

Modified Polytopic Vector Analysis To Identify and Quantify a Dioxin Dechlorination Signature in Sediments. 2. Application to the Passaic River

NOÉMI BARABÁS,*
PIERRE GOOVAERTS, AND
PETER ADRIAENS†

Department of Civil and Environmental Engineering,
University of Michigan, Ann Arbor, Michigan 48109-2125

Persistent contaminants such as dioxins have been documented to undergo dechlorination reactions in the laboratory; however, little is known about the importance of these reactions in the field. Polytopic vector analysis (PVA) is a statistical pattern recognition technique for multivariate data traditionally used to identify fingerprints of contaminant sources. A modified PVA algorithm with uncertainty analysis was used to model dechlorination fingerprints and sources. The technique was applied to 351 sediment core-derived dioxin samples from the lower reach of the Passaic River, New Jersey. A dechlorination fingerprint was identified with a highly positive 2,3,7,8-tetraCDD component and a highly negative heptaCDD component. The most important industrial source of 2,3,7,8-tetraCDD is a fingerprint related to 2,4,5-trichlorophenoxyacetic acid production. The dechlorination contribution to the data variance is $3.00 \pm 1.00\%$, corresponding to an average of $1.2 \mu\text{g}/\text{kg}$ of 2,3,7,8-tetraCDD per sample at the expense of heptaCDD. The possible occurrence of dechlorination was validated by comparing the local dechlorination contribution in the results to the value of the ratio 2,3,7,8-tetraCDD/total 2,3,7,8-PCDD, which indicates dechlorination in the laboratory. Bootstrap uncertainty analysis yielded the same dechlorination EM in 40% of the realizations. The results indicated that bootstrapping is an important statistical tool to quantify uncertainties with respect to the dechlorination EM and some of the source EMs.

Introduction

Sediments in major rivers and ports worldwide have been severely contaminated with persistent organic compounds such as dioxins (1). Under the reducing conditions found in sediments, dioxins undergo biotically—and/or abiotically—mediated dechlorination reactions, although very slowly (2). Depending on the prevailing redox conditions and activity of microbial consortia, dechlorination can proceed via several pathways from octaCDD (OCDD) to monochlorinated isomers (Figure S1, Supporting Information). The most toxic congener, 2,3,7,8-tetraCDD (TCDD) may transiently accumulate as the result of peri- (1,4,6,9) dechlorination (2, 3).

* Corresponding author phone: (734)615-5905; fax: (734)763-2275; e-mail: barabas@engin.umich.edu.

† Current address: Biomedware Inc., 710 Ridgeway Ln., Ann Arbor, MI 48103-1535.

These reactions have been demonstrated in the laboratory, but their occurrence and relevance must also be evaluated in the field.

Many severely contaminated sites, such as the Passaic River (NJ) (4), have large databases that lend themselves to sophisticated multivariate data analysis. Polytopic vector analysis (PVA) is a multivariate pattern recognition technique that unmixes complex mixtures into several contributing patterns (i.e., the distribution of the contaminants in different emission source categories (end-members)) and their contribution to each sample (5). Various statistical techniques (6–9) have been applied at the same site by several authors in order to identify sources that have contributed to sediment contamination. Several different sources were found to contribute to the dioxin/furan load in the river and the estuary. Using PVA in subsurface sediments, end-members were identified to be representative of combustion sources, sewage sludge, and PCBs, while four EMs remained unidentified (10). In surface sediments, the authors of ref 11 found sewage sludge and three unidentified patterns. The authors of ref 12 found sewage sludge, *o*-chloranil, recycled pulp and paper mills/chlorine production, combustion/incineration, PCBs/graphite electrode sludge, and a signature possibly related to a 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) production facility. Combined sewer overflows (CSOs) receive industrial, commercial, and municipal effluents and were found to be a significant source of dioxins and furans (6).

As presented in a companion paper (13), a modified PVA algorithm (M-PVA) was developed to allow for the recognition of a dechlorination signature in a mixing model of dioxins and furans by using criteria derived in laboratory experiments. The incorporation of reactivity in PVA was used to re-estimate the fingerprints and contributions of dioxin sources and dechlorination in artificial, reference data sets. The results from four artificial data sets indicated a reasonable estimation of the dechlorination fingerprint and a need for a sensitivity analysis due to variability in the output. In this work, M-PVA is applied to polychlorinated dioxin and furan data from Passaic River subsurface sediment cores (4).

The goal of this paper is to estimate dioxin reactivity in subsurface sediments using M-PVA, to validate the dechlorination EM using comparisons with laboratory observations and to evaluate the impact of uncertainties on model results.

