Magnitude and origin of polychlorinated biphenyl (PCB) and dichlorodiphenyltrichloroethane (DDT) compounds resuspended in southern Lake Michigan

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[1] Polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDT) compounds are introduced into the water as a result of large-scale storms and sediment resuspension in the southern basin of Lake Michigan. Settling and suspended sediments, as well as air and water samples, were collected in southern Lake Michigan over a 12 month period. Analysis of contaminant fluxes on settling particles shows that approximately 370 kg of PCBs and 110 kg of DDT compounds are resuspended in southern Lake Michigan during a single basin-wide event (January 1999). Examination of contaminant signals indicates strong regional and temporal source-receptor relationships between settling, suspended, and surficial sediments. The settling, suspended, and bottom surficial sediments in the shallow waters of the southern coastal region are enriched in lower molecular weight PCBs. The sediments in the water column and on the lake bottom in the deeper regions are enriched in higher molecular weight PCBs. Furthermore, falling sediments collected in the deeper regions of the lake are enriched in 4,4′-DDT. The unique contaminant signal in deep water regions is surprising and suggests a source/receptor relationship among the bottom sediments and the sediments suspended and settling above them.   INDEX TERMS: 4863 Oceanography: Biological and Chemical: Sedimentation; 4857 Oceanography: Biological and Chemical: Pollution; 1615 Global Change: Biogeochemical processes (4805); 9345 Information Related to Geographic Region: Large bodies of water (e.g., lakes and inland seas); KEYWORDS: persistent organic pollutants, sedimentation, principal component analysis, non-point source

1. Introduction

[2] The bottom sediments of the Great Lakes are contaminated with persistent organic contaminants, including polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDT) compounds [*Eisenreich et al.*, 1989; *Golden et al.*, 1993; *Oliver et al.*, 1989; *Pearson et al.*, 1997; *Schneider et al.*, 2001; *Wong et al.*, 1995]. Resuspension of sediments may be an important continuing source of these compounds and could explain why concentrations of these compounds in Great Lakes fish continue to exceed the FDA action level and water quality objectives defined by Annex I of the Great Lakes Water Quality Agreement. PCBs and DDT both contribute to states' and provinces' decisions to set fish consumption advisories, and for good reason. PCBs are implicated as endocrine disrupters [*Kester et al.*, 2000; *Walkowiak et al.*, 2001], immuno-depressants [*Weisglas-Kuperus et al.*, 2000], and known neurotoxins [*Schantz et al.*, 2003]. Consumption of PCB-contaminated fish is correlated with learning disabilities and developmental delay in the children born to Great Lakes' fish eaters [*Buck et al.*, 2000; *Jacobson and Jacobson*, 1996]. DDT is no longer viewed as a probable cause of breast cancer [*Safe*, 2000; *Snedeker*, 2001], but studies have shown that the DDT and its degradation products are endocrine disruptors [*National Research Council*, 1999].

[3] Lake Michigan has a long and intense history of exposure to these contaminants. *Golden et al.* [1993] estimated the total inventory of PCBs and DDT (parent and major degradation products) compounds in the lake to be 75,000 kg and 35,000 kg, respectively. The majority of these contaminant burdens are considered permanently buried, but some fraction of the surficial sediments may

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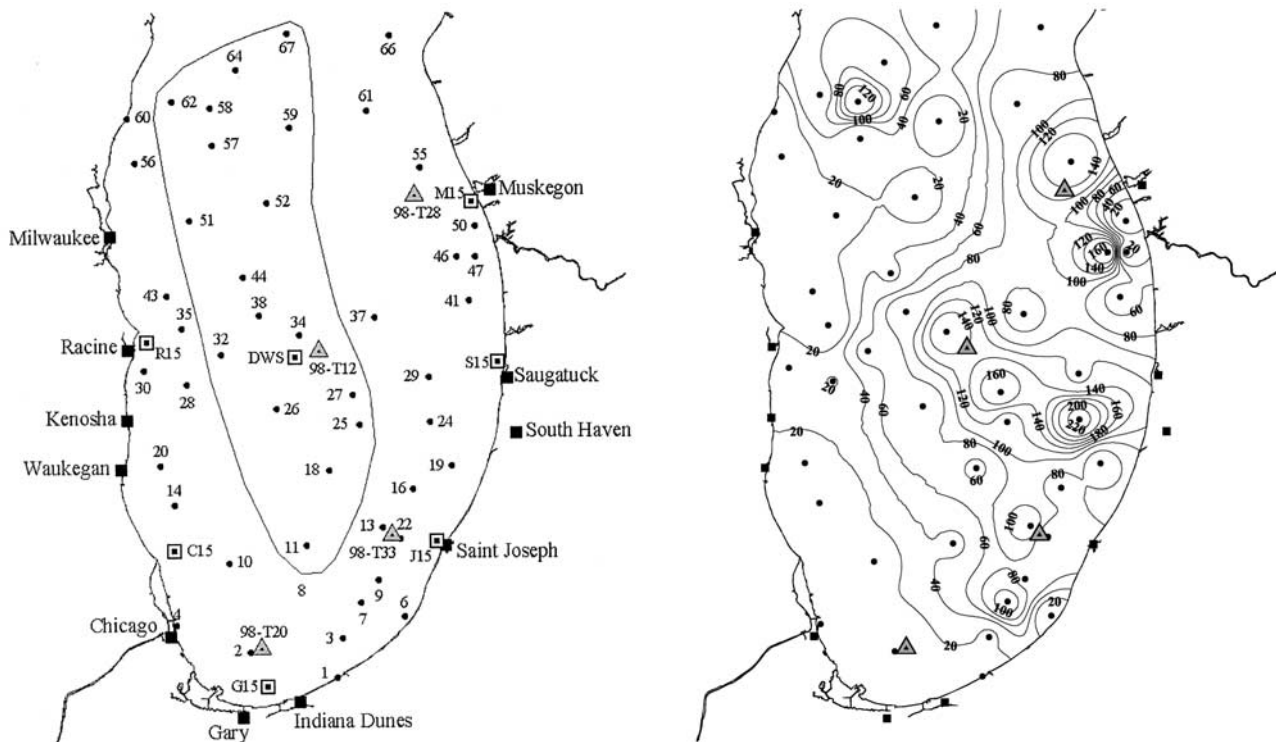
Figure 1. (left) Location of water (squares), sequencing sediment traps (triangles), and surficial sediment (points) sampling sites. The sites in the outlined region (labeled central and deep in Figures 4b–4d) show statistical similarity in the PCB congener distribution patterns. (right) Concentrations of ΣPCB, ng g^{-1}, in surficial sediments. The lines represent regions of constant concentration.

be reintroduced in the water column through resuspension. Of greatest concern is those regions of the lake where concentrations of PCBs and DDT in surficial sediment remain very high. A detailed survey of surficial sediment PCB concentrations was conducted as part of the U.S. Environmental Protection Agency's Lake Michigan Mass Balance/Environmental Monitoring and Assessment (LMMB/EMAP) field study in 1994–1995. The results show that the highest concentrations of surficial PCBs in the southern basin are found in the regions of highest sediment accumulation, primarily at depths exceeding 60 m [*U.S. Environmental Protection Agency* (*U.S. EPA*), 2001] in the central and eastern region (Figure 1). However, this distribution does not follow the lake bathymetry. Currents and prevailing circulation trends also have major impacts on the contaminant accumulation. An earlier survey of surficial sediments conducted in 1975 report similar distributions of ΣDDT [*Frank et al.*, 1981].

[4] Bottom sediments may be resuspended during the wintertime unstratified period. This may be an important source of contaminants to the lake. However, it is not clear if the most highly contaminated sediments, found in the deepest waters, are accessible to mixing under any conditions. Bottom sediments in more than 60 m of water can occasionally be resuspended under intense mixing during winter storms when the lake is isothermal [*Baker et al.*, 1991; *Eadie et al.*, 1984; *Hawley and Lee*, 1999; *Hawley et al.*, 1996; *Schneider et al.*, 2002] but coastal surficial sediments are expected to be the most important source of the sediment transported to in the open and deep waters of southern Lake Michigan [*Eadie et al.*, 1996, 2002].

Nearshore sediments are regularly resuspended, transported laterally and deposited into deeper regions. For example, in reporting a detailed field investigation of sediment transport in southern Lake Michigan, *Hawley and Lee* [1999] concluded that coastal sediments transported laterally is the major source of the settling sediment at the deeper sites in southern Lake Michigan. Also, *Edgington and Robbins* [1990], using radionuclide tracers, described how the southern basin of Lake Michigan is subjected to intense focusing processes that move sediment to deep regions.

