axis) and 7 (z-axis) % of the information in the X-matrix. It is clear that the majority of data points come very close together. It is of interest to find that the PCP and PCP-Na are within the majority of the sediment and sludge samples. The effluent samples #1 to #6 and samples #60 to #69 are separated from the majority of the other samples as well as some other groups; e.g. PCB or trichlorobenzene, come outside this sphere. However, there is no statistical significant separation (with 95 % confidence). One reason is

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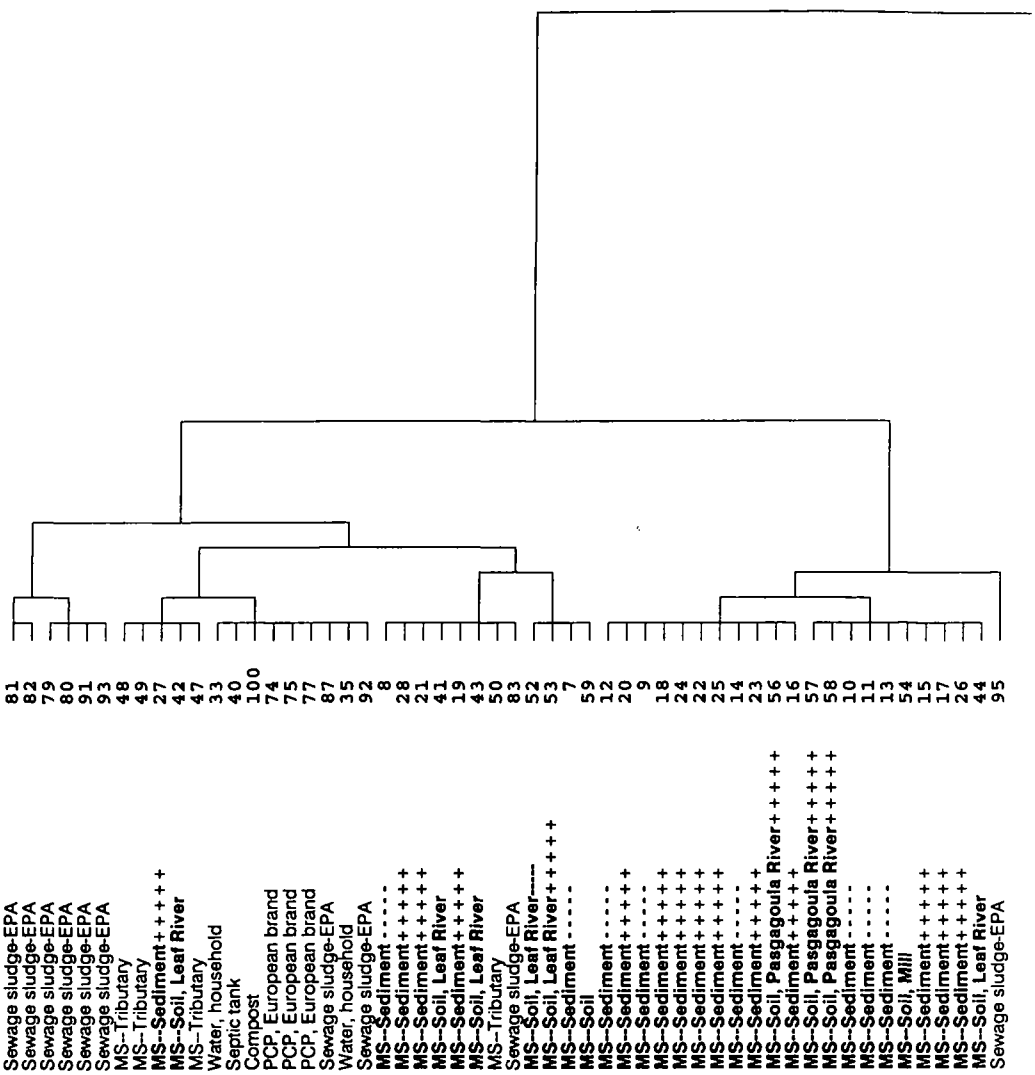
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82 Sewage sludge-EPA
79 Sewage sludge-EPA
80 Sewage sludge-EPA
91 Sewage sludge-EPA
93 Sewage sludge-EPA
48 MS--Tributary
49 MS--Tributary
27 MS--Sediment+++++
42 MS--Soil, Leaf River
47 MS--Tributary
33 Water, household
40 Septic tank
100 Compost
74 PCP, European brand
75 PCP, European brand
77 PCP, European brand
87 Sewage sludge-EPA
35 Water, household
92 Sewage sludge-EPA
8 MS--Sediment-----
28 MS--Sediment+++++
21 MS--Sediment+++++
41 MS--Soil, Leaf River
19 MS--Sediment++++
43 MS--Soil, Leaf River
50 MS--Tributary
83 Sewage sludge-EPA
52 MS--Soil, Leaf River----
53 MS--Soil, Leaf River++++
7 MS--Sediment-----
59 MS--Soil
12 MS--Sediment------
20 MS--Sediment+++++
9 MS--Sediment-----
18 MS--Sediment++++++
24 MS--Sediment++++++
22 MS--Sediment++++++
25 MS--Sediment++++++
14 MS--Sediment-----
23 MS--Sediment+++++
56 MS--Soil, Pasagoula River+++++
16 MS--Sediment++++
57 MS--Soil, Pasagoula River+++++
58 MS--Soil, Pasagoula River+++++
10 MS--Sediment-----
11 MS--Sediment-----
13 MS--Soil, Mill
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17 MS--Sediment+++++
26 MS--Soil, Leaf River
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95

