

GEOSTATISTICAL INTERPRETATION OF DIOXIN REACTIVITY IN SEDIMENTS

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Introduction:

The interpretation of spatial and temporal information on the distribution of dioxins in contaminated environments is affected by differences in the various source patterns, spatial heterogeneity, and potential reactive mechanisms prevailing in sediments. Research during the last decade has emphasized correlations between known dioxin source patterns, and those observed in sediments using principal component analysis and polytopic vector analysis^{1,2,3}. Environmental reactive processes, such as dechlorination of dioxins in freshwater and estuarine sediments, are complex and involve several interrelated factors that may be physical, chemical or microbiological in nature. Much research has been devoted so far to laboratory experimentation, which allowed a better understanding of the mechanisms governing the degradation of these contaminants and to construct numerical models that predict, to some extent, laboratory observations from a few environmental descriptors^{4,5,6,7,8}. Based on dechlorination fingerprints in solid free and sediment environments, it was inferred that microorganisms predominantly affect dechlorination reactions by changing the redox state of the sediment organic matter, which dominates the reactivity⁹.

The extrapolation of these results to the field requires the modeling of the distribution in space of the contaminant concentrations and of the environmental factors controlling their degradation.

The objective of the current study is to determine dominance of biotic vs. abiotic dechlorination pathways as indicated by the ratios of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD to Total 2,3,7,8-PCDD (Ratio 1 and 2 respectively) as functions of salinity and TOC. Field measurements of dioxin concentrations, salinity and TOC and laboratory results on dechlorination pathways will be integrated through geostatistical analysis, in order to simulate and map the predominant degradation pathways in the river sediments.

Methods and Materials

Field Data: Dioxin (2,3,7,8 congeners) and TOC data were acquired from the U.S. Environmental Protection Agency and from a database of New Jersey sediment data compiled by the National Oceanic and Atmospheric Administration^{10,11}. The data set includes 94 sediment cores that were taken along 27 equally spaced (~370 m) transects in the Passaic River in 1995. Most transects consist of a mid-stream and two flanking cores about 48 m apart. Samples represent depth-averaged concentrations from approx. 30 cm core intervals, and 16 depth categories (0 to 5 m) were considered for the analysis. Salinity data are from a study conducted for the New Jersey Environmental Protection Agency in 1985 and correspond to 4 different tide/flow scenarios.

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Statistical Analysis: An exploratory data analysis has been conducted on the measured congeners and on Ratio 1 and 2. For each depth, a principal component analysis allowed one to summarize the correlation pattern of dioxin congeners and look at their relation with environmental variables, such as TOC.

Data locations were accounted for in the analysis using geostatistics¹². The first step was the computation of semivariograms, which measure the spatial variability in 3 dimensions. Due to the meandering nature of the river, physical distances between samples cannot be described by a mere Euclidean distance since some of them would necessarily be measured over land. To ensure that all distances are measured within the water, sample coordinates were transformed, which amounts at mathematically "un-bending" the meanders (Figure 1). Semivariograms were modeled and used to interpolate each variable on a 3-D grid using ordinary kriging, followed by a transform of coordinates back into the original space.

Results and Discussion

The exploratory data analysis revealed strong differences between TOC and ratios, both in terms of univariate distribution (histogram) and patterns of spatial variability. While the TOC histogram is fairly symmetric, the distribution of Ratio 1 is bimodal (Figure 2). For Ratio 2, the distribution is strongly positively skewed, which required a log-transform of the data before processing.

The semivariograms of the three variables have been computed and modeled in 3 directions: the flow direction (x), the transverse direction (y) and the vertical direction (z). The parameters of the models are:

$$\begin{aligned}\gamma_{R1}(\mathbf{h}) &= 0.01 + 0.055 \text{ Sph}(h_x/600, h_y/25, h_z/2.5) + 0.08 \text{ Sph}(0, 0, h_z/5) \\ \gamma_{R2}(\mathbf{h}) &= 0.2 + 0.7 \text{ Sph}(h_x/200, h_y/50, h_z/1.2) + 0.4 \text{ Sph}(h_x/1300, h_y/70, 0) \\ \gamma_{\text{TOC}}(\mathbf{h}) &= 5 + 18 \text{ Sph}(h_x/300, h_y/25, h_z/1.8) + 6 \text{ Sph}(h_x/2000, 0, 0)\end{aligned}$$

Where \mathbf{h} is the distance vector (h_x, h_y, h_z) and Sph is a function of \mathbf{h} , known as the spherical model¹².