[5] The first objective of this study was to determine the magnitude of organic contaminants resuspended in southern Lake Michigan, primarily during the winter period when the lake is not thermally stratified. The magnitude of resuspended PCB and DDT contaminants was examined using sequencing sediment traps deployed in the region. The second objective was to determine the source of the contaminated, resuspended sediment. To accomplish this, we exploit subtle but significant differences in PCB congener profiles. We examined the PCB congeners and DDT compounds in settling sediment, suspended sediment, and surficial bottom sediment.

[6] A series of field sampling efforts was conducted in southern Lake Michigan. The sampling strategy was designed to study large-scale resuspension events and organic contaminants. Sampling included: (1) settling trap material collected over one year in 1998–1999; (2) water, air, and suspended sediments collected during four sampling expeditions during the unstratified period of the same year. These samples are compared with data from a large survey of Lake Michigan surficial sediment. The locations of the

Table 1. Dates and Locations of Sequencing Sediment Trap Deployments

Station	Deployment Dates	Trap Depth, m/Station Depth, m
T12	June 1998 to May 1999	30/160
T20	October 1998 to March 1999[a]	12/25
T28	June 1998 to May 1999	30/110
T33	October 1998 to March 1999[a]	62/67

[a]Not a continuous chronology of samples.

samples collected through these three field efforts is illustrated in Figure 1. This work represents the first time the complex chemical signals from organic contaminants have been used to examine the magnitude and source of sediments and contaminants resuspended in the open waters of a large lake.

2. Methods

[7] This work was conducted as part of Episodic-Events-Great Lakes Experiment (EEGLE), a multi-investigator and multidisciplinary study of resuspension in southern Lake Michigan. The EEGLE project included deployment of sequencing sediment traps to capture settling sediment coordinated with a series of sampling expeditions timed to capture changes in the lake as a result of large-scale sediment resuspension. The sampling expeditions included sampling of air (vapor phase is reported here), and water (separated into suspended sediment and dissolved fractions).

[8] Sequencing traps were successfully deployed at four locations in southern Lake Michigan, and collected samples between May 1998 and May 1999. The locations and deployment periods of the trap collection at these stations is listed in Table 1. From the two most northern stations (T12 and T28; Figure 1), the traps were successful in collecting the full carousel of 23 samples. Because of problems caused by zebra mussel contamination, the deployment at station T20 yielded only nine noncontinuous samples, while a battery failure at station T33 caused the trap to stop sampling after the twelfth bottle. Bottles from traps deployed at three other locations experienced problems with the batteries and the bottles from these sites were used as blanks. Details of the sediment trap collection procedures has been described elsewhere [*Bogdan et al.*, 2002; *Muzzi and Eadie*, 2004; *Schneider et al.*, 2002].

[9] Water and air samples were collected during four sampling expeditions in the winter and spring of 1999. The water samples each consisted of 500 to 1200 L of lake water collected at less than 2 m depth. The particulate and dissolved phases in water and the particulate and gas phases in air are operationally defined by the separation on glass fiber filters and XAD-2 resin in series. These methods have been described elsewhere [*Achman et al.*, 1993; *Hornbuckle et al.*, 1993; *U.S. EPA*, 1997].

[10] All sediment trap, suspended, dissolved-, and vapor-phase samples collected were analyzed for a total of 98 individual PCB congeners and/or congener groups and 25 pesticides at the University of Iowa. The extraction of the sediment trap bottles with a 1:1 acetone:hexane solvent mixture used a repetitive sonication and centrifugation procedure to allow the analysis of the solids as well as the overlying water and chloroform preservative.

[11] The extraction of glass fiber filters and XAD used in the suspended and dissolved water sampling included a 24 hour Soxhlet reflux with a 1:1 acetone:hexane mixture. The concentrated extract was passed through a glass column of 3% deactivated silica gel with sequential elutions of hexane, 40:60 dichloromethane:hexane, 30:50 dichloromethane:methanol to clean and fractionate the sample by compound. Just prior to gas chromatographic analysis, each sample was injected with internal standards PCB 2,4,6-trichlorobiphenyl (IUPAC 30) and 2,2′,3,4,4′,5,6,6′-octachlorobiphenyl (IUPAC 204). Surrogate PCB congeners 3,5-dichlorobiphenyl (IUPAC 14), 2,3,5,6-tetrachlorobiphenyl (IUPAC 65), and 2,3,4,4′,5,6-hexachlorobiphenyl (IUPAC 166) were added to every sample prior to sonication or Soxhlet extraction.

[12] PCB analysis of the first fraction eluting from the silica gel column was performed using a Hewlett-Packard 6890 Gas Chromatograph equipped with a DB-5 60 m capillary column (J&W Scientific) [63]Ni microelectron capture detector (GC/μECD). The pesticide analysis of the first and second fractions was performed using mass spectrometry negative chemical ionization (GC/NCI) operated in select ion mode (CI-SIM) on the same Hewlett-Packard 6890 Gas Chromatograph. For the DDT compounds, ions 318, 352 and 355 were monitored in CI-SIM mode for quantification. The linearity of the detector response was confirmed for all compounds.

[13] The contaminant signals from the air, water, and settling sediment samples are compared to those reported for surficial (top centimeter) bottom sediments collected as part of the LMMB/EMAP. Only that sediment data that had passed all the U.S. EPA's LMMB/EMAP quality control measures as of 2/1/02 were used here. Three sampling techniques were used to acquire the uppermost layer of bottom sediment. Box cores were obtained wherever possible, mostly in depositional and some transitional regions. If a box core could not be used because of sediment composition (silt overlying clay), then a gravity core was used. If a gravity core could not be used then a PONAR grab sampler was used. The methods used for sample handling and chemical analysis of the LMMB/EMAP samples are comparable to the methods used for settling and suspended sediments.

2.1. Quality Control

[14] The quality of the data was evaluated through recoveries of added surrogate compounds, field and lab blanks, and quantitation limit studies. Of the 103 sediment trap samples collected and analyzed in this study, 17 (16.5%) were lab blanks and 19 (18.4%) were field blanks. Field blanks resulted from sequencing sediment traps that were deployed in southern Lake Michigan but did not operate properly, and hence the sample bottles did not open up to collect the settling particles in the lake. These field blanks, filled with deionized water, chloroform and a small amount of lake water, were in the lake for over 6 months.

[15] The mean surrogate recoveries (±95% confidence interval) during PCB detection were 74% ± 3.5% for congener 14, 78% ± 3.7% for congener 65, and 84% ± 2.6% for congener 166. By GC/NCI, the recoveries for surrogate congener 166 were 86% ± 3.0%, indicating comparable detector response. All samples were corrected for

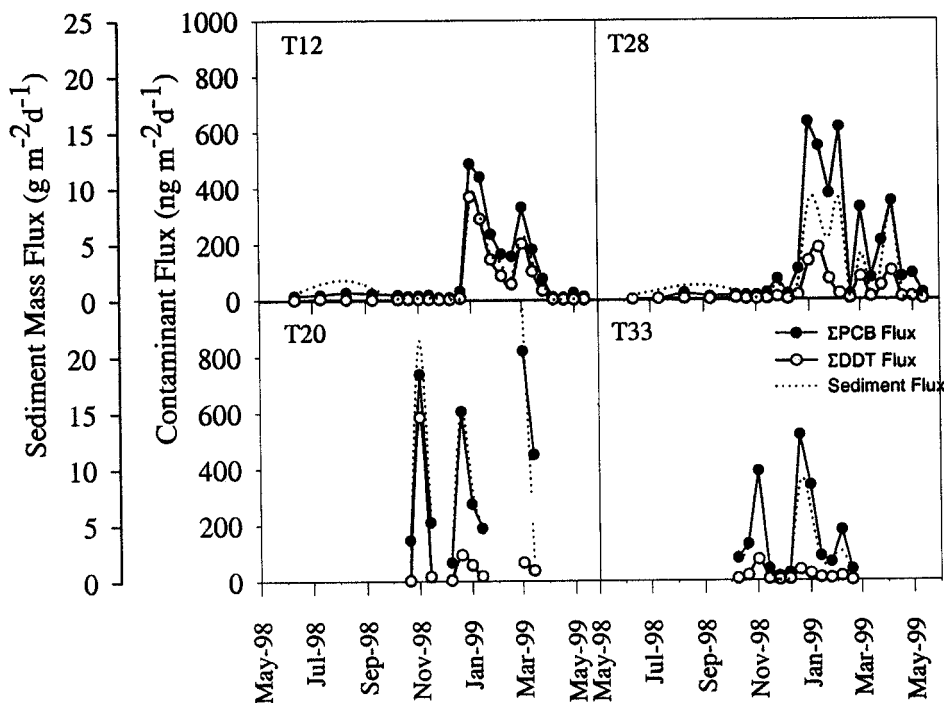**Figure 2.** Downward flux of sediment, ΣPCBs, and ΣDDT. The dates correspond to the first day of sediment collection. The points represent the integrated flux value for a collection period. Breaks in the connecting lines indicate time periods when sediment was not collected.

surrogate recovery. ΣPCB and ΣDDT in the field blanks, at the 95% confidence level, were 1.8 ng $\pm$ 0.72 ng and 0.62 ng $\pm$ 0.66 ng, respectively.

