

## Determination of Rates and Extent of Dechlorination in PCB-Contaminated Sediments During Monitored Natural Recovery

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Lake Hartwell

by NRMRL involved characterization of dechlorination in sediments using PCB congener fingerprinting and polytopic vector analysis (PVA).

NRMRL conducted studies to evaluate the long-term recovery of PCB-contaminated sediments via reductive dechlorination, including the magnitude, extent, and rates of ortho and meta plus para dechlorination reactions with sediment depth and time (4, 5). The information learned is summarized in this *Sediment Issue*, which is intended to be used as a reference for site managers and U.S. EPA decision makers who may be considering MNR as a contaminated sediments management strategy. The data summarized in this *Sediment Issue* were generated during field studies conducted by NRMRL in cooperation with U.S. EPA Region 4 at the Sangamo-Weston/Twelvemile Creek/Lake Hartwell Superfund Site in Pickens County, SC.

### Introduction

In aquatic environments affected by contaminated sediments, risk management strategies focus on either removing the contaminated material or interrupting exposure pathways by which contaminants might pose an ecological or human health risk over time. This is generally achieved by dredging, capping, or MNR. MNR relies on naturally occurring processes to reduce risk to humans and/or ecological receptors, including physical, biological, and chemical mechanisms

### Purpose

The National Risk Management Research Laboratory (NRMRL) of the U.S. Environmental Protection Agency (U.S. EPA) is developing effective, inexpensive remediation strategies for contaminated sediments. This program theme includes the study and development of field monitoring tools to evaluate Monitored Natural Recovery (MNR) processes in aquatic sediments (1). Previous researchers have demonstrated the potential for PCB dechlorination in sediments using other evaluation methods, such as chiral chemistry (2) and laboratory microcosms (3). In contrast, the approach taken

that act together to contain, destroy, or otherwise decrease the bioavailability or toxicity of contaminants in sediment (1).

In the case of PCB-contaminated sediments, where buried sediments are anaerobic and ample organic carbon is present, PCBs may undergo metabolic transformation through a process known as reductive dechlorination (6-8). This metabolic transformation is mediated by bacteria, resulting in a hydrogen substitution for a chlorine on the PCB molecule. Generally, higher-chlorinated PCBs are more susceptible to transformation via reductive dechlorination, resulting in the accumulation of lower-chlorinated PCBs (9).

Reductive dechlorination preferentially removes chlorines from the meta and para positions of PCBs (6), depicted in Figure 1, which has been shown to lead to the conservation of biphenyl rings and ortho chlorines. Dechlorination of meta and para chlorines can result in relative detoxification through elimination of coplanar-like congeners and aryl receptor-mediated toxicity (10, 11) and through the transformation of generally more toxic, higher-chlorinated congeners to generally less toxic, though more mobile, lower-chlorinated congeners (12).

Dechlorination patterns can be evaluated by measuring historical dechlorination patterns in vertical sediment core profiles and by multivariate receptor modeling, such as PVA. PVA, a sophisticated statistical procedure, is a self-training receptor/mixing model that separates complex mixtures into several contributing patterns and determines their contributions to each sample (13). PVA has been used increasingly for the characterization of PCB sources and to determine the transformation of PCBs in complex environmental settings (7-9, 14-16).

## Methods

**Identification and Characterization of Weathered and Dechlorinated PCB Congener Patterns.** Detailed PCB analysis of 107 congeners (PCB molecules) was used to measure historical dechlorination patterns in vertical sediment core profiles. Assuming the PCB source remains unchanged, congener shifts (patterns showing an accumu-

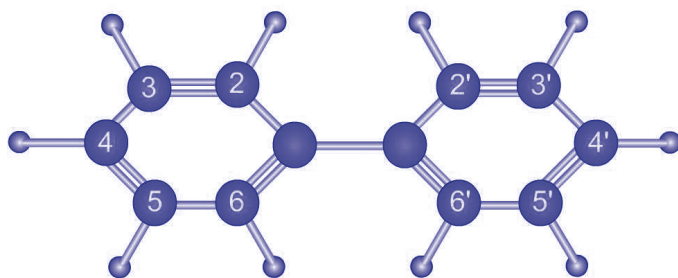


Figure 1. Meta (3,3',5,5') and Para (4,4') Positions of PCB Molecule.

lation of lower-chlorinated congeners and a corresponding decrease in higher-chlorinated congeners) are characterized by comparing surface sediment congener distributions with the distributions in buried sediments.