Figure 2 shows the directional semivariograms with the anisotropic model fitted for Ratio 1. The distances of spatial correlation range from 5 m in the z-direction to 600 m in the x-direction. The larger sill of the vertical semivariogram indicates that the ratio values are more variable in the vertical direction; for example, the variability observed longitudinally over 1 km is already present over a depth interval of 0.7 m. For Ratio 2 and TOC, the variability is largest in the horizontal plane.

The semivariogram models are used to simulate the spatial distribution of the three variables which can then be combined to derive a map of activity.

Acknowledgments

The authors would like to acknowledge support from the Office of Naval Research and the National Science Foundation. Since this communication has not been approved by either agency, no endorsement should be inferred

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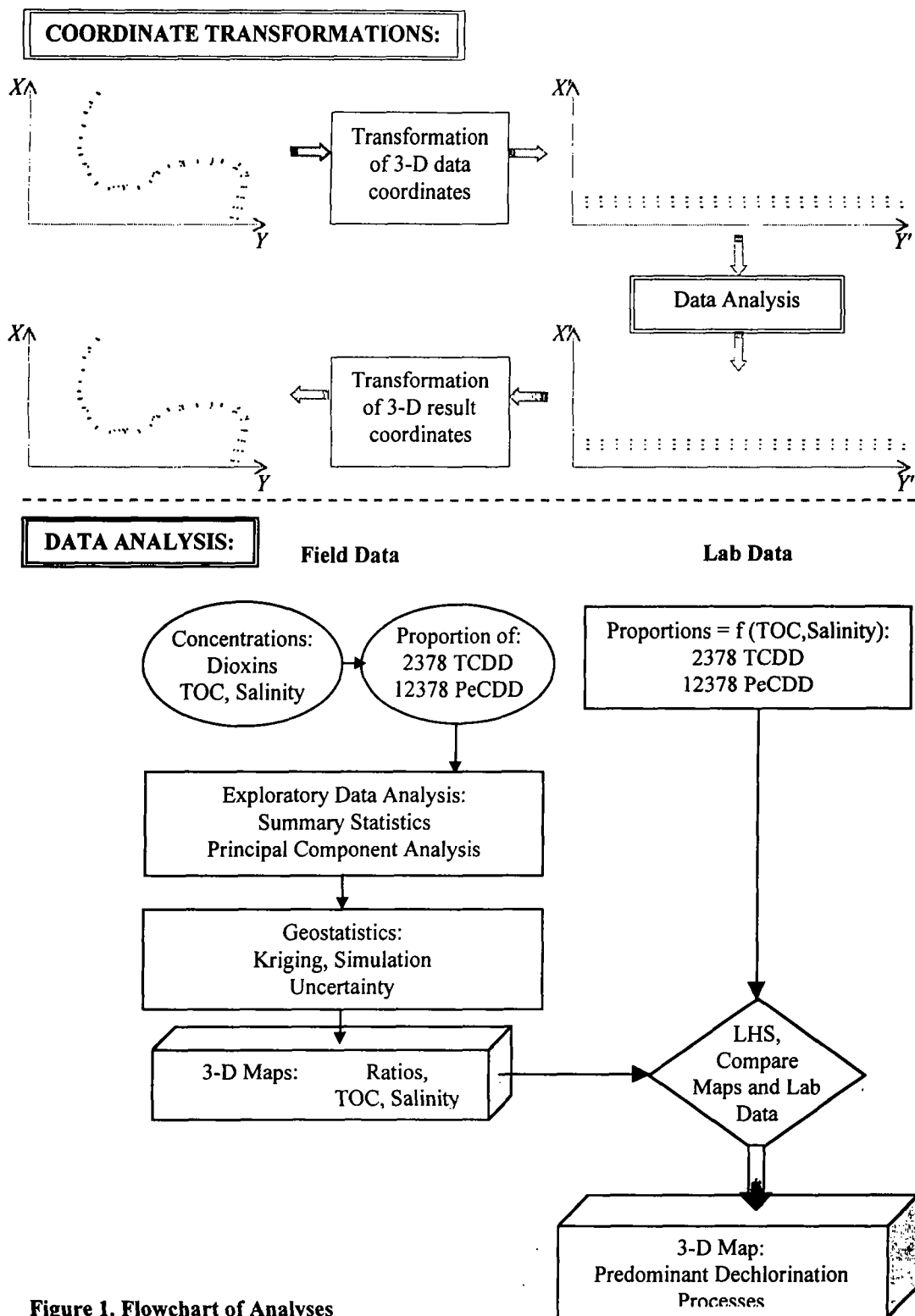