[16] A quantitation limit (QL) for the settling sediment data was determined to distinguish sample compound masses that are significantly larger than the field blanks. The QL was calculated as three times the standard deviation of the compound mass in the field blanks. The QL was determined on a congener or compound specific basis and compared to the contaminant masses in the samples. As a result of high QL values, 10 PCB congeners were excluded from the entire data set. For the remaining congeners, the QL for ΣPCB was 5.0 ng/sample. For the DDT group, the QL ranged from 0.10 ng/sample for 4,4′-DDD to 4.4 ng/sample for 4,4′-DDE. Figures in the auxiliary materials illustrate the low level of potential contamination in the settling sediment[1].

2.2. Statistical Analysis (Normalization, SAS)

[17] PCB congener patterns in 164 samples were analyzed for correlations using principal component analysis (PCA) in SAS Analyst, version 8 (SAS Institute, Cary NC) with Varimax rotation. Prior to PCA analysis, each PCB congener mass was normalized to the total PCB concentration in the sample. PCA was performed with a normalized matrix of the PCBs in 16 suspended sediments, 18 dissolved phase, 12 vapor phase, 67 settling sediment traps, 47 bottom surficial sediments, and 4 Aroclor mixtures. Some deletion or summation of specific

congeners was necessary to match the sets, resulting in a suite of 76 congener groups (see table in auxiliary material). Principal component analysis reduces the number of variables that describe the data set and identify a few variables or dimensions (eigenvectors) that adequately distinguish groups of samples from each other [*Dunteman*, 1989]. Without such a method it would be difficult, if not impossible, to compare the patterns of the 76 PCB congeners in the 164 samples to one another.

3. Results and Discussion

3.1. Resuspension of PCBs and DDT Compounds

[18] Sediment and contaminant settling fluxes exhibit highly episodic behavior in southern Lake Michigan, corresponding to regional storms during the unstratified period. In the 1998–1999 unstratified season, five resuspension events were recorded by the sequencing sediment trap systems (Figure 2). Two of the events were recorded at all the operating trap deployment sites: the first in late December through early January and the second in the first week of March. The December/January event was particularly strong. It was triggered by a storm in the eastern region on 30 December followed by another storm in the western region on 2 January (UCAR Nowcast archives). Recorded wave heights from tripods deployed near St. Joseph, Michigan City and Milwaukee reached a peak on 30 December 1998 (Hawley, NOAA/GLERL, personal communication), the largest between October and May of that year. On the same day, a resuspension event was recorded by Acoustic Doppler Current Profiler (ADCP) deployed near St. Joseph [*Beletsky et al.*, 2000].

Table 2. ΣPCB and ΣDDT Resuspension During the December/January Event

Site	Days[a]	Start Day[b]	End Day[b]	n[c]	ΣPCB		ΣDDT	
					ng/m^{2}[d]	kg[e]	ng/m^{2}[d]	kg[e]
T12	48	1 Jan. 1999	18 Feb. 1999	4	15,947	462	10657	309
T28	36	1 Jan. 1999	6 Feb. 1999	3	18,727	543	4716	137
T20	36	20 Dec. 1998	25 Jan. 1999	3	8,547	248	1341	39
T33	24	20 Dec. 1998	13 Jan. 1999	2	10,332	300	757	22

[a]Number of days of elevated sedimentation during the December/January event period.
[b]Inclusive dates of sediment trap bottle collection during the December/January event period.
[c]Number of sediment trap bottles recording the December/January event period.
[d]Compound flux over the December/January event period.
[e]Mass of compound resuspended over the entire southern basis (29,000 km^2) if each trap was representative of the entire region.

[19] The mass of contaminants associated with the December/January event can be estimated from the settling fluxes, the resuspension event period, and relevant lake area coverage. The latter is unknown, but is illustrated by calculating a contaminant mass flux as if each trap were representative of the entire region. Table 2 includes the contaminant fluxes and length of the December/January event period for each trap. This method has major uncertainties that cannot be quantified, especially since the western region included no traps and we do not know if measured chemical fluxes are representative. However, if each trap were representative of the entire southern region, then ΣPCB resuspension ranges from 250 to 540 kg of material resuspended. ΣDDT resuspension ranges from 22 to 310 kg of material resuspended. Clearly PCBs have a more uniform impact, varying by about a factor of two, than does DDT - perhaps reflecting more years of input and subsequent distribution within the lake for PCBs. An average estimate of resuspension is ~370 kg of ΣPCB, consistent with the 400 kg estimate for a single event in the previous year [*Bogdan et al.*, 2002]. There is greater uncertainty in the DDT estimate because of the larger variance between fluxes at the traps, but an average is ~100 kg DDT compound resuspended. We do not know of any previous estimate of DDT resuspension in the open waters of the Great Lakes.

[20] Resuspended contaminants may not be an ecological hazard. We do not know if desorption of contaminants from the resuspended sediment occurs. Even if desorption is thermodynamically feasible, there may be insufficient time before the sediment returns to the lake bottom. It is possible that there is no net change in contaminant burden, or in ecosystem exposure, especially since biological productivity is very low during the periods of the most active resuspension.

3.2. Contaminant Concentrations on Settling and Bottom Sediments

[21] The variation in contaminant concentrations in settling sediments may be used to identify sources of the resuspended sediments. For some compounds the variation is related to major resuspension episodes. For example, ΣDDT concentrations in settling sediment increase during major resuspension events (p = 0.001 for the entire data set; Figure 3). This effect was not statistically significant for ΣPCBs (Table 3), consistent with other reports [*Bogdan et al.*, 2002; *Schneider et al.*, 2002]. Concentrations of ΣDDT in settling sediment ranged from <2 ng g^{-1} to 44 ng g^{-1}, with

the highest values observed in January to March at the central T12 trap site. These are similar to concentrations reported for bottom sediment in southern Lake Michigan. Sampling of bottom surficial sediments completed in 1975 [*Frank et al.*, 1981] and in 1991 [*Golden*, 1994; *Golden et al.*, 1993] report concentrations ranging from 20 to 70 ng g^{-1} in the area below the T12 trap deployment site and exceeding 40 ng g^{-1} in the eastern region near site T33.

[22] The parent insecticide, 4,4′DDT was found in only one of the settling traps, T12, and only during the major resuspension period of January through March. 4,4′DDT is usually found in low concentrations in natural systems, as the compound has been banned in the U. S. for over three decades. DDT is reductively dechlorinated to DDD and dehydrochlorinated to DDE and both products were also present in the technical mixture. The latter dominates in all the settling sediment samples analyzed for this study, and is the major DDT compound in the surficial sediment [*Golden et al.*, 1993]. Parent 4,4′DDT was not found in the other traps, suggesting that T12 has a source of resuspended sediment that is not shared across the basin. A comparison of the ratio of these two compounds (4,4′DDT/4,4′DDE) finds similar values in bottom sediments of the depositional zones and in the January to March settling sediments at T12. The ratio is statistically the same: 0.30 ± 0.02 for surficial sediment from Golden et al. and 0.33 ± 0.06 for settling sediment in the T12 trap analyzed in this study. Frank et al. do not report concentrations of all the DDT compounds but does report that in the southern depositional zones, the parent DDT component represented 30.5% of the ΣDDT. In settling sediment the ratio approaches or equals zero at the other three traps. From these findings, we hypothesize that the settling sediments captured in the open lake T12 site are different, either in character or origin, from those captured at the three coastal sites. This hypothesis is further evaluated using PCB congener patterns below.