Congener-specific PCB data are evaluated using PVA. The use of a multivariate, variance-based technique, such as PVA, offers broad insight into mixing systems at a very high level of detail (sample-level resolution) using only data concerning the response variables of a system (13). PVA provides estimated compositions of contributing PCB fingerprints (end-members) directly from the analysis of the ambient data. The end-member (EM) refers to the original Aroclor formulation that the PVA analysis has determined and points to as being the original material that caused the contamination. In other words, PVA analysis is applied to a PCB data set that is comprised of an environmentally altered PCB congener composition (e.g., weathered, degraded), and the result of the analysis is an identification of the original Aroclor(s) that the contamination came from some time ago. PVA also provides estimates of the relative contribution of each EM in each sample. Only after the EM patterns are resolved are they compared to literature-reported source and alteration patterns (e.g., Aroclor compositions, PCB dechlorination patterns, and other weathering patterns). Using an exploratory approach with minimal *a priori* assumptions helps ensure that unknown or unforeseen PCB source or alteration mechanisms are not overlooked. Use of PVA, in conjunction with other forensic analysis approaches, can be important for understanding long-term fate and formulating efficient remediation strategies.

**Determination of Dechlorination Rates.** Sediment age dating, using lead-210 ( $^{210}\text{Pb}$ ) and cesium-137 ( $^{137}\text{Cs}$ ), and linear relationships between meta plus para chlorine concentrations and sediment age are used to determine dechlorination rates (4). These rates are compared with literature-reported rates and to rates calculated using this equation by Zwiernik *et al.* (17):

$$\text{MDR} = 1.16C_e + 6.37 \quad (r^2 = 0.960)$$

where MDR (nmol Cl/g sediment/week) is the maximum dechlorination rate and  $C_e$  ( $\mu\text{g/L}$ ) is the aqueous phase PCB concentration. The aqueous-phase PCB concentrations were estimated based on equilibrium-partitioning coefficients, fraction of organic carbon, and total PCB (t-PCB) concentrations. The magnitude and extent of PCB dechlorination is measured by plotting ortho chlorines and meta plus para chlorines per biphenyl molecule (i.e., mole chlorine/mole PCB) with sediment depth. Linear regression analysis is used to determine the rate of meta plus para removals over time (as will be shown in later examples in this *Sediment Issue*).

## Challenges

Challenges associated with using PCB dechlorination and the above methods to assess the extent of natural recovery include:

- **Direct Access to Reference Data Sets** – Direct comparison of the congener patterns observed in sediments under study to known or historic dechlorination patterns can greatly facilitate interpretation; however, raw historic data often are unavailable.
- **Assuming Relativeness of Surface Sediment Distributions to the PCB Source** – It is assumed that surface sediments are characteristic of the PCB source; however, if historical data from surface sediments are unavailable, this assumption may be impossible to prove.
- **Consistency of Dechlorination** – Dechlorination may be very extensive in most of the cores, but it may not be consistent from core to core or at various depth intervals within a single core.
- **Dechlorination Rates** – Rates of dechlorination are derived from the laboratory and may be higher than dechlorination rates measured directly in the field.
- **Analytical Limitations** – Chemical analysis may result in the coelution of certain PCBs, making it impossible to calculate the numbers of meta and para chlorines per biphenyl molecule separately. In order to address coeluting congeners in this study, the meta and para chlorines were summed so that the magnitude and extent of PCB dechlorination were measured using ortho chlorines and meta plus para chlorines per biphenyl molecule (i.e., moles chlorine/mole PCB). However, as subsequently noted later in this *Sediment Issue*, three factors were considered before summing the meta and para chlorines to calculate dechlorination rates: 1) the uniformity of source material in the sediments, 2) the conservation of ortho chlorines with sediment depth and time, and 3) the linear relationship between the meta and para chlorines and time.