Materials and Methods

Sampling Site and Data Sources. The study area is a 10-km section of the Passaic River in New Jersey, under investigation by the U.S. EPA as part of its evaluation of the Diamond Alkali Superfund site. Historical industrial activity as well as nonpoint sources have resulted in elevated levels of dioxins in the sediments (14, 15). The river is part of the Hudson–Raritan tidal estuary. The sediments are cohesive and fine-grained (16) and have a very high organic carbon content (5–40%) (4). Polychlorinated dibenzo-*p*-dioxin and -furan data for 2,3,7,8-substituted congeners (PCDD/PCDF) were acquired from the U.S. EPA and from a database of New Jersey sediment data compiled by the National Oceanic and Atmospheric Administration (17, 4). The sample set consists of 94 cores taken along 27 transects (Figure 1). In this analysis, all dioxin and furan congener data are used except for OCDD. Furan data were included because the maximum number of factors that can be found in factor analysis is given here by the number of variables (13). Since data are only available for seven 2,3,7,8-substituted dioxin congeners in the sediments, furans had to be included to allow a PVA model of

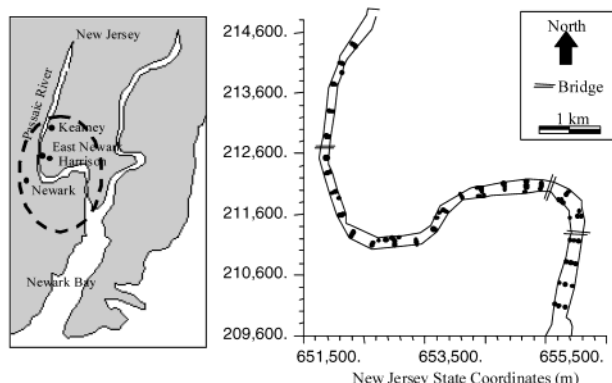


FIGURE 1. Study site (left) and locations of sediment cores (right).

more than seven factors in order to statistically detect low variability contributions by dechlorination.

Observations represent depth-averaged concentrations from approximately 30-cm core intervals. About 9.0% of the data were below the detection limit (DL) and were reset to half of the DL (10, 12). The distributions of the congeners are highly positively skewed and bimodal for some congeners (see Figure S2, Supporting Information). No dating was performed for this work, but the sediment in undisturbed locations dates back to before the year 1954 (the approximate start of the ^{137}Cs peak), apparent by a slow rise preceding the peaks in ^{137}Cs activity.

Data Treatment Methods. Several adjustments were necessary on the original data set. Samples with any missing data were removed for factor analysis. Some samples were reported at depth intervals that overlapped with other samples in the same core and were removed. In an initial PVA outlier analysis as described by Johnson (18), samples with 10 or more congeners reported at the DL were identified as outliers (70 samples) and were also eliminated from the data set (19). OCDD was eliminated for statistical and chemical reasons noted below. The total number of subsurface samples used is 351 (Table S1, Supporting Information). At each location, the concentrations were normalized to the sample PCDD/F total.

Exclusion of OCDD. There are two major reasons that OCDD was eliminated. The first reason is that properties of its distribution could lead to skewed results. OCDD is present at much higher concentrations in samples than other congeners, even OCDF (Figure S3, Supporting Information). This could lead to a dominant, artifact presence of OCDD in a large number of fingerprints. The low coefficient of variation (standard deviation over average) supports this hypothesis. Since the variability is low relative to the mean, OCDD is less important than other congeners in accounting for differences between EMs. Furthermore, in most actual source fingerprints, OCDD is ubiquitous and present in much higher concentrations than other congeners, so its value as an identifier of sources is limited as well. The second reason is that dechlorination may be difficult to identify in the presence of OCDD. Dechlorination of dioxin congeners has only been observed at the parts-per-trillion (ppt) to subparts-per-million (ppm) level, with the main impact of chlorine removal observed for the di- to heptaCDD congeners. Whereas concentration changes were observed for OCDD as well, no clear correlation was found with the accumulation of lesser chlorinated congeners. Hence, the interpretation of laboratory-based dechlorination patterns excluded OCDD (2).

Excluding OCDD has disadvantages as well. There is a risk that with the elimination of OCDD, some fingerprints characterized mostly or exclusively by this congener would not be detected. Such a fingerprint may exist, since Baker

and Hites (20) have found a large discrepancy in the global mass balance of dioxins between total known mass emissions and total mass deposition. Most of that discrepancy can be attributed to OCDD alone with 40 times more deposition than emissions (20). This indicates that the bulk of OCDD in the environment does not have a direct anthropogenic source, rather it may be the result of chemical reactions of non-dioxin compounds (precursors) after release into the environment, such as pentachlorophenol (20), and possibly natural sources (21). Including OCDD may allow such a fingerprint to be found, but it will not aid in the identification of dechlorination processes in the Passaic River.