3.3. PCB Congener Distributions Vary Spatially

[23] A Principal Component Analysis (PCA) was conducted to examine similarities between sediment samples collected throughout the southern Lake Michigan basin. PCBs are very good analytes for the PCA method because each sample is described by many variables (congeners) with patterns that are difficult to identify or group by inspection. This method has been used to examine sources of PCBs in biota [*Vuorinen et al.*, 1997], sediments [*Ashley and Baker*, 1999], water [*Bremle and Larsson*, 1997; *Offenberg and Baker*, 2000] and air [*Helm and Bidleman*,
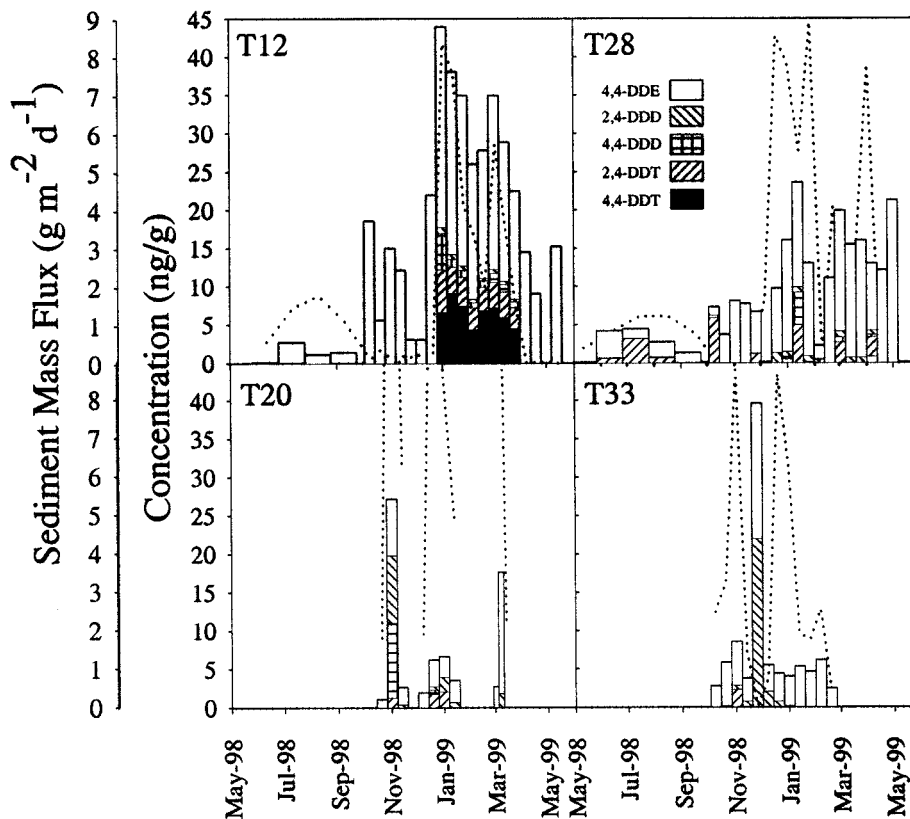
Figure 3. Concentrations (ng/g) of the DDT compounds measured in settling sediment. The dotted line is the downward flux of sediment.

2003]. In this study, PCA successfully identified PCB congener pattern differences and similarities between bottom sediments, suspended sediments, settling sediments, water and air.

[24] The first two principal components of the normalized matrix, which describe 72% of the total variability in the data, are plotted in Figure 4a. The first principal component (PC1) is an apparent measure of the molecular weight, hydrophobicity, and/or chlorination of the PCBs in a sample. Samples with congener distributions dominated by lower chlorinated congeners exhibit lower PC1 scores. Gas-phase and dissolved-phase samples are an example, in this study and others, of congener distributions enriched in the less chlorinated congeners (PCBs with two, three, and four chlorines). A correlation between chlorine number and PC1 was found and is illustrated in the auxiliary material. Chlorine number, Cl#, is defined in equation (1) and the results for various sample matrices are illustrated in Figure 5.

$$Cl\# = \frac{\sum_{i}^{76} (congener_i \cdot Cl_i)}{\sum PCB}. \qquad (1)$$

[25] $Congener_i$ is the mass of congener i in the sample, Cl_i is the number of chlorines in congener i, $\sum PCB$ is the sum of the 76 congeners masses in the sample. For the total data set, the correlation between PC1 and Cl# is significant but only

describes about half of the variability ($r^2 = 0.45$). For a subset of only the sediment samples plotted in Figures 4b–4d, the correlation is much stronger ($R^2 = 0.86$, see also auxiliary material). We conclude PC1 is primarily, but not exclusively, identifying the pattern differences due to PCB chlorination, molecular weight, or cocorrelated compound properties.

[26] The second principal component (PC2) best describes pattern differences for trap samples collected during periods of low resuspension and settling. This set of samples is labeled 'low-sed settling' in Figure 4a. These are trap samples that collected a small amount of settling sediment (<2 g m^{-2} d^{-1}). PC2 may be related to analytical

Table 3. Measured Concentrations of Contaminants in Sediment (Average ± Standard Deviation)

Study Period	Sediment Matrix	ΣPCB, ng/g (All for the Same 76 Congeners)	ΣDDT, ng/g
1998–1999 high sed[a]	settling sediment	60 ± 34	16 ± 12
1998–1999 low sed[b]	settling sediment	110 ± 150	8 ± 8
1999	suspended sediment	24 ± 20	6 ± 10
1994–1995	surficial bottom sediment	62 ± 58[c]	NA[d]
1991	surficial bottom sediment[e]	126 ± 4	69 ± 7.1

[a]During periods of high sediment settling fluxes (>2 g m^{-2} d^{-1}).
[b]During periods of low sediment settling fluxes (<2 g m^{-2} d^{-1}).
[c]U.S. EPA, Lake Michigan Mass Balance Program.
[d]DDT concentrations are not available for 1994–1995 surficial sediment.
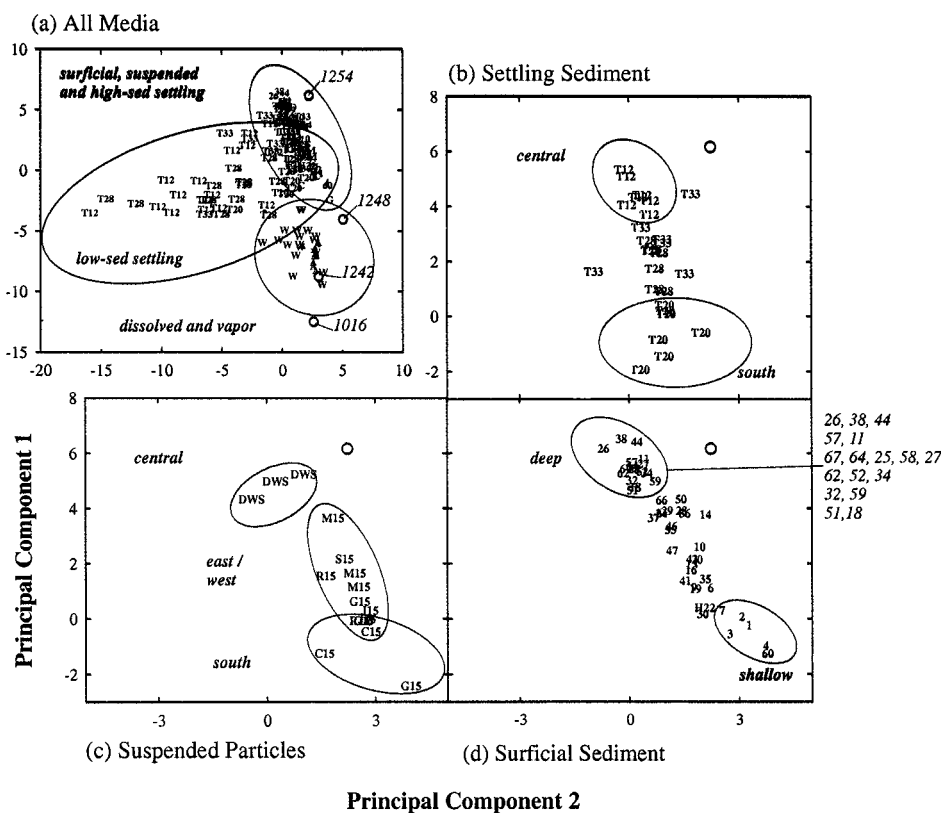[e]*Golden* [1994] site 18, near site 34 of this study, four 1 cm increments.

Figure 4. Principal component analysis (PCA) plots for sediment-associated PCBs in southern Lake Michigan. (a) The result of the PCA for all sample types. The dissolved- and gas-phase samples are represented as W and A, respectively. The open circles represent four of the major Aroclor mixtures. The remaining sample types (settling sediment, suspended sediment, and surficial bottom sediment) are represented by their site abbreviation (see Figure 1). (b)–(d) The results of the same PCA analysis, with the sample types separated for visual clarity. In Figure 4b, only settling sediment samples collected during periods of high (>2 g m^{-2} d^{-1}) downward sedimentation fluxes are shown.

sensitivity and detection limits. The samples with low PC2 scores have a large number of undetected congeners (see auxiliary material). However, PC2 is still a valuable component as it allows a statistical explanation for removing the 'low-sed settling' samples from additional analysis.

[27] Figures 4b–4d are plots of the same results as in Figure 4a, with sample groups plotted separately for clarity. Three major findings result. First, the PCA consistently groups together those sediment samples collected in the deep waters of the southern basin, regardless of the sediment's 'state' of suspension, settling or accumulation in bottom sediments. This grouping includes settling sediment collected at site T12 during resuspension events, suspended sediment collected at the DWS site, and surficial bottom sediment collected in deep water (see samples with PC1 scores near 5 in Figures 4b–4d). In all these cases, the congener distributions are enriched in highly chlorinated congeners (high PC1 scores). This type of signal would be expected from older sediment. *Jeremiason et al.* [1994], suggested that weathering of PCB patterns in the Great Lakes is primarily a function of volatilization of congeners rather than microbial degradation or sediment burial and results in enrichment of highly chlorinated PCBs and loss of the more volatile congeners. This is a subtle effect,

however, and would probably not be detected without the PCA. (Congener distributions for representative samples and homolog distributions for all samples are provided in the auxiliary material. Concentrations of surficial sediment for each grouping in Figure 4d are also provided in the auxiliary material.)

