IMPLICATIONS OF PCB DECHLORINATION ON LINEAR MIXING MODELS

Glenn W. Johnson[1] and John F. Quensen[2]

[1] Energy & Geoscience Institute, Department of Civil and Environmental Engineering. University of Utah, 423 Wakara Way, Salt Lake City, Utah 84108
[2] Dept. of Crop and Soil Sciences, Michigan State University, East Lansing, MI 48824-1325

Introduction

Linear mixing models are often used in investigation of sources and environmental fate of polychlorinated biphenyls (PCBs). They have proven a valuable tool in gaining insight into large data sets from field areas where sources and alteration processes could not be predicted *a priori*.[1] However, PCB dechlorination represents an environmental process that can confound the conceptual mixing model. A dechlorinated end-product does not necessarily behave as a linearly mixing source pattern. Successful inference of source and process requires sensitivity to and understanding of such mechanisms, and how they might affect such models.

In this paper, we use the linear mixing model polytopic vector analysis (PVA) to analyze data from published dechlorination experiments.[2] The impetus for this study was the observation that linear mixing models have provided insight to the presence of dechlorination, but interpretation of the results could be ambiguous when samples have undergone considerable dechlorination.[3] The objective of this paper is to demonstrate and evaluate the behavior of a linear mixing model method on a well-understood data set. In this case we apply PVA to experimental data whereby a single source (Aroclor 1248) underwent a known environmental fate mechanism: anaerobic dechlorination. If the source and process involved behave as two linearly mixing end-members, we would expect resolution of a two-component system, where one "end-member" was unaltered Aroclor 1248, and the other was the extreme alteration product.

Methods and Materials

Experimental data were taken from an Aroclor 1248 experiment reported in Quensen et al.[2] Aroclor 1248 was dechlorinated by anaerobic microorganisms eluted from Hudson River sediments. The Hudson River microorganisms preferentially removed *meta* and *para* chlorines via a type of dechlorination described in the literature as *process C*.[4-6] Quensen and colleagues also reported results for other Aroclors. This experiment is used for demonstration in this paper because that data set reduced to 3 principal components without loss of information, thus making it more amenable to visualization. The dechlorination experiments were conducted over a 20 week period, with 3 replicate samples collected and analyzed at each of six timer intervals: time-zero and four week intervals, through to Week 20. Congener specific PCB data were reported based on quantitation of 87 peaks. Additional information regarding experimental methods may be found in Quensen et al.[2]

The resulting data set was composed of 18 samples and 87 PCB peaks. Seventy-six of those 87 peaks were not reported below laboratory detection limits in any samples, and these 76 peaks were retained for statistical modeling. The data were modeled using the multivariate statistical method polytopic vector analysis (PVA). The PVA algorithm has evolved over a period of 40 years, primarily within the mathematical geology literature. The development and formalism of the PVA algorithm is outlined by Johnson.[7] The conceptual mixing model involves resolution of three

parameters of concern in a mixed system: (1) the number of components in the mixture, (2) the chemical composition of each source, and (3) the relative proportions of each source pattern in each sample. The analysis is performed in two steps. In Step 1, the number of components in the system is determined through a principal components analysis (PCA) and subsequent dimensionality analysis.[7] In Step 2, an iterative process is used to determine the chemical source compositions and the mixing proportions. This involves fitting a simplex (in three dimensions: a triangle) around the data cloud such that all samples are enclosed within the simplex.

Results and Discussion

The goodness-of-fit diagnostics were in good agreement, indicating the presence of three components. A three end-member model was resolved. The results are shown graphically on Figure 1. The simplex fit around the data cloud is illustrated, as are locations of the samples.