Polytopic Vector Analysis (PVA). The goals of PVA are to determine (i) the number k of contributing source categories (or end-members, EM), (ii) the component profile or pattern of each EM, and (iii) the contribution of each EM to each sample (loadings). PVA decomposes a data matrix \mathbf{X} of p samples and N variables into a loading matrix \mathbf{A} and an end-member matrix \mathbf{F} such that (Figure 2 in ref 13):

$$\mathbf{X}_{p \times N} = \mathbf{A}_{p \times k} \mathbf{F}_{k \times N} + \mathbf{E}_{p \times N} \text{ and } k \leq N \quad (1)$$

Due to the multitude of contributing sources, processes, and errors, when $k < N$, the data are reproduced only approximately leaving an error term $\mathbf{E}_{p \times N}$. The decomposition is based on a multivariate analysis of a similarity matrix (variance-covariance, correlation, etc.) by principal component analysis (PCA) and subsequent rotation of PC axes until all loadings and EM components are positive (Figure S2, Supporting Information in ref 13). This constraint models the linear mixing of positive sources with positive contaminant contributions.

The modified procedure (Figure 2 in ref 13) starts with the traditional algorithm (T-PVA) and a sensitivity analysis to find the number of positive, source EMs, $N(\text{EM})^+$. This is followed by the modified code (M-PVA), allowing some relaxed EMs (with negative values) $N(\text{EM})^-$ and implements new constraints on one of these to model the dechlorination EM (EM_{dechl}). Then

$$k = N(\text{EM})^+ + N(\text{EM})^- \quad (2)$$

The theoretical details of the M-PVA procedure are described in a companion paper (13). In the following, additional procedures are described that are necessary when analyzing real data.

T-PVA: Determining $N(\text{EM})^+$. Traditionally, k is determined by repeating the initial PCA step using an increasing number of principal components (1 to N). For each model size, the data are re-estimated using eq 1, and the scatterplots of data versus estimates are assessed for each variable (18). (Other more traditional measures exist, but the scatterplots used here, also called coefficient of determination plots, have been determined to be better indicators.) In addition to the correlation between data and estimates, a new criterion is introduced: the persistence of end-members in the context of a sensitivity analysis. In contrast to the scatterplots, this analysis necessitates a complete PVA run beyond PCA for each model size with EM patterns calculated for each. Then, EMs that persist through all or most models (with slight variation) are identified. The added advantage of this approach is that it allows estimating uncertainty due to an important model parameter for each end-member and its contributions to total data variance by evaluating the standard error across models.

M-PVA: Determining $N(\text{EM})^-$ and EM_{dechl} . The appearance of a dechlorination EM is, of course, not guaranteed. Furthermore, dechlorination may contribute little to overall variance, and it is not known a priori whether a dechlorination EM will be detected by M-PVA because it could be easily

masked by errors. In addition, even if EM_{dechl} is detected, it is not known a priori in which position it will appear, so the dechlorination constraints cannot be applied initially. The following strategy was used and is recommended:

(i) Determine whether EM_{dechl} exists:

(a) Allow maximum number of relaxed EMs ($N - N(EM)^+$) and inspect each for compatibility with dechlorination criteria (13).

(b) If a possible EM_{dechl} is found in first M-PVA run, apply dechlorination constraint to it in a second run (i.e., if the 10th EM is found to show dechlorination properties, the constraint should be applied to the 10th EM).

(c) Inspect if constrained EM still fulfills dechlorination criteria (if not, try constraint on another relaxed EM; if none of the constrained EMs fulfill criteria, dechlorination cannot be identified: stop).

(ii) If EM_{dechl} is found, while retaining constraint, reduce the number of relaxed EMs to minimum necessary for EM_{dechl} to appear.

(a) Reduce stepwise $N(EM)^-$ from maximum ($N - N(EM)^+$) to 1 and perform full PVA for each model.

(b) Observe how EM_{dechl} changes and quantify standard error.

The second step above constitutes a sensitivity analysis for EM_{dechl} , testing the robustness of PVA independently of the data set, relative to the parameter k . Source EMs and means and standard errors can be calculated. It may be necessary to retain at least two relaxed EMs, since for $N(EM)^- = 1$, the dechlorination EM may not appear. The additional relaxed, unconstrained EM(s) could reflect measurement error, noise, or other processes.