[28] Second, the PCA groups together those sediment samples collected in shallower waters of the southern region of the lake, regardless of the sediment sample matrix (suspended, surficial, or settling). Of these six sites, site 7 has a very high ΣPCB concentration (107 ng/g). The remaining sites of this 'shallow' group have much lower ΣPCB concentrations (7.7 ± 9.1 ng/g). In all these cases, the congener distributions are enriched in the less chlorinated congeners (low PC1 scores).

[29] Thirdly, the bottom surficial sediment samples collected on the eastern and western coastal regions are indistinguishable with respect to PCB patterns, unlike the deep water sites and the shallow coastal region (Figure 4d). The ΣPCB concentrations are statistically different, however, even if the patterns are not. PCB concentrations are significantly higher ($p < 0.001$) among surficial sediments collected in the eastern region (87 ± 60 ng/g) as compared to those in the western region (13 ± 7.6 ng/g). Our trap
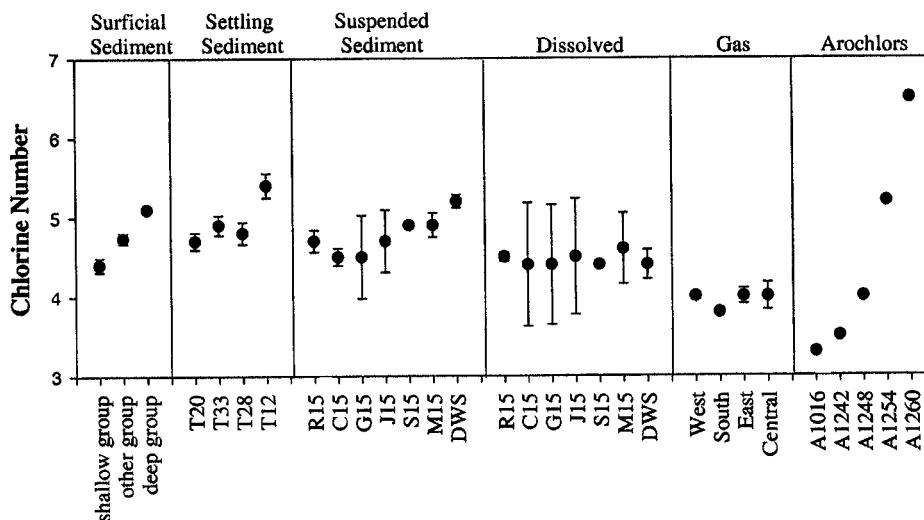
Figure 5. Chlorine numbers for samples organized by media and collection region, except for the Aroclor mixtures, which are organized by molecular weight. The solid circles represent the average chlorine number for the sample group; the bars represent one standard deviation.

deployment and sampling expeditions did not include the western coastal region so settling sediment cannot be directly compared with the bottom sediment in this region.

3.4. PCB Congener Signals in Sediments Vary Over Time

[30] PCB congener signals in the settling sediments change over the course of the year. Figure 6 describes this change in PCB signal for all four traps. The PCB signal is represented as the first principal component (PC1) so that it can be plotted two dimensionally. At sites T12 and T28, the sites with the complete annual record, this change is most evident. Since PC1 is primarily a function of a shift in molecular weight, or chlorination, the resuspension events are associated with heavier PCBs. PC1 is not completely a function of molecular weight, however. As discussed above, during the stratified period of low rates of sediment settling, the first principal component is not well correlated with molecular weight. So the PC1 scores during the spring, summer and early fall are not necessarily representative of molecular weight. In general, however, large storms resuspend high molecular weight PCBs, especially in the deeper regions of the lake. At other times of the year, the background PCBs in the suspended and settling sediments consist of more of the lower chlorinated congeners.

[31] The PCB signal starts to change prior to the major settling periods. At both the T12 and T28 sites, a series of steadily increasing PC1 scores are observed during the four to six weeks prior to the major event. No corresponding increase in settling fluxes is observed. At this time, the lake is still stratified at T12, but coastal regions of the lake are beginning to turn over. Particles collected in traps during this pre-event time may be reflective of coastal resuspension processes that move sediment from the coastal margins into the deep lake.

4. Conclusions

[32] During intense resuspension, the sediments on the bottom of southern Lake Michigan share the same chemical signal as the suspended and settling sediments in the water column above or nearby. This indicates a common source of sediments in each region, which we have classified as shallow, deep and a group of 'other' sites located in both the eastern and western coastal region.

[33] The sediments in the shallow regions of the lake have a distinct chemical signal. The settling, suspended and bottom surficial sediments in the shallow waters of the southern coastal region are more enriched in lower molecular weight PCB congeners than elsewhere. There are several known sources of contaminated sediment in the extreme southern region of the lake, including the Grand Calument River and Indiana Harbor Ship Canal [*U.S. EPA*, 2003]. While *Offenberg and Baker* [2000] found that the Gary region was a source of higher PCB content particles, we found that the bottom surficial and settling sediments are not unusually contaminated. We did not find evidence of major sediment release from the canal during resuspension events, probably because flows from the canal are well controlled. Sediment in this region does not accumulate. It is rapidly transported to deeper regions. Therefore the chemical signal is reflective to background inputs, including atmospheric deposition [*Green et al.*, 2000; *Offenberg and Baker*, 2000; *Paode et al.*, 1998; *Simcik et al.*, 1999].

[34] The sediments in the deep waters of the open lake have a distinct chemical signal. The sediments in settling, suspended, and surficial bottom sediments are enriched in higher molecular weight PCB congeners and the settling sediment is more enriched in 4,4′-DDT. This chemical signal is consistent with older sediments that have retained the less volatile contaminants and lost the lighter and more volatile compounds. The presence of 4,4′-DDT is notable. Detection of 4,4′DDT only in the central T12 trap suggests that deeper sediments were accessible only during the most intense storm related turbulence.

[35] The unique contaminant signal in deep water regions is surprising and suggests a source/receptor relationship among the bottom sediments and the sediments suspended and settling above them. Two explanations are proposed.
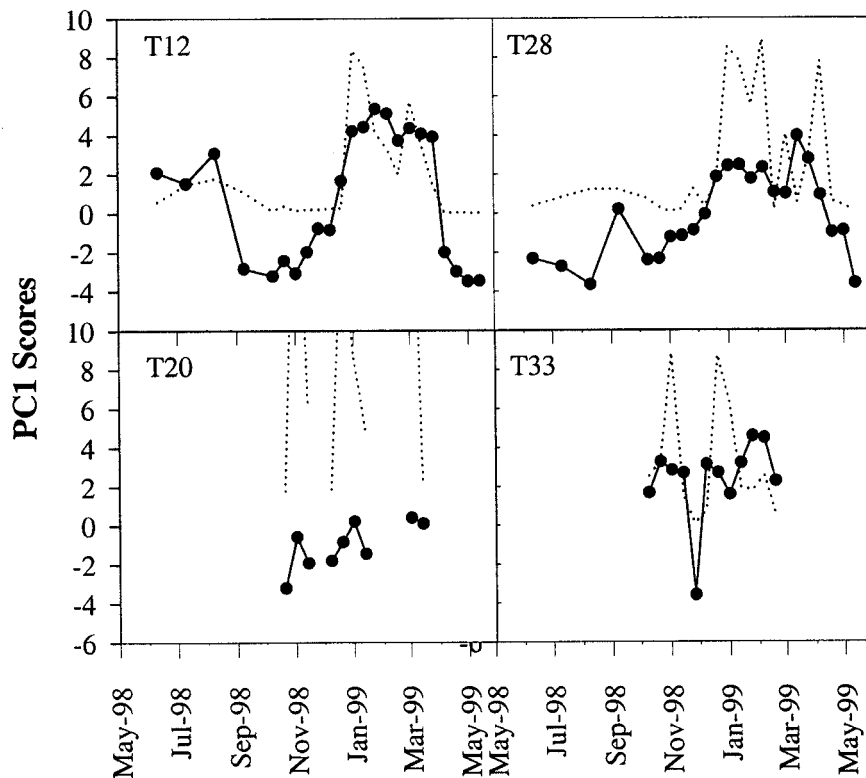
Figure 6. PC1 scores for settling sediment versus the first day of collection. Since PC1 scores are correlated with increasing PCB chlorine number, increasing PC1 scores can be interpreted as increasing PCB chlorination in the sample. The axis scale is the same for PC1 scores (solid points and line) and for sediment mass flux (g m^{-2} d^{-1}, dotted line) for each plot.