## Case Study

### Lake Hartwell Superfund Site

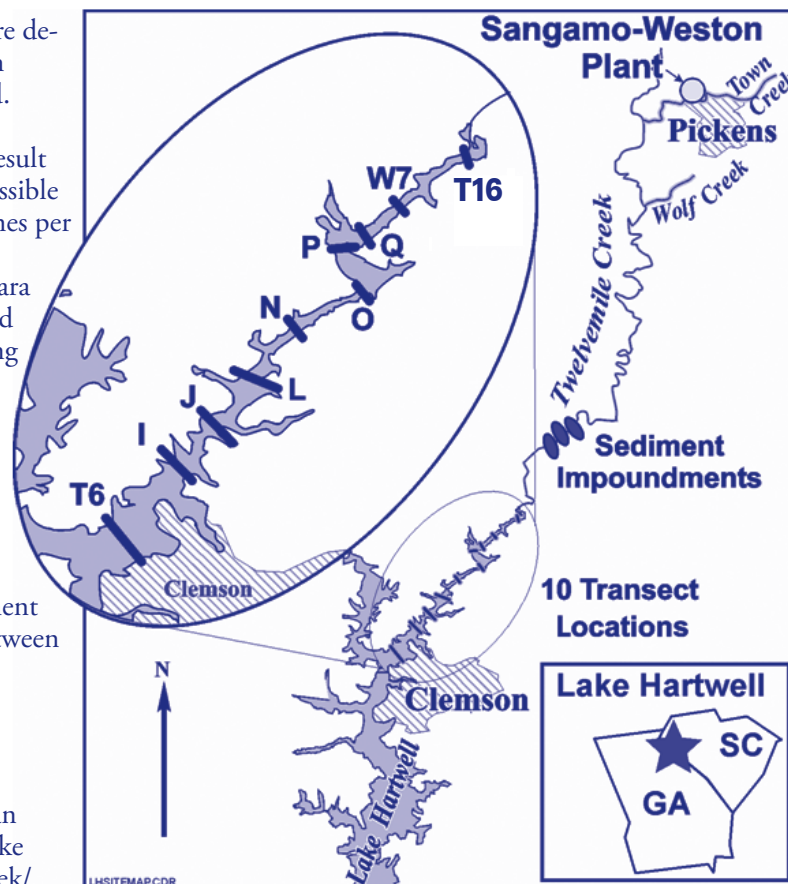
The methods described were conducted as part of an evaluation of the recovery of PCB-contaminated lake sediments at the Sangamo-Weston/Twelvemile Creek/Lake Hartwell Superfund site (Pickens County, SC), shown in Figure 2. The Sangamo-Weston plant manufactured capacitors from 1955 to 1978 using dielectric fluids containing Aroclors 1016, 1242, and 1254.

Though the Sangamo-Weston plant no longer exists, waste disposal practices dating back to earlier operations led to PCB-contaminated sediments in Lake Hartwell, downstream of the Sangamo-Weston plant (18).

A total of 280 samples from 18 sediment cores and surface sediment samples were collected during two annual events conducted in 2000 and 2001. Sediment sample locations are shown in Figure 2 as alpha-numeric transects. Sediment samples were analyzed for 107 PCB congeners, particle size distribution, total organic carbon (TOC), moisture content, and radioisotopes ( $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ ).

**1. PCB Dechlorination: End-Member Characterization.** PCB congener fingerprinting and PVA were used for identification and characterization of weathered and dechlorinated PCB congener patterns.