Bootstrap Uncertainty Analysis. A companion paper (13) indicated that a dechlorination contribution to variability as low as 4% impacts the M-PVA results even when no error is present in the system. Given that error is always present in environmental data and because dechlorination of dioxins is by its nature a slow process, a bootstrap-based uncertainty analysis (22, 23) was conducted. The data were resampled with replacement 100 times and M-PVA repeated to evaluate the impact of uncertainty on the model relative to the deterministic approach described above.

Results and Discussion

Source End-Member Analysis. Scatterplots for each variable in models of increasing size suggest that between 8 and 13 EMs are necessary in the model to account for sufficient variability in the data (Figure S4, Supporting Information). It is important that any residual variance (evident in the scatter) not be related to dechlorination. Otherwise, a dechlorination EM may go undetected in the model, even when present in the system. With 13 EMs, residual scatter for each variable is symmetrical about the 1:1 line (characteristic of error), and the coefficient of determination (CD), a measure of correlation between estimates and data (18), ranges from 0.86 to 1.00 except for 1,2,3,7,8,9-HxCDF, for which CD was 0.51. Sufficient variance is accounted for to allow even a low contribution of dechlorination to be contained in the model rather than in the excluded residuals. A few potential outliers remain, and their effect was assessed on source and dechlorination EMs. The impact on sources is discussed in the Supporting Information. Most importantly, however, the dechlorination EM is not affected by these outliers (Figure S6, Supporting Information).

The sensitivity analysis (summarized in Supporting Information and Figure S7) indicates a 10- or 13-EM model. The 10-EM model is chosen because the compositions of the additional three EMs are highly variable. Interestingly, the end-members tend to be very stable. The analysis shows that PVA results are less sensitive to k than previously assumed (24). Thus uncertainties about the fingerprints of various

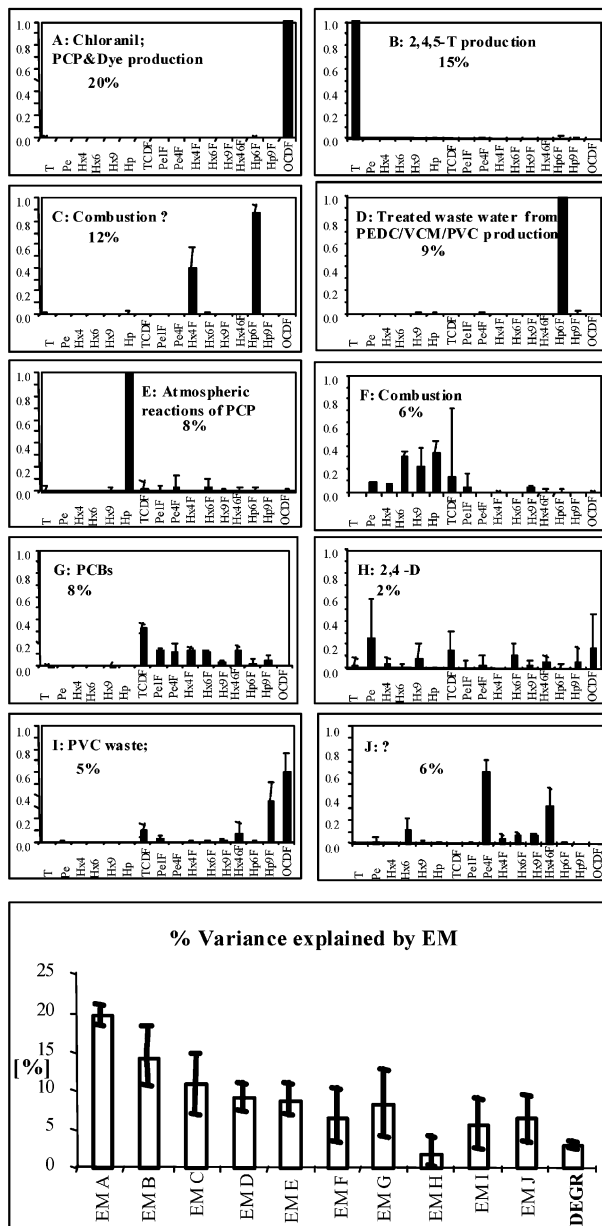


FIGURE 2. Source EM identification and the variance explained by each. The bars represent the average, and the error bars represent the standard error (deviation) calculated from the results of three different models. The y-axis is the proportion of a congener in the EM.

sources and model uncertainty regardless of the number of retained end-members are more relevant issues for decision-making than the actual value of k .

When applying M-PVA in the next step, the source end-members retain their identity, indicating that M-PVA is also robust. For comparison with source fingerprints (Figure S5, Supporting Information), the final source EM patterns from M-PVA (see numerical results in Table S2a, Supporting Information) are shown with the mean value and one standard error of each component across all models (Figure 2).