First, the sediments in the water column may have been resuspended from the surficial bottom sediments directly below them. While this is a reasonable explanation for the signals observed in the shallower regions, it is less plausible for those deeper regions of the lake. Sediments settling in deep regions are expected to originate from surficial sediments in coastal regions. The average depth of the sediments with similar chemical signals in this group is 120 m, a depth considered inaccessible to resuspension. In fact, there is clear satellite evidence that transport of some sediment from coastal regions to the open lake is ongoing during intense resuspension events [*Eadie et al.*, 2002].

[36] A second explanation is that the spatial differences between sediments in deep and shallow waters are a result of sorting by particle size or transport. Particle sorting by size is likely to occur during resuspension events: Larger particles fall more rapidly and close to their sources while finer particles fall slower and further from their source [*Digiano et al.*, 1993; *Roberts et al.*, 1998]. Higher molecular weight organic contaminants tend to associate with finer particles of higher organic carbon content. The combined effect of these factors may result in spatial and temporal differences in PCB signatures in the lake. We cannot address this fully as the particle size distributions and organic carbon contents by size in all the settling, suspended, and surficial sediments of our study are not available. However, we do not think that this effect can completely explain our observations. A PCB pattern difference as a result of particle size would have resulted in significant differences between the PCB patterns in settling, suspended and surficial sediments. In fact, we observe strong similarities in these sediments, when paired in time and space. We therefore conclude that deep and highly contaminated sediments are resuspended during high-intensity large-scale storms in unstratified waters.

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The Magnitude and Origin of PCB and DDT Compounds Resuspended in Southern Lake Michigan

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10 pages: 2 Tables and 7 Figures

Table S1. Concentrations of ΣPCB (sum of 76 congener groups) in bottom surficial sediment. The sites are categorized as deep, shallow, and other based on the groupings identified by the principal component analysis of the PCB congener patters (see Figure 4 and text), not by the actual depth of the water column.

A. 'Deep' sites

site	ng/g	Region	Method	Water Depth (m)
11	39.1	South	S	87
18	59.1	Central	S	127
25	116.1	Central	S	124
26	73.1	Central	B	148
27	172.3	Central	S	145
32	62.3	Central	G	111
34	151.1	Central	S	157
38	90.6	Central	P	125
44	39.2	Central	P	93
51	12.9	East Central	P	89
52	14.4	Central	P	86
57	20.9	Central	P	91
58	135.2	Central	S	152
59	8.4	Cemtral	P	80
62	54.8	East Central	S	129
64	65.7	Cemtral	P	140
67	26.1	Central	P	149
average	67.1			**120**
stdev	50.3			27

B. 'Shallow' sites

site	ng/g	Region	Method	Water Depth (m)
1	0.6	South	P	6.2
2	1.4	South	P	20
3	18.7	South	P	26
4	16.4	South	P	8
7	106.7	South	S	47
60	1.3	Eastern	P	8
average	24.2			**19**
stdev	41.3			16

C. 'Other' sites

site	ng/g	Region	Method	Water Depth (m)
6	4.9	Eastern	P	17
9	79.0	Eastern	G	55
13	113.2	Eastern	G	79
16	76.1	Eastern	G	60
19	73.7	Eastern	G	45
22	60.9	Eastern	S	52
29	118.5	Eastern	S	82
37	75.5	Eastern	S	110
41	56.1	Eastern	S	58
46	180.8	Eastern	S	73
47	16.6	Eastern	S	47
50	5.2	Eastern	P	29
55	152.8	Eastern	S	90
61	89.5	Eastern	S	138
66	67.7	Eastern	S	98
24	224.9	Eastern	S	73
10	15.3	Western	P	51
14	8.5	Western	P	41
20	16.2	Western	P	45
28	19.9	Western	P	80
30	25.6	Western	P	18
35	5.4	Western	P	52
43	5.7	Western	P	46
56	5.7	Western	P	71
average	62.4			**63**
stdev	60.7			28
ave east	87.2			
std east	60.4			
ave west	12.8			
std west	7.6			

Table S2. Congener groups analyzed for this study. The order is the same as is displayed in Figure 6 in the article, minus those highlighted in yellow. Those in yellow were eliminated from the analysis due to high QL values. ΣPCB is the sum of the remaining compounds.

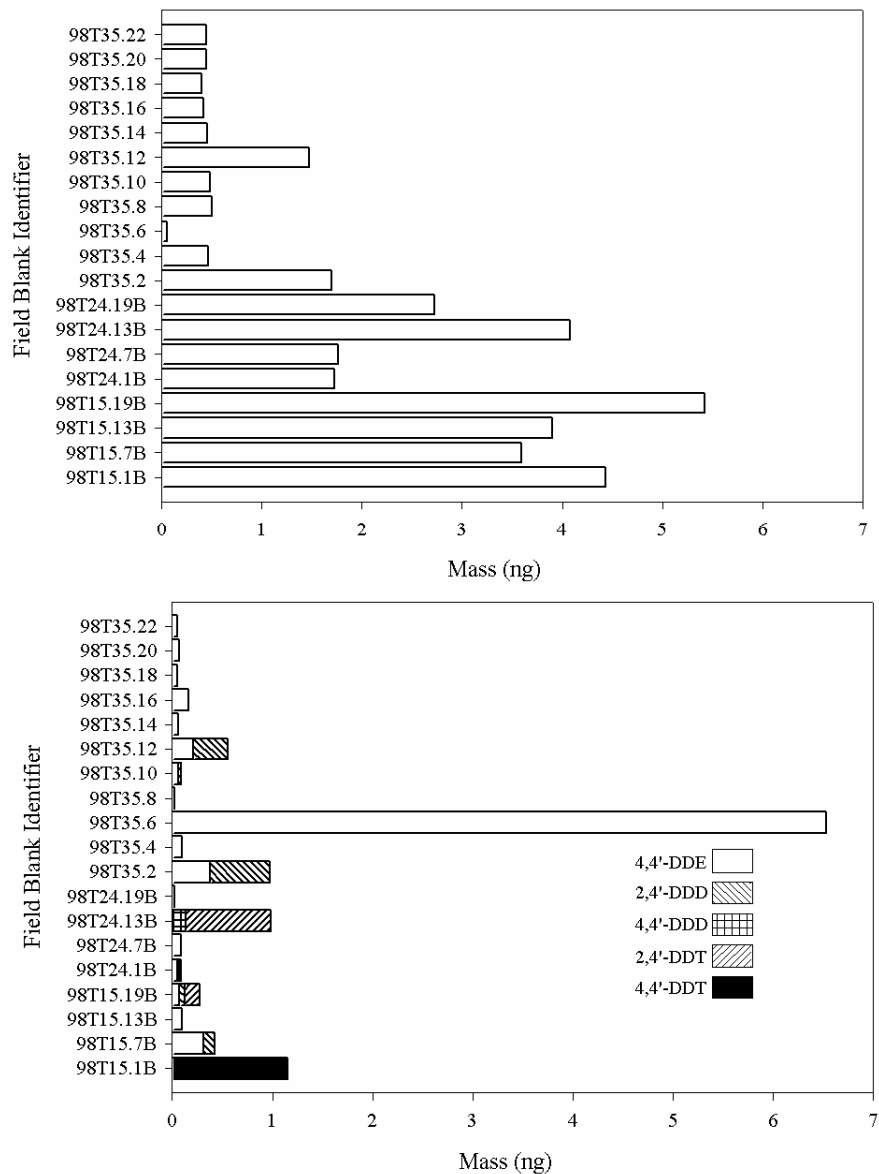|	
4+10	81+87
7+9	85
6	136
8+5	110+77
19	82
12+13	151
18	135+144
15+17	107
24+27	123+149
16+32	118
29	134
26	114+131
25	146
31	153+105+132
28	141
33	137+176+130
53	163+138
51	158
22	178+129
45	187+182+175
46	183
52	128
49+43	185
47	174
48	177
44	202+171+156
37+42	157+200
41+71	172
64	197
40	180
100	193
63	191
74	199
70+76	170+190
66	198
95	201
91	203+196
56+60	189
84+92	208+195
101	207
99	194
119	205
83	206
97	209