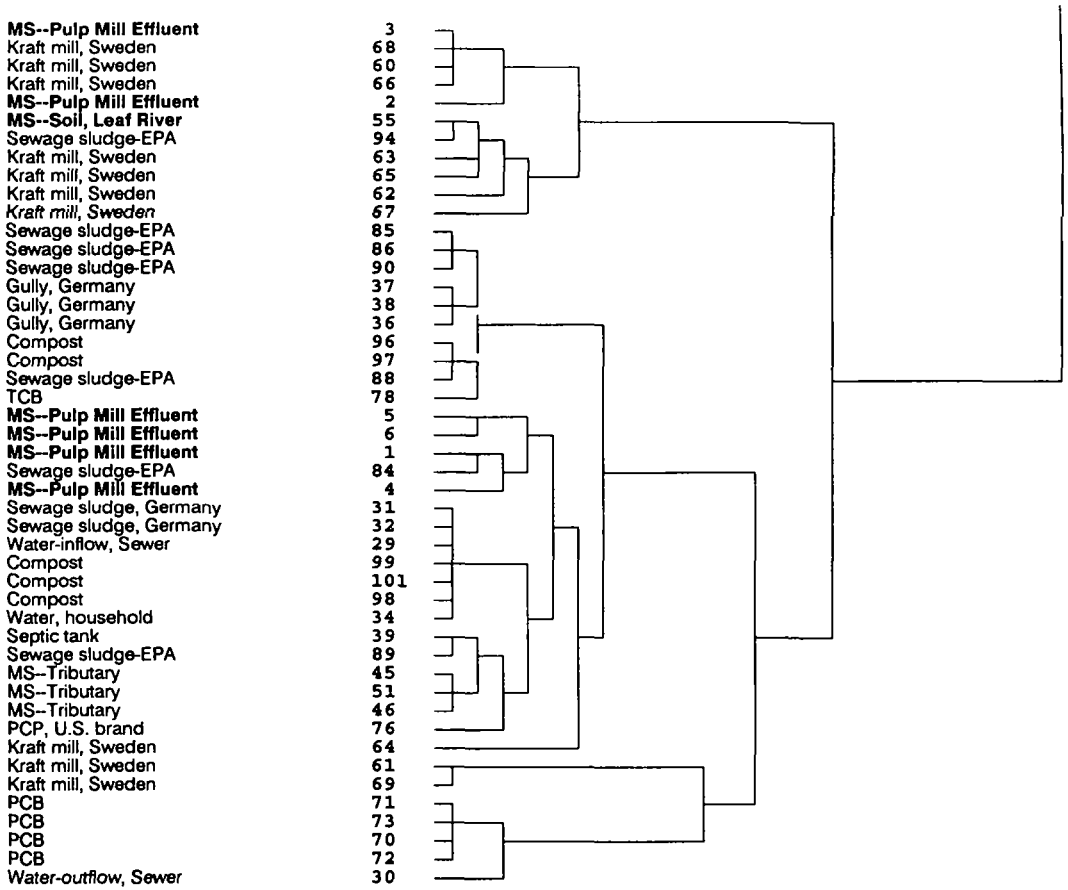

Fig. 1: Dendrogram of the cluster analysis: Ratio 2,3,7,8-substituted congener/I-TEQ
(The 38 soil and sediment samples and the 6 pulp mill effluent samples from the Leaf and Pascagoula Rivers are written in bold letters;
"MS" indicates that a sample has been taken in the State of Mississippi)

that there is no distinct group from which the mill effluent samples (#1 to #6) can be separated. The second group consisting of samples #7 to #101 is fairly heterogeneous. Another problem is the large portion of congeners with concentrations below the detection limit within the data set used. A second PLS analysis confirms that there is no separation of the sediment samples in groups upstream and downstream the mill.