Of the 10 source EMs obtained through M-PVA, five have been identified previously (6, 10–12): PCB byproduct, combustion, possibly sewage sludge, production of pentachlorophenol (PCP)/chloranil/dyes, and 2,4,5-T production. In addition, there are new EMs identified as treated wastewater from vinyl chloride monomer (VCM) and poly(vinyl chloride) (PVC) production, PVC production waste,

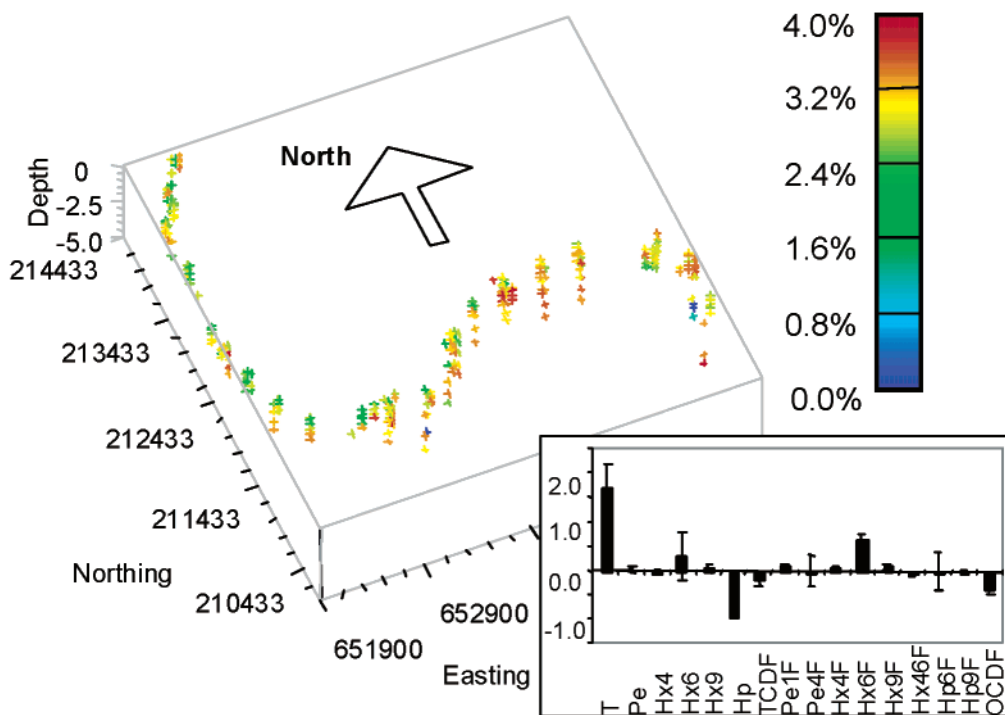


FIGURE 3. Dechlorination EM (3% average contribution to variance) (with the x-axis representing proportion of the congeners in the EM) and the spatial distribution of its loadings.

atmospheric PCP (or sewage sludge), and 2,4-dichlorophenoxyacetic acid (2,4-D). End-member C exhibits features of some combustion EMs, but its identity is uncertain. EM J is also unidentified (see Figure S5 in Supporting Information for source fingerprints used in identification). The validation of the source fingerprints is discussed in the Supporting Information.

Dechlorination End-Member Quantification. This EM (Figure 3, insert) occurred in three out of five possible models with a mean variance contribution of 3.0% and a standard error of 0.5% for the models with two, three and four relaxed EMs. Although not necessary, in all models, unconstrained, relaxed EMs (except EM_{dechl}) have a negligible net contribution of 0.00% to the overall variance. The dechlorination fingerprint shows that heptaCDD decreases in favor of TCDD with some 1,2,3,6,7,8-hexaCDD production. OctaCDF is similarly depleted resulting in 1,2,3,6,7,8-hexaCDF production. The intermediate congeners do not show net accumulation or depletion within uncertainty bounds. This EM occurs throughout the river, with an average sample contribution of $3.0 \pm 1.0\%$ increasing to up to 7.0% at isolated locations (Figure 3; Table S2b, Supporting Information). The variance contribution of the dechlorination EM is the most uncertain parameter in the analysis, and tests with artificial data suggest that this contribution may be overestimated by a factor of 5 (13).

Validation and Interpretation of EM_{dechl} . Further field data interpretation and correlation to laboratory observations are required to determine whether model results correspond to real world processes.