Figure S1. Field blanks for settling sediment. 4,4'-DDE was detected in 17 of 19 field blank bottles, 2,4'-DDD was detected in 5 bottles, 2,4'-DDT was detected in 3 bottles, 4,4'-DDD was detected in 2 bottles and 2,4'-DDT was detected in only one field blank bottle. Bottle 98T35.6 is an 4,4'-DDE outlier (greater than 3 standard deviations from the mean) and was discarded from the calculation of the MDL. Field Blank Identifiers 8T35, 98T24, and 98T15 were collected from failed traps deployed near Benton Harbor MI, St. Joseph MI, and Racine Wisconsin, respectively.
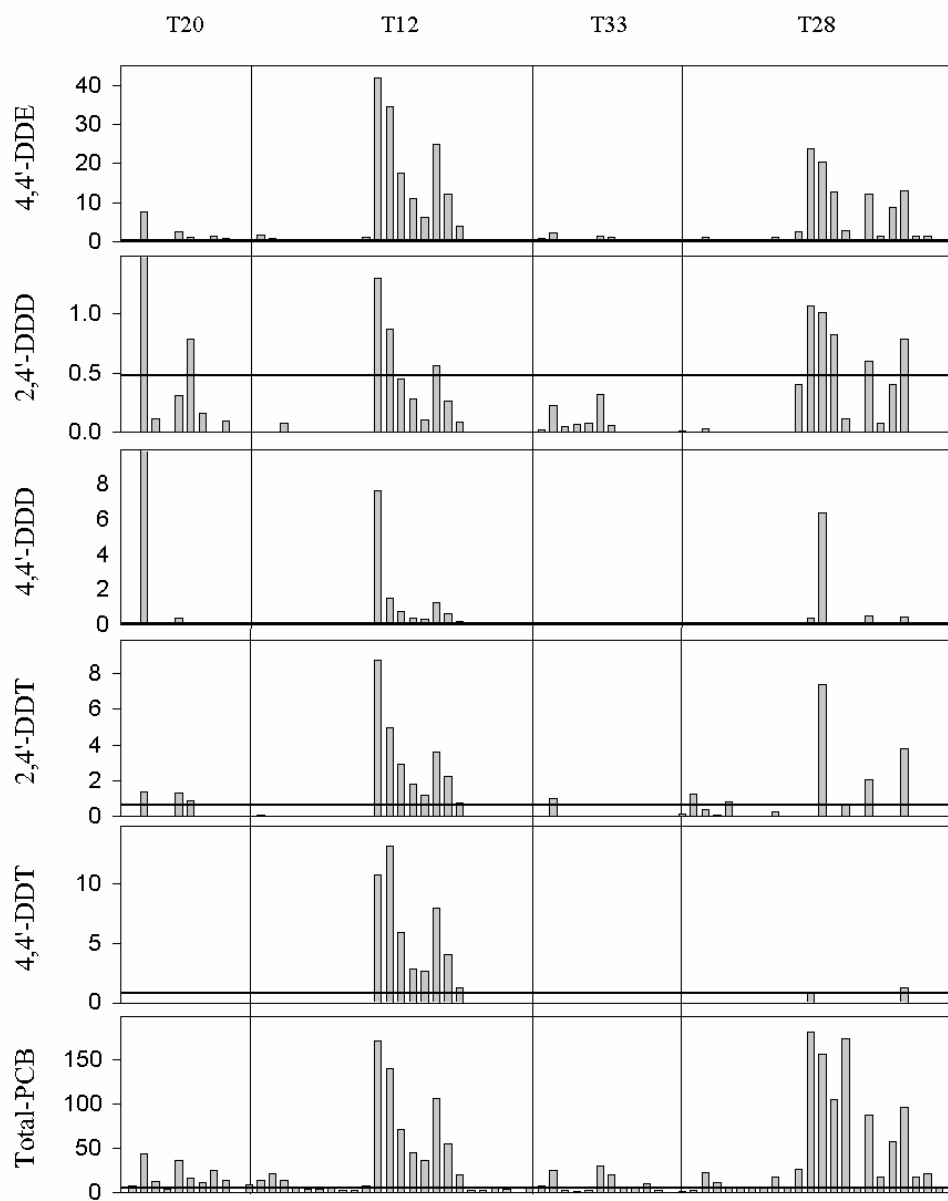
Figure S2. DDT compounds and ΣPCB mass (ng) in settling sediments (bars) and Calculated quantitative limits (horizontal line).
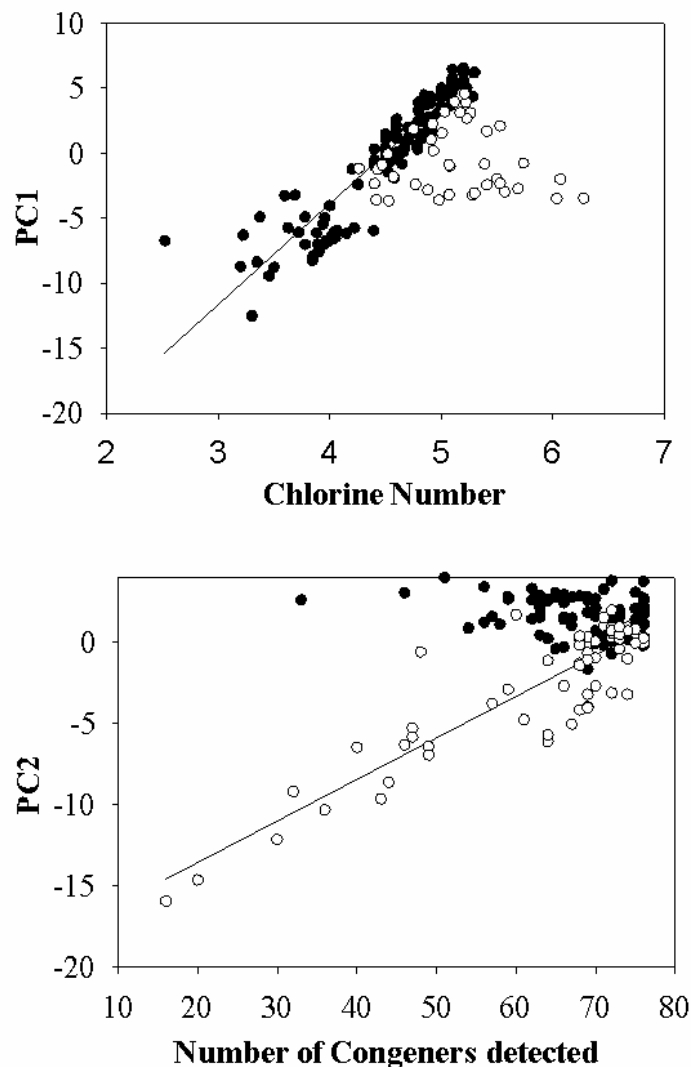
Figure S3. Relationship between principle components and characteristics of the samples. In both plots, the black circles represent settling sediment samples collected when the sedimentation rate exceeded 2 g m^{-2} d^{-1}. The open circles are settling sediment samples collected at lower settling fluxes. The top plot illustrates that PC1 is correlated with the chlorine number (defined in the text) for the sample. The correlation is strongest for the high sedimentation samples (R^2 = 0.86, regression line included) and is less strong for the whole data set (R^2 = 0.45). The bottom plot illustrates that PC2 is correlated with the number of PCB congeners detected in the sample. The correlation is strongest for the low sedimentation samples, where the least amount of sediment was collected (R^2= 0.80, regression line included). For the total data set, R^2 = 0.41.