Congener shifts were characterized by comparing surface sediment congener distributions with the distributions in



**Figure 2. Location Map of Lake Hartwell Transects.** Lake Hartwell sediment cores were collected at 10 transect locations. Surface sediment samples were collected in Twelvemile Creek and in Town Creek above and below the former Sangamo-Weston plant. Reprinted with permission from (5). Copyright 2005, American Chemical Society.

buried sediments and then matched with literature-reported dechlorination patterns from other sites. Examples of congener distributions (mole percent) are shown in Figure 3 for surface and buried samples from the Transect L core collected in 2000. Congeners are plotted as they appear chromatographically, from left to right and generally from low to high molecular weight (from lower-chlorinated to higher-chlorinated congeners). Figure 3-c illustrates the net congener shifts from high to low chlorinated congeners due primarily to dechlorination, although other weathering mechanisms such as biotransformation, sorption, and benthic mixing also may have been involved. Negative concentrations in Figure 3-c represent a net concentration loss, while positive concentrations represent a net concentration gain. Comparison of the surface and buried congener distributions in the Transect L core reveals a congener shift from higher- to lower-chlorinated congeners with sediment depth and age.

PVA results were used to determine PCB source and dechlorination EM patterns and their distributions in each of the cores. Analysis of PVA goodness-of-fit diagnostics indicated a four end-member model.

Figure 4 shows the congener profile of the first end-member (EM-1) as an example. The similarities between congener profiles were evaluated by calculating the cosine theta ( $\cos \theta$ ) values (19). The  $\cos \theta$  value represents the cosine of the angle between two multivariate vectors, in this case the two matrices formed by the congeners used for each respective sample. A  $\cos \theta$  value of 0 would indicate two completely dissimilar, orthogonal vectors, and a  $\cos \theta$  value of 1.0 would indicate two identical vectors. The  $\cos \theta$  values were calculated for various Aroclor mixtures compared to EM-1, including mixtures of Aroclors 1016, 1242, 1248, and 1254. Comparison of EM-1 with the 50/50 Aroclor 1248/1254 mixture shown in Figure 4-b