4. Discussion

The cluster analysis using the Ward Method is a powerful tool to determine similarities and dissimilarities based on full-congener PCDD/PCDF analyses. Data evaluation can be performed independent of the matrix analyzed or the concentrations found. The MDA proved to be a very sensitive method to classify new samples into a framework of well described known samples that belong to different characteristic groups. However, MDA is not a good method for identifying groups when most samples fall into one group. The MDA has problems when a substantial amount of congeners have non-detectable concentrations. The mathematically and statistically deduced conclusions have also been confirmed by a scientific plausibility check, taking into consideration the state of the knowledge regarding transport and environmental fate of PCDD/PCDF.

Some general conclusions can be drawn from both methods:

- Most of the soil and sediment samples in Mississippi exhibit the same pattern as found in background samples; in other words: the PCDD/PCDF patterns and profiles cannot be attributed to special point sources (pulp mill, PCB, trichlorobenzene).
- Sediment samples from the tributaries exhibit some similarity to the US American PCP-Na sample (#76) and not the European brands.
- It cannot be distinguished between sediment samples above and below the pulp mill, a potential point-source for sediment contamination.
- Along the river's flow neither the pattern nor the profile of the sediments undergoes changes, e.g. in all three evaluations of the cluster analysis sediment #9 taken 22 miles above the mill and sediment sample #25 taken 59.3 miles below the mill are within the same group of samples. Thus, they exhibit the highest possible degree of similarity.

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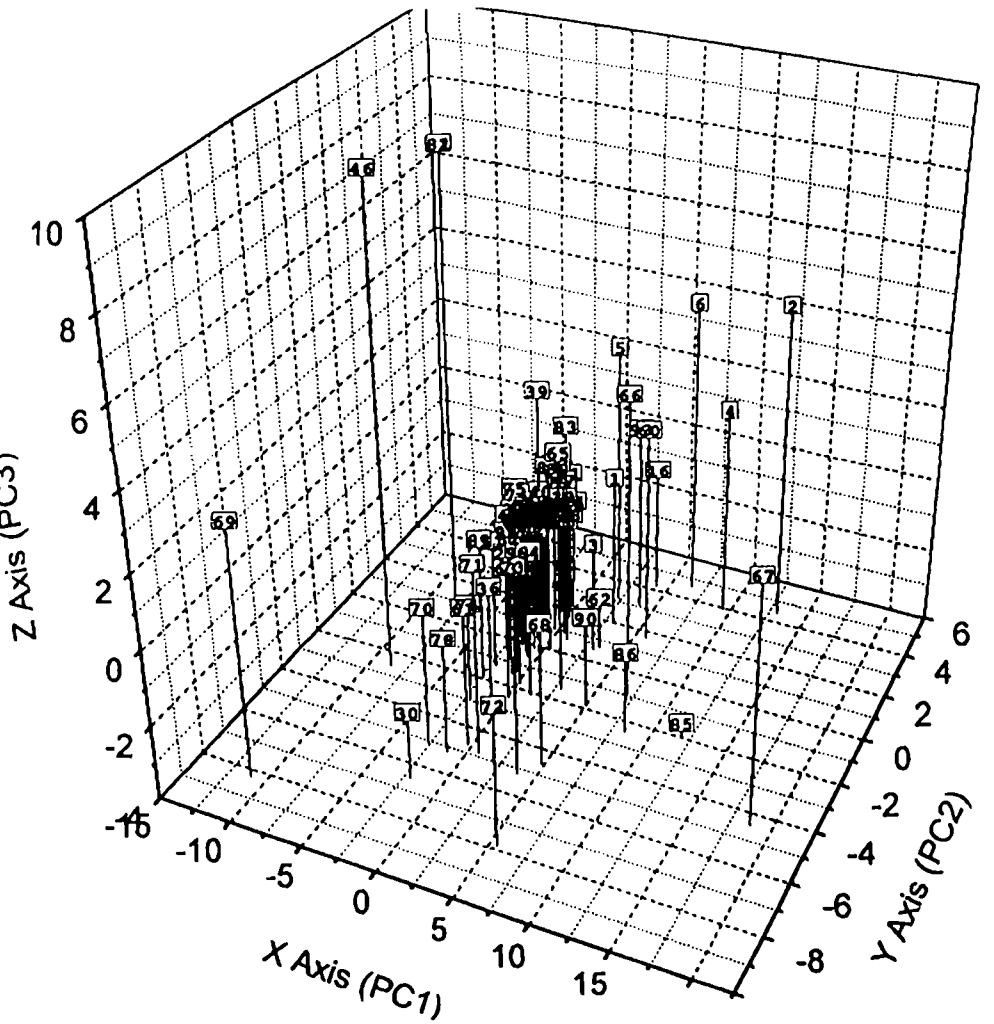

Fig. 2: PCA-Plot of 101 samples evaluated

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