Figure 1. Flowchart of Analyses

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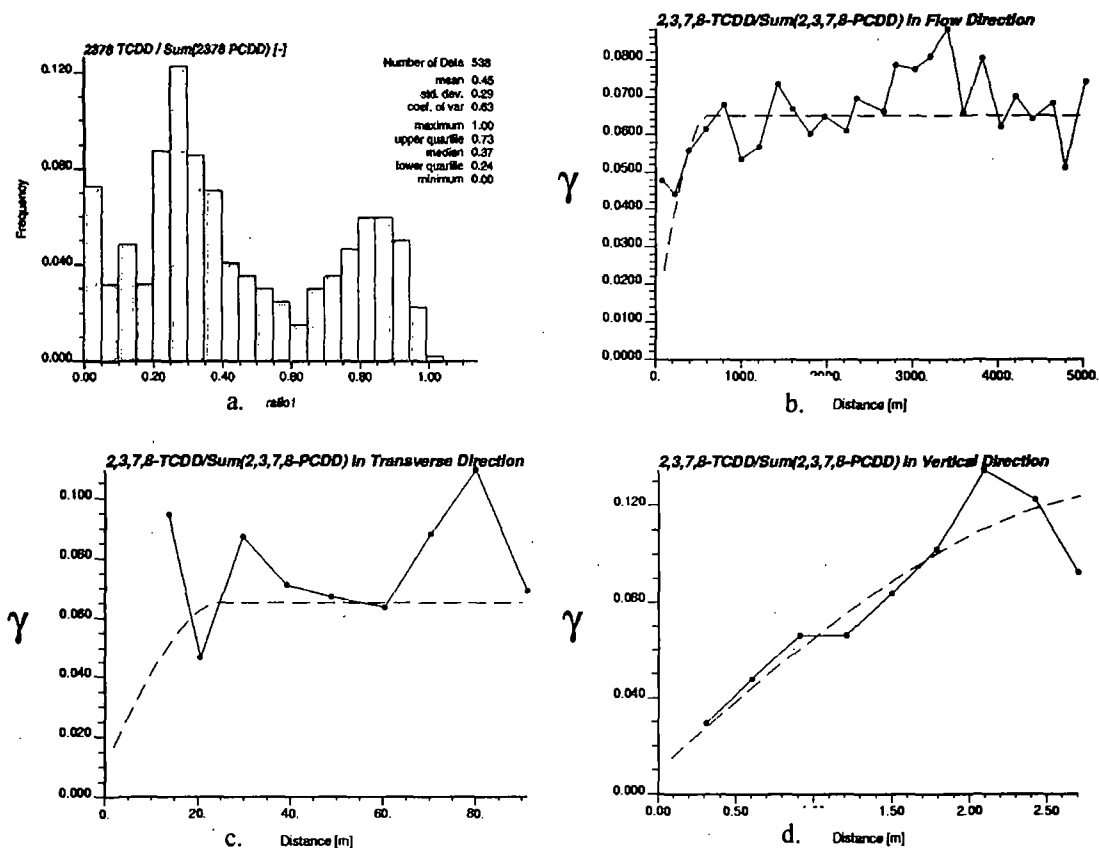


Figure 2. Histogram and Semivariograms for the Ratio 2,3,7,8-TCDD to Total 2,3,7,8-PCDD

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