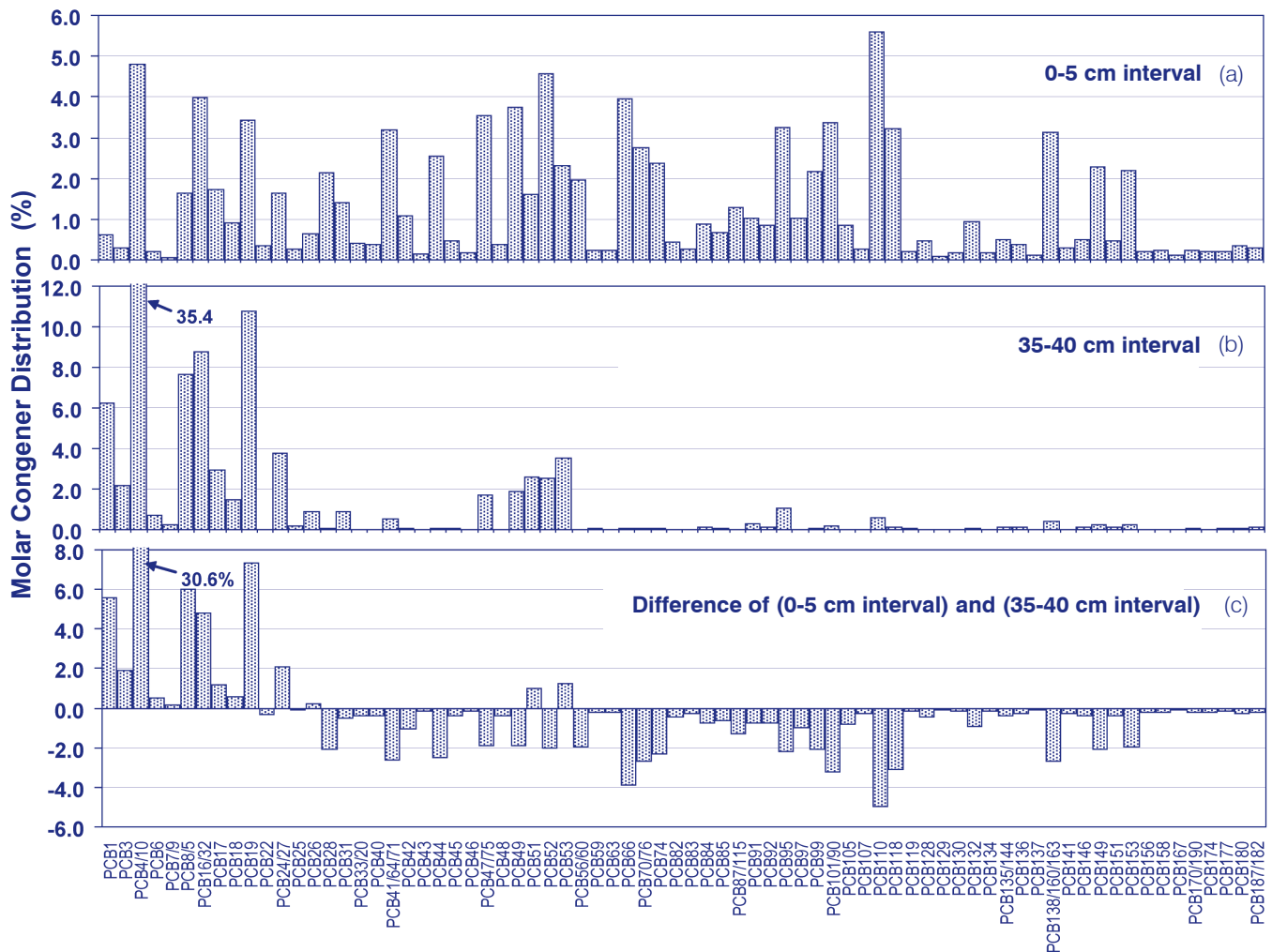


Figure 3. Congener Distributions Showing Dechlorination Characteristics for Lake Hartwell Sediments. Panel (a) shows Transect L (year 2000) surface sediment (0-5 cm) congener distribution; panel (b) shows the congener distribution in the 35-40 cm interval of the year 2000 Transect L core; and panel (c) shows the net dechlorination in the 35-40 cm interval by subtracting the congener distribution in panel b from panel a. Reprinted with permission from (4). Copyright 2005, American Chemical Society.

resulted in the highest  $\cos \theta$  value of 0.93. Comparison of EM-1 with the 50/50 Aroclor 1242/1254 mixture shown in Figure 4-c resulted in a  $\cos \theta$  value of 0.83. Both values are close to 1.0 and suggest strong similarities between these two Aroclor mixtures and EM-1. Congener profiles for EM-2 through EM-4 are provided by Magar *et al.* (5).

**2. PCB Dechlorination: Rates and Extent.** An evaluation was conducted to determine the extent of reductive dechlorination by the preferential loss of meta and para chlorines, the conservation of ortho chlorines with sediment depth and age, and the historical transformation of higher-chlorinated PCB congeners (congeners with four or more chlorines) to mono-, di-, and trichlorobiphenyl congeners with sediment depth and time. The magnitude and extent of PCB dechlorination was measured by plotting ortho chlorines and meta plus para chlorines per biphenyl molecule (i.e., moles chlorine/mole PCB) with sediment

depth, as shown in Figure 5. The loss of meta and para chlorines and the conservation of ortho chlorines with sediment depth suggests that the PCBs in the sediments underwent reductive dechlorination after burial.

Dechlorination rates were determined on a sample-by-sample basis for the Lake Hartwell site by plotting the numbers of meta plus para chlorines per biphenyl molecule (moles chlorine/mole PCB) with sediment age. Linear regression was used to determine the rate of meta plus para chlorine removals over time. Results of the linear regression analyses and corresponding meta plus para dechlorination rates measured for 2000 and 2001 cores are shown in Table 1. Three factors made it possible to calculate meta plus para dechlorination rates in this study: 1) the source material was relatively uniform throughout the Lake Hartwell surface sediments, 2) ortho chlorines were well conserved with sediment depth and time (the number of ortho chlorines did not change with depth since the input composition did not change with time), and 3) the linear

