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

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Abstract

Sediment and soil data from a river system in South Mississippi and a potential point source of PCDD/PCDF have been evaluated by statistical and mathematical methods. None of the results could identify the pulp mill as the source of dioxin and furan levels found in the sediments and soils in the flood-plain.

Introduction

Pulp mills are known sources of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) (Rappe et al. 1986, Amendola et al. 1989). The main emissions of dioxins and furans from pulp mills occur *via* the effluents to receiving waters, such as rivers and lakes . Due to the strong adsorption of PCDD/PCDF to particulates dioxins and furans will be found in the sediments of the aquatic environment. The impact of dioxin contaminations from pulp mills are limited to the hydraulic transport (Götz et al. 1994). However, soils can be contaminated by such a point source if flooding of the river occurs.

Methods

The statistical methods used, Principle Component Analysis (PCA) (Wold et al. 1984) and cluster analysis, have been described in detail (Fiedler et al. 1994). We have evaluated sediment samples from above and below a kraft pulp mill in South Mississippi as well as soil samples which have been flooded repeatedly in the past. Using PCA and cluster analysis, we have compared 22 sediment samples and ten soil samples with the six effluent data from the pulp mill (see Table 1). The data base includes the 2,3,7,8-substituted PCDD and PCDF congeners as well as the homologues.

Table 1: List of samples used for statistical evaluation

ID-No.	Matrix	Abbreviation Fig. 2	References
1-6	Pulp mill effluents (Water)	Effluent	Internal data from mill
7-14	Sediments above mill	---sed	DEQ
15-18	Sediments below mill	+++sed	DEQ
29-34	Soil at Leaf River	Soil LR	Eco Logic 1994
35	Soil on mill property	Soil-Mill	Eco Logic 1994
36-38	Soils at Pascagoula River	Soil-PR	Eco Logic 1993

A three-step cluster analysis was applied to full-congener PCDD/PCDF analyses. Thus, each sample is characterized by a multitude of ratios to determine similarities and dissimilarities. Here, the TEQ of the individual 2,3,7,8-substituted congener is divided by the total TEQ of the sample. This method weighs congener concentration according to the assigned I-TEF (International Toxicity Equivalency Factor). This procedure leads to a pattern in which the Cl_8DD is not as dominating as in the original pattern of the soil and sediment samples. The results of these cluster analyses are plotted as dendrograms where short distances on a relative scale describe a high degree of similarity whereas long distances express low similarities, in other words: samples that are not very similar.

The Principal Component (PC) calculation is made with a SIMCA program packet version 3B (UMETRI). To remove the differences in the concentrations between samples each PCDD and PCDF value of a sample is normalized against the sum of all variables. To ensure that all variables have equal influence within the calculation, the variable is scaled to the same standard deviation. Before starting the PC calculation the data are centred by removing the variables' average values. In the evaluation presented in this paper two PC components are calculated.

Levels below the detection limit were treated as zero or missing data in both methods.

Results

The plots obtained from the PCA are shown in Figure 1 and the dendrogram is given in Figure 2.

The PC1-axis (x-axis) of the PC plot (see Figure 1) explains 51 % and the PC2 (y-axis) explain 18 % of the total normalized and scaled data variation. The pulp mill water emissions (samples 1 to 6) are clearly separated from the soil and sediment samples (sample Nos. 7 to 39) which from an own cluster at the left of Figure 1.

The results obtained from the PC calculation could be confirmed by the cluster analysis. From Figure 2 it can be seen that it is not possible to group the sediment samples into two groups, one above the pulp mill and one below the pulp mill. In other words, it is not possible to distinguish sediment below the mill from sediment above the mill. As a result, from the dioxin analyses an impact or influence from the pulp mill can not be seen.

As can be seen in both plots the soil samples do not form distinct groups but are mixed with the sediment samples. Thus, the statistical and mathematical evaluation confirms that the soil samples have similar PCDD/PCDF profiles and patterns to the sediment samples. These findings have been expected as the soil sampling sites are located in the flood-plain.