Laboratory experiments have indicated that the ratio of 2,3,7,8-TCDD to total 2,3,7,8-PCDDs (excluding OCDD) tends to increase during dechlorination, particularly in the presence of labile organic matter and in sediments (2, 3, 25). The elevated (>0.5) values for the ratio have been explained by a shift to predominantly peri-dechlorination (removal of 1,4,6,9 chlorines; Figure S1, Supporting Information) in the presence of organic (humic) matter, which also appear to prevail in Passaic River sediments. The interpretation of field data collected from several geographically distinct sites has indicated that a lateral (removal of 2,3,7,8 chlorines) dechlorination

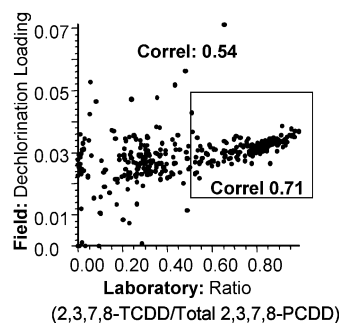


FIGURE 4. Relationship between laboratory-derived indicator ratio (2,3,7,8-TCDD/total 2,3,7,8-PCDD, excluding OCDD) and field-derived loadings.

mechanism can also dominate, resulting in a so-called "1,4-pattern" (26). The contribution of lateral 1,4,6,9-TCDD ranged from 3 to 66%, depending on the site. Since the PVA analysis included all 2,3,7,8-substituted congeners (except OCDD) available for the Passaic River site, the aforementioned ratio was used as an independent indicator of dechlorination in the field. When the field loadings of the dechlorination EM are plotted against this ratio, the correlation is high ($\rho = 0.71$) for values above 0.5, suggesting that the field and laboratory outcomes converge (Figure 4).

Given that the dechlorination pattern represented by EM_{dechl} suggests a possible accumulation of the most toxic congener (2,3,7,8-TCDD), which is also a characteristic of 2,4,5-T production, the absolute concentration contribution of dechlorination to this component is evaluated and compared to contributions by the 2,4,5-T EM. The absolute concentration contributions of TCDD to each sample s by an end-member i ($T_{i,s}$) can be back-calculated using its loadings ($a_{s,i}$), the end-member contribution ($f_{i,T}$) to TCDD and the total sample concentration of dioxins and furans (C_s) (each sample is normalized to C_s before PVA) such that

$$T_{i,s} = C_s a_{s,i} f_{i,T} \text{ for each } s \text{ with } \sum_{i=1}^k T_{i,s} \leq T_s \quad (3)$$

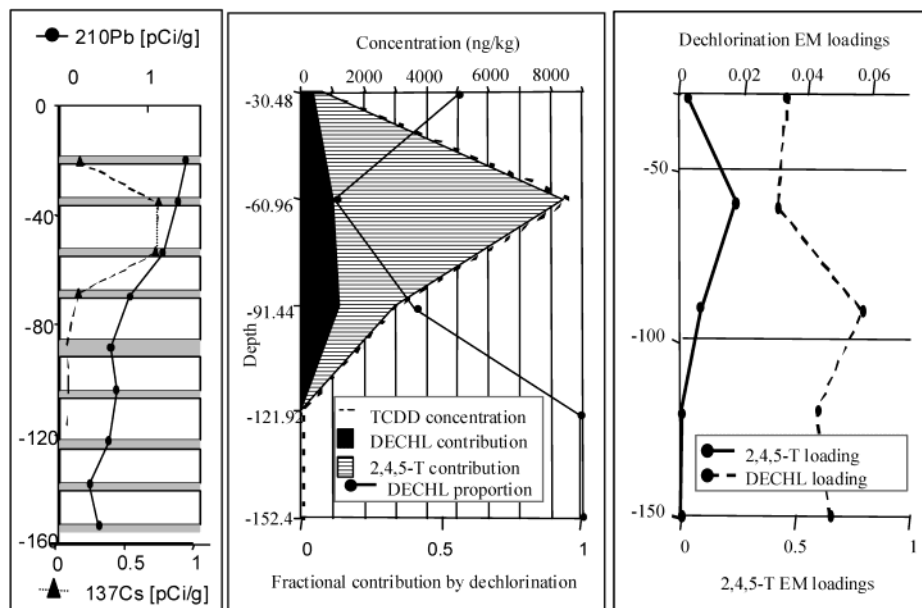


FIGURE 5. Depth profile of the contribution of 2,4,5-T and dechl end-members to total sample TCDD concentration in a core (center), end-member loading profile (right). (Linear interpolation between depths for easier recognition only.) ^{137}Cs and ^{210}Pb concentration depth profile on the left shows that the core is structured (i.e., undisturbed) so that depth represents time.

where $s = 1, 2, \dots, p$; a and f are individual elements of matrixes **A** and **F**; and T_s is the total sample concentration of TCDD. The proportion of $T_{i,s}$ in a given sample is then $T_{i,s}/T_s$.