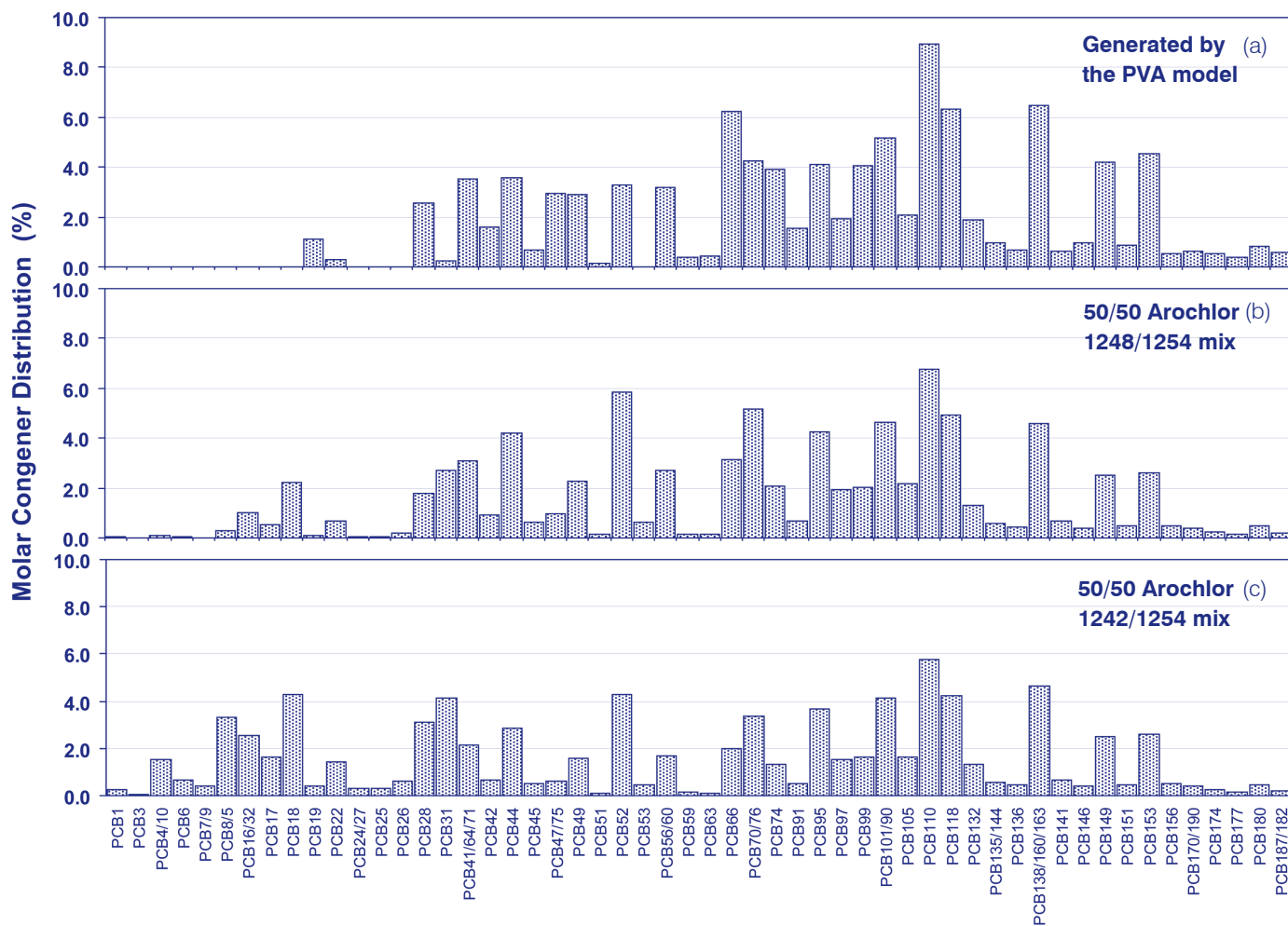
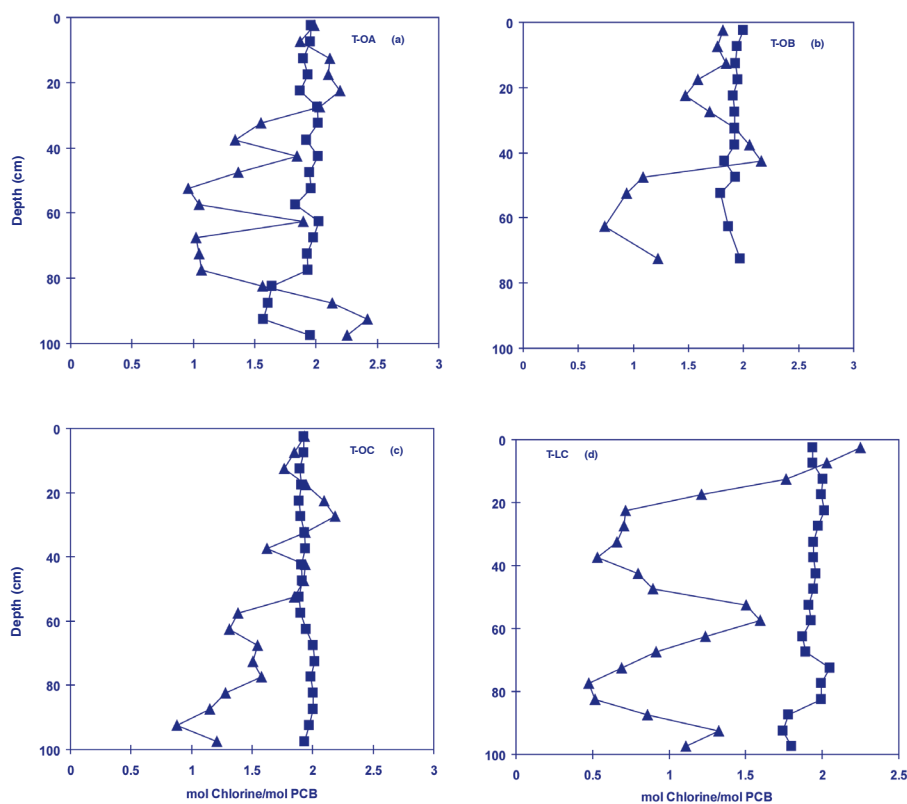