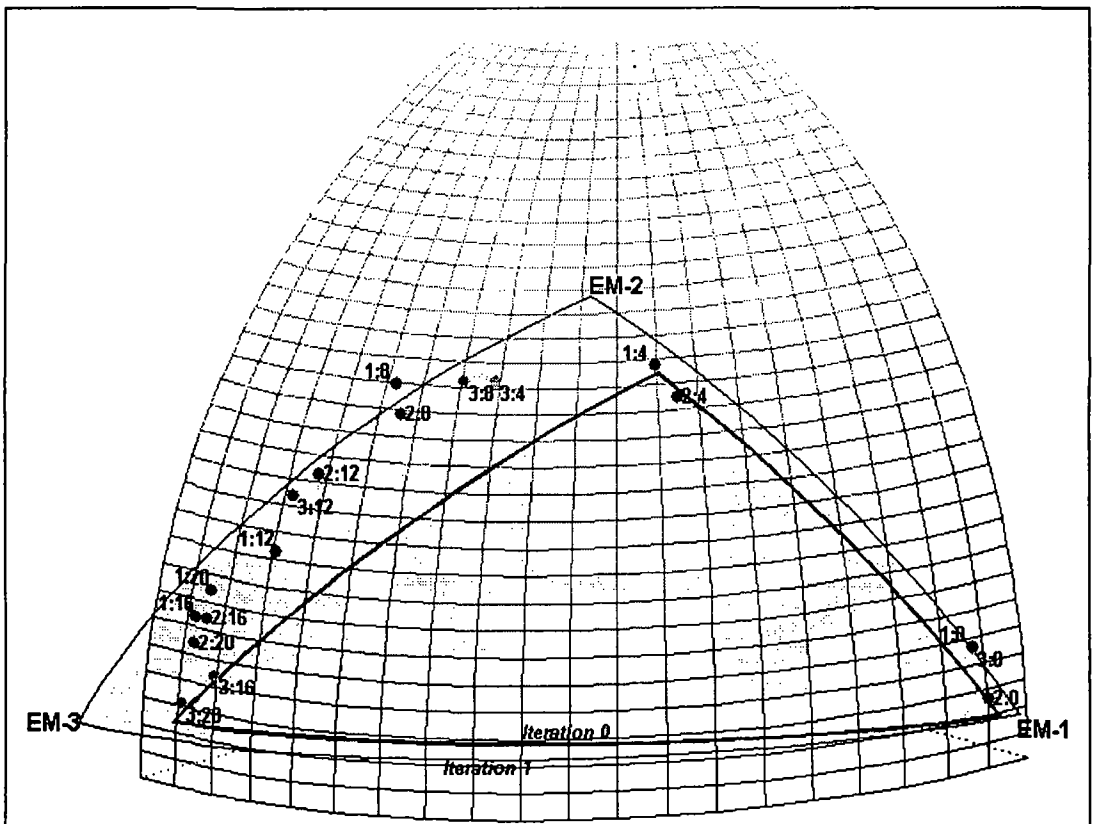

Figure 1. Quensen Aroclor 1248 dechlorination experiment data plotted in 3 principal component space. End-members (EMs) resolved through PVA are shown plotted at vertices of the shaded triangle. Sample nomenclature indicates experiment number, and time interval (e.g. Sample 3:12 is Replicate 3: Week 12).