Using this approach, the average absolute concentration contribution by the 2,4,5-T EM is $9.8 \mu\text{g}/\text{kg}$ (standard deviation: $70.4 \mu\text{g}/\text{kg}$), and the average proportion of 2,4,5-T-derived TCDD is 60% with a standard deviation of 30%. In 12% of the samples, this end-member does not contribute at all. Dechlorination contributes an average of $1.2 \mu\text{g}/\text{kg}$ (standard deviation: $5.9 \mu\text{g}/\text{kg}$) to TCDD concentrations, and its average proportion is 33% (standard deviation: 25%). Only 1.7% of the samples have no contribution by this end-member. Thus, the single most important direct source of TCDD across the site is the 2,4,5-T EM, followed by dechlorination. Industrial sources with no TCDD emissions contribute to the sediment TCDD concentrations indirectly by supplying the parent compounds to the dechlorination pathway.

The results of these calculations are exemplified for a core at which one of the highest dechlorination loadings (6%) is found (Figure 5). The sample concentration of TCDD peaks at a depth of 61 cm with the contribution of the 2,4,5-T EM. The contribution by dechlorination peaks just below at 91 cm. However, the proportion of the sample concentration due to dechlorination is highest below the concentration peak, where TCDD concentrations are the lowest. Most importantly, dechlorination is the dominant (proportion > 50%) source of TCDD at low concentrations, particularly in deep (122 and 152 cm) samples. The dechlorination loading also peaks below the concentration peaks where concentrations are lower. A plot of dechlorination proportion versus sample concentration for all samples reveals that this pattern applies throughout the site (Figure 6): the absolute contribution of dechlorination seems to be strongly influenced by dioxin concentration. Using (traditional) PVA on PCBs, Imamoglu and Christensen (27) were similarly able to relate a dechlorination-related EM to contaminant concentrations (although for PCBs, the dechlorination-concentration relationship is different). When the dechlorination proportion was plotted against depth, no apparent correlations could be observed (data not shown), whereas it would be expected that the proportion increases with depth (time). However, there are two confounding factors with regard to temporal

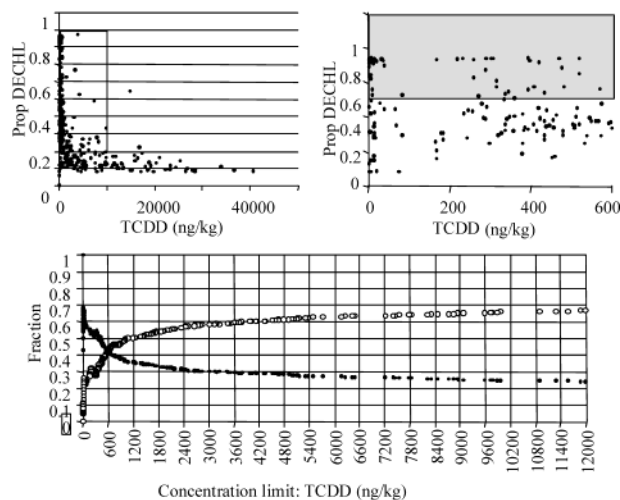


FIGURE 6. Proportional contribution of dechlorination to sample TCDD concentrations as a function of sample TCDD concentration for all (top left) and low (top right) concentrations. The shaded area denotes the 40% of the samples below 600 ng/kg in which dechlorination dominates (proportion > 50%) other sources. Bottom: Fraction of samples in which the 2,4,5-T EM (white) and the dechlorination EM (black) dominate below concentration limit.

patterns: (i) the competing concentration dependence and (ii) sediment disturbance by erosion and re-deposition processes. On the basis of a preliminary analysis of radio-nuclide data (^{210}Pb and ^{137}Cs), about half of the cores are structured (not disturbed). Another study of earlier samples at the same site dated the samples and also found about half of the cores to be structured (10). This means that at least in some cores a depth pattern could be observed. Since this is not the case, concentration may be more important than age in affecting dechlorination. The highest proportions of dechlorination contribution to TCDD are found in low-concentration areas either above or below concentration peaks. Below $10 \mu\text{g}/\text{kg}$, the dechlorination proportions increase above 20% (boxed-in area in Figure 6, left), and below $0.6 \mu\text{g}/\text{kg}$ 40% of the TCDD concentrations are dominated by dechlorination (shaded area in Figure 6, right). This observation supports preliminary laboratory data, which