Figure 4. Congener Profile of EM-1. (a) Generated by the PVA model; (b) 50/50 Aroclor 1248/1254 mix; and (c) a 50/50 Aroclor 1242/1254 mix for comparisons. Reprinted with permission from (5). Copyright 2005, American Chemical Society.



**Figure 5.** Numbers of Ortho (■) and Meta Plus Para (▲) Chlorines per Biphenyl Molecule (Moles Chlorine/Mole PCB) with Sediment Depth for Sediment Cores Collected in 2001. Figures include (a) Cores T-OA, (b) T-OB, (c) T-OC, and (d) T-LC. Adapted from (4). Copyright 2005, American Chemical Society.

relationship observed between the number of meta plus para chlorines and time.

For comparison to rates calculated using the equation by Zwiernik et al. (17), the average dechlorination rates for the 2000 and 2001 transect cores (i.e., 0.0403 and 0.0266 mole Cl/mole PCB/yr, respectively, from Table 1) correspond to  $2.9 \times 10^{-6}$  mole Cl/g PCB/week and  $2.2 \times 10^{-6}$  mole Cl/g PCB/week, assuming 261 g/mole for Aroclor 1242 (the MDR equation was calculated using experiments with Aroclor 1242) and 52 weeks per year. Thus, average dechlorination rates assuming a sediment PCB concentration of 60 mg/kg (60,000 nanograms/gram) equates to 0.174 and 0.132 nmole Cl/g sediment/week for 2000 and 2001, respectively.

An inverse of the dechlorination rate indicates the time required for chlorine removal. Thus, for the average dechlorination rate for 2001 transect cores, the amount of time for chlorine removal would be about 33 years.