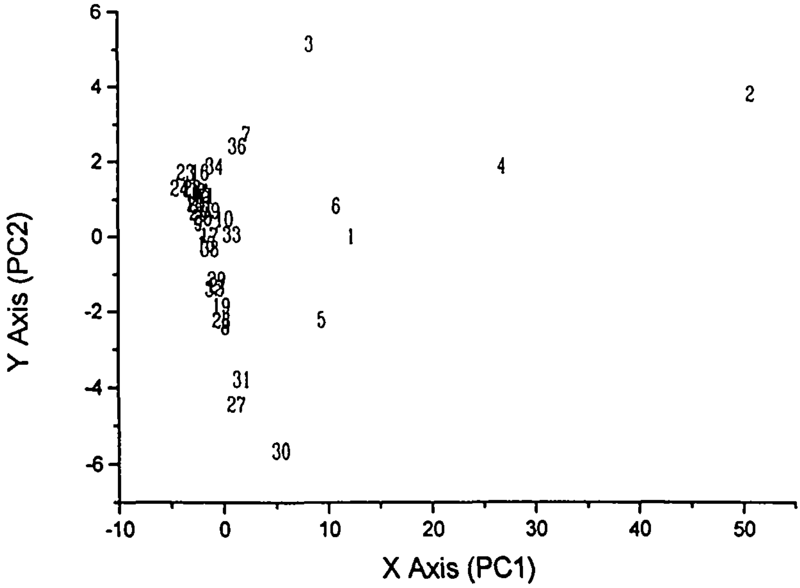

Figure 1: Principal Component (PC) plot of the samples shown in Table 1

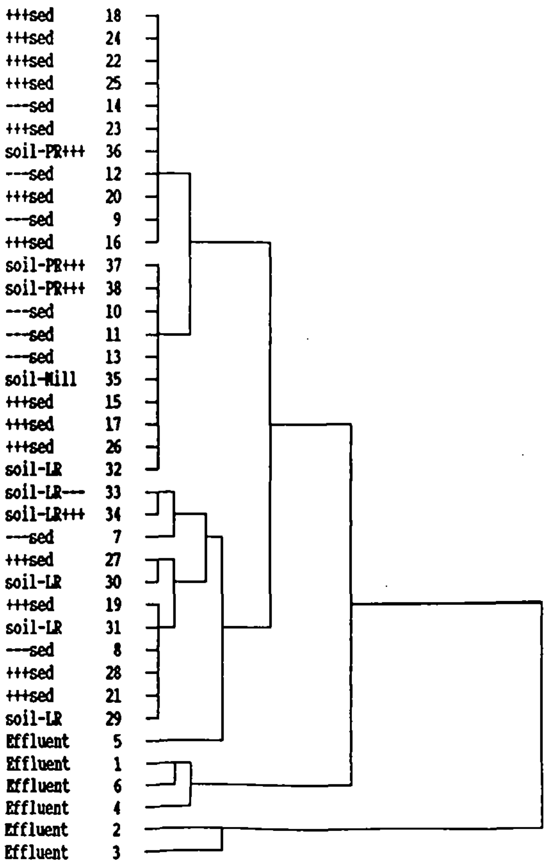

Figure 2: Dendrogram of cluster analysis when evaluating the contribution of the 2,3,7,8-substituted congener to the total I-TEQ of the sample

Moreover, Figures 1 and 2 clearly show that the six effluent samples from the pulp mill form an distinct group; in other words, none of the sediment and soil samples exhibits a similarity to the mill's effluents. Moreover, the cluster analysis (see Figure 2) shows that the mill's effluent samples #2 and #3 are somewhat different from the effluent samples #1, #4, #5, and #6. This finding is in accordance with a change in the bleaching process: Samples #2 and #3 have been taken at a time when the pulp mill utilized some amount of molecular chlorine in its five stage bleaching process whereas the four other samples were analyzed when the mill was operating at greater than 99 % chlorine dioxide substitution.

Conclusions

The statistical and mathematical evaluation, PCA and cluster analysis, of sediment, soil, and pulp mill effluent samples in a river system in South Mississippi showed that the pulp mill during all times of its operation (from 1984 until now) had a clearly discernible dioxin pattern that does not reflect any similarity to the sediment and soil patterns from above and below the mill. Thus, the pulp mill could not be identified as a point source for PCDD/PCDF contamination in the river system.

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