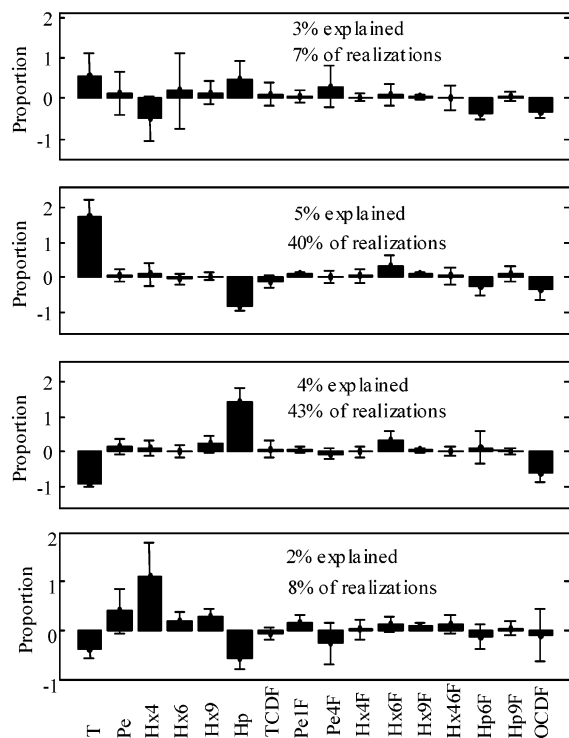


FIGURE 7. Relaxed and constrained EM as calculated in 100 bootstrap realizations. The dechlorination EM, as defined in this paper, occurred in 40% of the realizations.

indicated that elevated dioxin concentrations may inhibit anaerobic respiration, probably due to uncoupling of electron flow (2, 3). The threshold concentration below which dechlorination dominates the 2,4,5-T EM and other source contributions is 0.6 $\mu\text{g}/\text{kg}$ (Figure 6, bottom).

Uncertainty Analysis. Bootstrapping using 100 resampled data sets did not yield a unique dechlorination-like pattern; instead, four different types of relaxed and constrained end-members appear (Figure 7). The dechlorination pattern obtained from deterministic M-PVA arises consistently (small standard deviation) in 40% of the realizations with an average variability contribution of 5%, while an opposite pattern with an increase in heptaCDD and decrease in 2,3,7,8-tetraCDD is present in 43% of the realizations with an average variability contribution of 4%. The other two patterns (simultaneous increase or decrease in both of these congeners) occur in 7 and 9% of the realizations, respectively, with 2–3% of variability explained. This outcome indicates that there is still uncertainty about the uniqueness of a potential dechlorination signature in the sediments. Whether the other three patterns represent reactive end-members cannot be confirmed because of insufficient understanding of dioxin dechlorination pathways.

The impact of bootstrapping on the source end-members indicated that only EMs A–E and, in at least 50% of realizations, G consistently appear with little variation in their contributions (results not shown). The other source EMs previously determined fail to appear in any of the realizations, indicating that the deterministic approach alone may be insufficient to reliably extract all source information.

Environmental Significance. In previous applications of PVA, dechlorination was inferred from the relative differences of source fingerprints and end-member profiles but only in applications with PCBs (23, 26). That approach is a valid exploratory strategy, but it cannot take into account variability in end-member profiles. Fingerprints for dioxins are much less well characterized and much more highly variable in the same source category (e.g., combustion) than the Arochlor/

Clophen mixtures of PCBs. This fact, while rendering source identification more difficult, also makes qualitative inferences on dioxin reactivity unreliable. Modified PVA, as presented here, allows for direct modeling of dechlorination while also addressing uncertainty.

This is the first time that dechlorination of dioxins in the field is estimated directly from field data. The convergence between laboratory and field scale analyses is an important milestone in the research on dioxin reactivity and lends credence to the occurrence of natural dioxin dechlorination, as hypothesized in Gaus et al. (26) for other sites. This convergence underscores the need of integrating research at these two scales. To further validate this approach, methods must be developed to propagate the uncertainty resulting from bootstrapping into the mapping of concentrations and interpretation of individual sediment cores.

The juxtaposition of a deterministic and probabilistic application of M-PVA reasserts the challenge inherent in solving a problem with an infinite solution set. Resolving fingerprints at the edge of resolvable variance also adds unknowable uncertainties. Nevertheless, the approach presented here yields opportunities for hypothesis testing in the area of environmental forensics, where ultimate decisions must be made using a combination of different sources of evidence. Ultimately, the outcomes must be validated using targeted field sampling.

Acknowledgments

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Supporting Information Available

Diagram of dechlorination pathways; histograms of dioxin and furan data, their means, standard deviations, and coefficients of variation; CD plots for the final model size; fingerprints of identified sources; discussion of source EMs; outlier and sensitivity analysis; numerical results (matrices **A** and **F**) for final M-PVA model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Note Added after ASAP Posting

This paper was released ASAP on 02/04/2004 with an incorrect number in the Abstract (third sentence from the end). The correct version was posted on 02/10/2004.

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