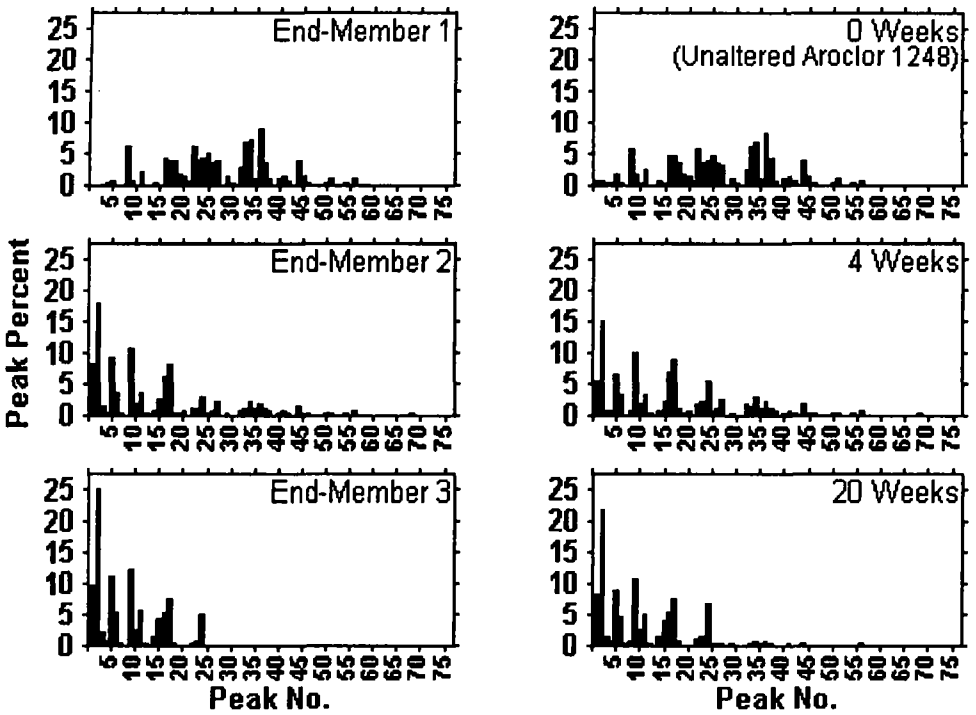

Figure 2. Comparison of PVA-derived end-member fingerprints to samples from Quensen Aroclor 1248 dechlorination experiment. Peak numbers for 76 PCB peaks used in PVA model shown along the x-axis.

In contrast, interpretation of the other part of the PVA solution, the end-member mixing proportions, is problematic. For example, the sample collected and analyzed at 12 weeks (Replicate 1) is reported back as a mixture composed of 7% EM1 (Unaltered Aroclor 1248), 32% EM2 and 62% EM3. Results in such a format are adequate given the conceptual mixing model, but are not at all intuitive when applied to data from a dechlorination series.

Figure 2 shows a comparison between the PVA-derived end-members and samples along degradation series that were closest to those end-members (See Figure 1). In each case the end-member compositions are more extreme than any of the measured samples. However, the derived fingerprint patterns are very similar to congener patterns observed along the degradation series. Given these results and no prior knowledge of the system under study, the analyst could readily infer a degradation series based on review of end-member patterns. End-member 1 (EM1) is unaltered Aroclor 1248. EM-2 is an intermediate dechlorination product, and EM-3 is the most extreme dechlorination product. Provided the analyst was sensitive to the various dechlorination processes described in the literature, he/she could readily infer the presence of *process C* dechlorination based on such modeling results.

Data from the Aroclor 1248 dechlorination experiment did not react as one would predict, if indeed a dechlorination end-product could be modeled as a linearly mixing end-member. Three principal components (not two) were required to reproduce the data with fidelity. However, the derived end-member fingerprints were interpretable in the context of a degradation series. This highlights the utility of such experimental reference data sets in interpretation of modeling results of ambient data, and shows the importance of the analyst being sensitive to such processes. When such results indicate the presence of a process such as dechlorination, the analyst must be aware they are no longer within the realm of the conceptual mixing model.

The implications of this work are important because in a typical data analysis situation, the analyst does not know *a priori* what sources and processes might have impacted a system. Some tool must be used to gain initial insight into that system. Given the simple conceptual model of linear mixing of multiple sources, the mixing model will provide excellent results. Given the more complicated situation of sources confounded by a non-linear alteration process, the mixing model is acceptable as an exploratory data analysis tool because it still allows accurate inference of the process involved. The fingerprints derived will allow valuable insight into environmental fate process occurring in the field, but one must be careful not to blindly interpret the results in context of a quantitative source apportionment.

References

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