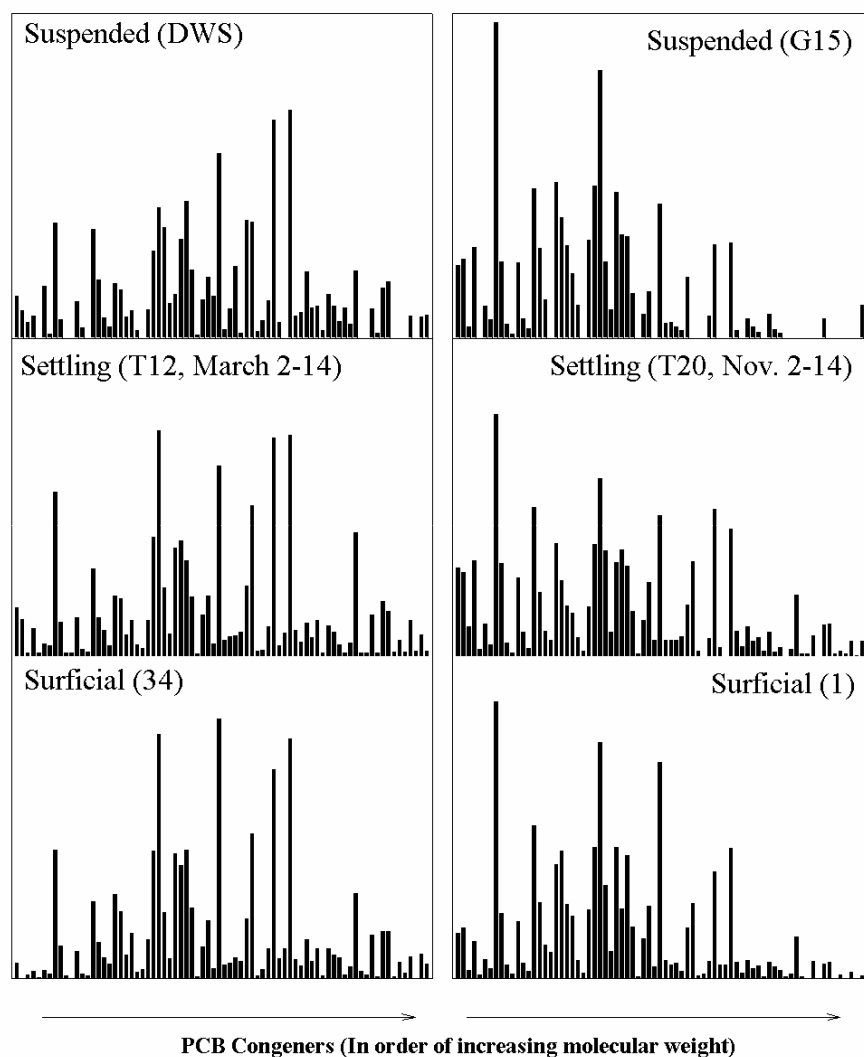
Figure S4. PCB congener distributions of suspended, settling, and surfical bottom sediments (top to bottom, respectively). The series of three plots on the left are grouped by PCA as deep and central site locations. The series of three plots on the right are grouped separately by PCA as shallow sampling locations. Most of sites in this grouping are from the southern coastal region
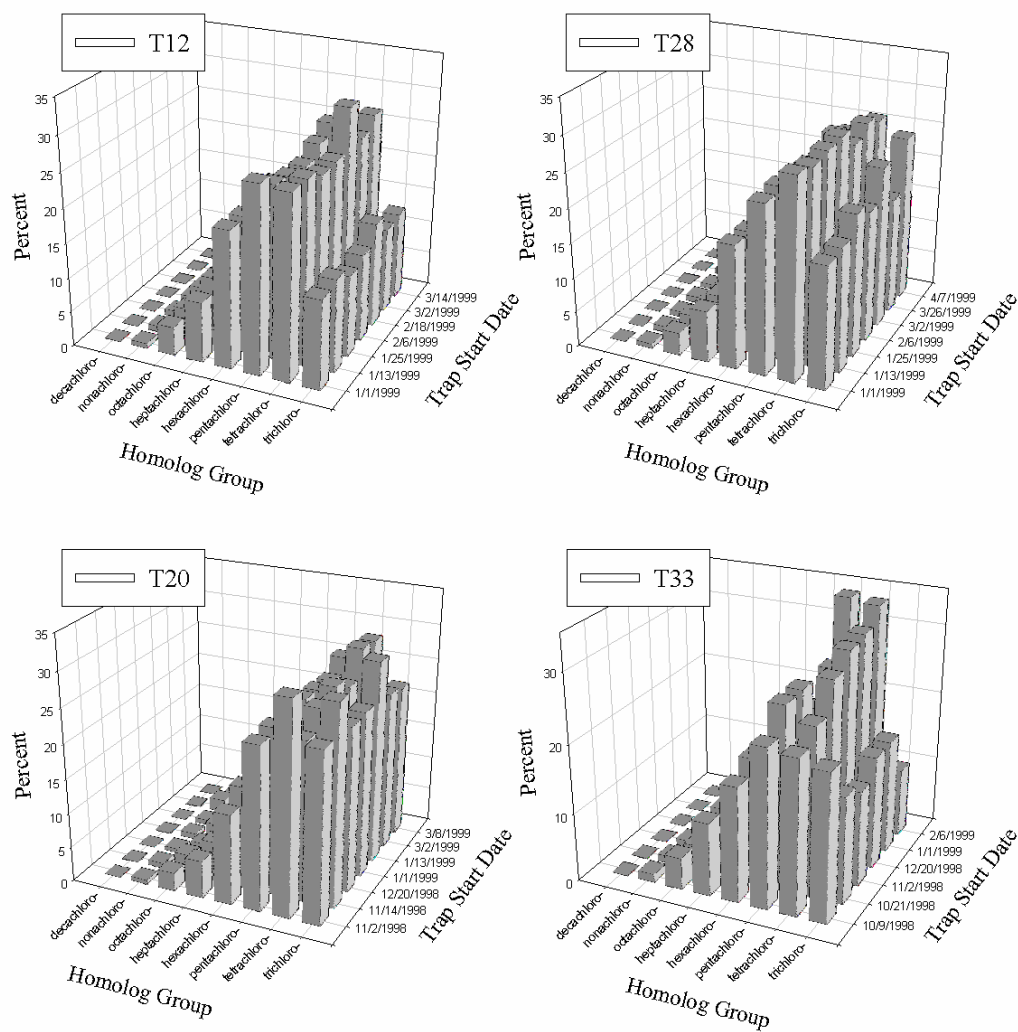
Figure S5. Percent of ΣPCB in each homolog for settling sediment samples collected during periods of high sedimentation (≥ 2 g m^{-2} d^{-1}). As illustrated by the PCA and by sample Cl# (see text), settling sediment during resuspension events at site T12 is enriched in higher chlorinated homologs (4, 5, and 6 chlorines) compared to T20 for which the sediments are enriched in the lower chlorinated homologs (3 chlorines). It is interesting that the sediment congener distributions at T33 change over time, with more of the lower chlorinated PCBs present in the fall than in winter.
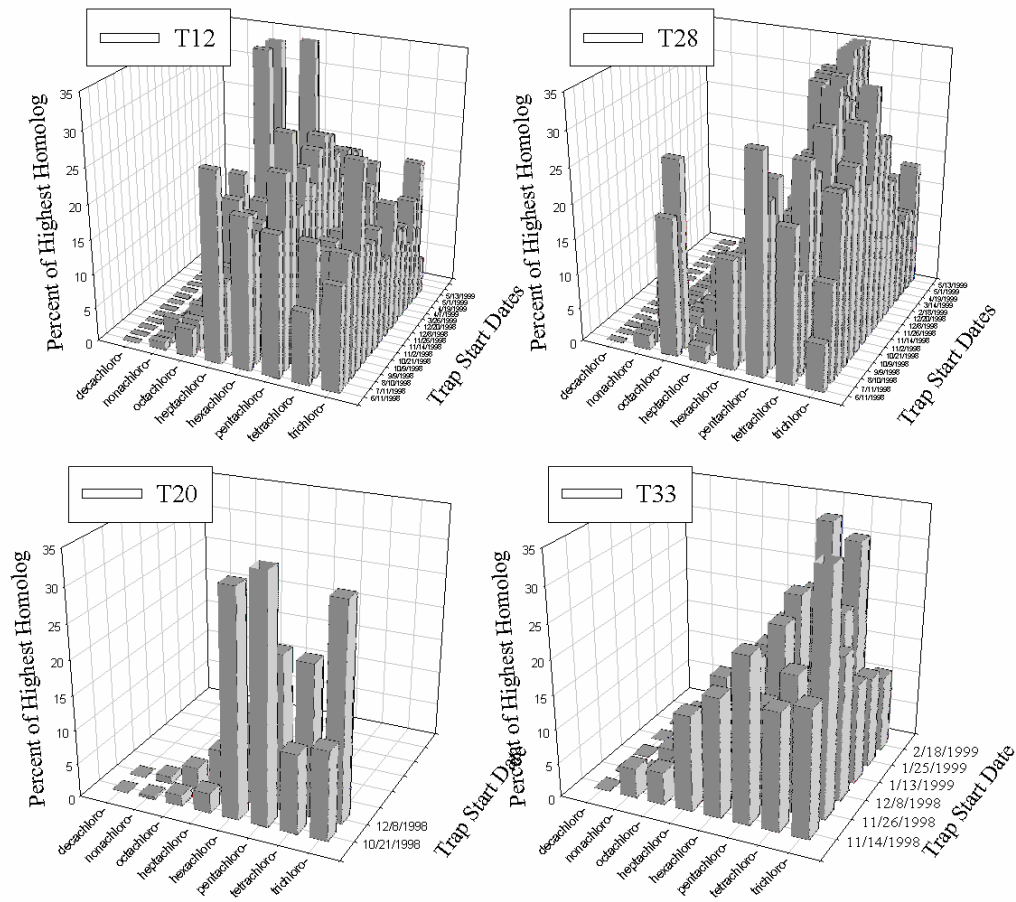
Figure S6. Percent of ΣPCB in each homolog for settling sediment samples collected during periods of lower sedimentation (< 2 g m^{-2} d^{-1}). Detection of PCBs in settling sediment during these periods is more difficult and approaches or fails detection limits. The homolog distribution signal is therefore more varied than observed in Figure S4.

Figure S7. Percent of ΣPCB in each homolog for air, water, and suspended sediment samples collected during expeditions. As illustrated by the PCA and Cl# analysis, gas-phase samples are enriched in trichlorobiphenyls.