## Conclusions

At PCB-contaminated sediment sites, dechlorination may be an important component of the natural recovery of the sediments when anaerobic conditions

**Table 1.** Measured Dechlorination Rates Using Moles of Meta Plus Para Chlorines Over Measured Time Intervals for Buried Sediments.

Core	Depth Range (cm)	Date Range <sup>a</sup> (year)	No. of Samples	Percent Decrease (mole Cl/mole PCB/yr) (95% Confidence Limits)	Correlation Coefficient
<i>2000 Transect Cores<sup>b</sup></i>					
T-O	0 – 40	1981 – 1999	8	6.03 (6.01, 6.05)	0.92
T-N	0 – 40	1958 – 1997	8	3.21 (3.20, 3.23)	0.85
T-L	0 – 35	1979 – 1999	7	5.76 (5.73, 5.79)	0.89
T-I	0 – 60	1980 – 1999	11	6.25 (6.22, 6.27)	0.88
T-T6	0 – 20	1960 – 1998	4	2.81 (2.80, 2.82)	0.97
<b>Average</b>				<b>4.03 (4.02, 4.04)</b>	<b>0.79</b>
<i>2001 Transect Cores<sup>c</sup></i>					
T-OC	20 – 100	1952 – 2000	11	1.52 (1.50, 1.53)	0.68
T-LA	15 – 35	1962 – 1984	4	6.33 (6.29, 6.37)	0.94
T-LB	0 – 60	1987 – 2001	7	8.33 (8.31, 8.35)	0.97
T-IA	0 – 20	1993 – 2000	4	14.1 (14.1, 14.1)	0.99
T-IB	0 – 15	1996 – 2000	3	16.4 (16.1, 16.6)	0.85
<b>Average</b>				<b>2.66 (2.65, 2.68)</b>	<b>0.52</b>

<sup>a</sup> Dates were determined using <sup>210</sup>Pb and <sup>137</sup>Cs age dating techniques.

<sup>b</sup> The cores for the year 2000 were collected at the centerline of the 10 transects shown in Figure 2, i.e., one core to the depth indicated per transect.

<sup>c</sup> The cores for the year 2001 were collected laterally along (or across) three of the 10 transects shown in Figure 2. Three cores were collected to depth across Transect O (designated A, B, and C), three across Transect L (again designated A, B, and C), and two across Transect I (designated A and B).

exist and the source(s) of PCBs in sediment remain unchanged. Under anaerobic conditions, the primary metabolic pathway for PCBs is reductive dechlorination in which chlorine removal and substitution with hydrogen by bacteria result in a reduced organic compound with fewer chlorine molecules (6-8).

Reductive dechlorination of PCBs preferentially removes chlorines from the meta and para positions (6), which has been shown to lead to the conservation of biphenyl rings and ortho chlorines in laboratory dechlorinating enrichment cultures (14, 15). Generally, higher-chlorinated biphenyls are preferentially dechlorinated over lower-chlorinated congeners resulting in the accumulation of mono-, di-, and trichlorobiphenyls (9). As such, reductive dechlorination can be identified by the historical transformation of higher-chlorinated PCB congeners with sediment depth and time, and through the preferential loss of meta and para chlorines and the conservation of ortho chlorines. Determination of dechlorination rates is useful for predicting the number of years for chlorine loss to occur (i.e., for predicting when positive impacts of dechlorination could be observed).

PCB congener fingerprinting and multivariate receptor modeling such as PVA can be used as exploratory data analysis tools to characterize PCB sources and alteration patterns. PCB sources and alteration patterns are determined by comparing PVA EM patterns with known source patterns (i.e., Aroclors or Aroclor mixtures) and literature-reported alteration patterns. PVA also is used to characterize the vertical and lateral distributions of PCB source and dechlorination patterns.

Utilization of PCB dechlorination to assess the extent of natural recovery has proven to be a valuable tool; however, challenges associated with this tool may be encountered. Some of these challenges have been summarized herein to enable site managers to account for them in their research design and interpretation of results.

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