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Spatial and temporal variations of persistent organic pollutants impacted by episodic sediment resuspension in southern Lake Michigan

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Abstract

The impacts of large-scale, episodic sediment resuspension on the cycling of polychlorinated biphenyl congeners (PCBs) were examined using a spatially coordinated air and water sampling strategy conducted in southern Lake Michigan in the late winters of 1998, 1999, and 2000. We found no significant temporal changes in gas phase, dissolved phase, or suspended sediment PCB concentrations despite large-scale seasonal storms occurring before and after sampling campaigns. Only gas phase and suspended sediment PCBs varied spatially. Higher total suspended material (*TSM*) concentrations and fraction organic carbon (f_{oc}) were measured at sampling stations located in the near-shore region of southern Lake Michigan than at open-water sampling stations. Gas phase concentrations (ΣPCB_g) were higher in the west (0.436 ± 0.200 ng/m^3, $n = 11$) and south (0.408 ± 0.286 ng/m^3, $n = 5$) than the east (0.214 ± 0.082 ng/m^3, $n = 10$) and central (0.253 ± 0.145 ng/m^3, $n = 8$) regions of southern Lake Michigan. Dissolved phase concentrations (ΣPCB_d) averaged 0.18 ± 0.024 ng/L ($n = 52$); suspended sediment concentrations (ΣPCB_s) accounted for between 4% and 72% ($23 \pm 4\%$, $n = 52$) of the total ΣPCB concentrations ($\Sigma PCB_T = \Sigma PCB_d + \Sigma PCB_s$). Despite no consistent temporal variations in both dissolved phase or suspended sediment ΣPCB concentrations, there were temporal and spatial variations in the distribution shift between phases that can be linked to sediment resuspension, not a state of equilibrium. Specifically, our analysis suggests sediment resuspension results in preferential sorption of heavier, more chlorinated PCB congeners.

Index words

PCBs; POPs; Lake Michigan; Sediment resuspension; K_{oc}

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Introduction

Large-scale, episodic sediment resuspension has been shown to reintroduce large amounts of persistent organic pollutants (POPs) to southern Lake Michigan (Bogdan et al., 2002; Hornbuckle et al., 2004). The physical characteristics associated with spatial and temporal variations that influence sediment and its resuspension in southern Lake Michigan play an important role in the behavior of the POPs with which they are associated (Robinson et al., 2008). Previous studies of POPs in Lake Michigan (U.S. Environmental Protection Agency, 2004; Miller et al., 2001) have been designed to examine aggregate spatial and temporal concentrations in support of whole-lake, mass balance modeling efforts (Zhang et al., 2008). The study described here is unique as it was designed to specifically examine the impacts of episodic sediment resuspension on spatial and temporal POPs concentrations.

Large-scale sediment resuspension events may change the rate and magnitude of in-lake cycling of POPs because their fate is controlled, in part, by their partitioning to sediment (Eadie and Robbins, 1987). Eadie et al. (1999) found that total suspended matter (*TSM*) was 5 to 10 times higher during a major sediment resuspension event in 1996 at near-shore sites (5.0 to 10.2 mg/L, $n = 4$) than at offshore sites (1.0 to 1.2 mg/L, $n = 4$). They found a relationship between the composition of suspended sediment in Lake Michigan and that of the bluff material from the western shore of the southern basin (Eadie and Robbins, 2005). Robinson et al. (2008) further assessed seasonal variations of PCBs on sediment for a single location in 45 m of water off the coast from Grand Haven, MI. They found that sediment concentrations and congener profiles remained constant while dissolved PCB concentrations varied seasonally and inter-annually. Bogdan et al. (2002) determined approximately 400 kg of PCBs associated with sediment was resuspended in March 1998. In a follow-up study by Hornbuckle et al. (2004), it was determined that approximately 370 kg of PCBs was resuspended as a result of an episodic event in 1999. Similar estimates were made using data collected during other years with varying sediment resuspension intensity (Miller, 2003).

The distribution of POPs between the dissolved phase and suspended sediment is largely controlled by particulate organic carbon (*POC*) content (Eadie et al., 1990). This distribution is represented as the organic carbon-normalized partition coefficient, K_{oc}, and is a measure of the compound’s hydrophobicity, roughly equal to its octanol–water partition coefficient, K_{ow} (Robinson et al., 2008; ten Hulscher et al., 2005). Field-derived values for K_{oc} have been found to vary widely from those determined in the laboratory (Butcher et al., 1998; Gobas and Maclean, 2003; Pickard et al., 2001; ten Hulscher et al., 2005). These variations may be due to changes in sediment composition (Cornelissen et al., 2005; Delle Site, 2001). Specifically, sediment sorption properties may be affected by changes in organic carbon, which more closely mimic those of coal (Johnson et al., 2001). The influence of black carbon and changes in organic carbon on POPs partitioning have been observed in field-derived samples (Ghosh et al., 1999, 2000; Ghosh and Khalil, 2005).

The potential for large quantities of sediment-associated PCBs to be resuspended suggests that the water column burden and concentrations should vary significantly over time and space. The main hypothesis of the research presented here is that POPs concentrations in water were higher during sediment resuspension events rather than before or after sediment resuspension events. We examined data resulting from spatially and temporally coordinated air and water samples collected in southern Lake Michigan. Study-averaged spatial and temporal POPs concentration differences and their implications in whole-lake mass balances are discussed.

Experimental

Field-sampling methods

Field-sampling campaigns were conducted to capture the conditions before, during, and after a sediment resuspension event in each of the 3 years of this study. A field-sampling cruise was characterized as occurring during a “sediment resuspension event” using two sets of measurements. First, springtime sediment resuspension in southern Lake Michigan is brought about following sustained wind blowing primarily from the north along the longest fetch of the lake. Daily meteorological forecasts were carefully monitored to determine optimum conditions for sediment resuspension (Roebber and Gehring, 2000; Schwab et al., 2006). Second, data resulting from sequencing sediment traps were used to determine periods of highest sediment concentration. Personnel were event-responsive and mobilized within 24 h in order to capture sediment resuspension at its peak. Satellite imagery was used after field sampling as visual confirmation of sediment resuspension.

The first of eight field-sampling campaigns was initiated with two cruises of the *R/V Lake Guardian* in 1998. The first cruise commenced in January 1998, before, the year’s sediment resuspension event, while the second cruise was initiated in March 1998, during the sediment resuspension event. Results from this first field-sampling campaign have been reported by Bogdan (1999) and Bogdan et al. (2002) and are presented here for the purposes of examining the effects sediment resuspension on three years of field data. The second sampling campaign commenced with four cruises in 1999 with the first in February, before the sediment resuspension event, the second in March, during the resuspension event, the third and fourth in April and June 1999, after the sediment resuspension event. During the final field-sampling campaign, samples were collected during the sediment resuspension event in March 2000 and after the sediment resuspension event in May 2000. Field-sampling cruise dates are outlined in Table 1.

During the 1998 and 1999 field-sampling campaigns, water samples were collected at stations located in 15 m of water along the project transects (Fig. 1a) except for a station located in the center of the southern basin where the water column depth exceeded 150 m. This station was identified as the Deep Water Station (DWS) and was taken to represent background conditions unaffected by the near-shore sediment resuspension. Project transects were identified by the major city from which they were offshore: Racine, R; Chicago, C; Gary, G; St. Joseph, J; Saugatauck, S; and Muskegon, M. This sampling approach was utilized to examine the spatial variation along the areal extent of sediment resuspension expecting that hydrodynamic and industrial activities within the basin would influence chemical characteristics. A different sampling approach was applied during the 2000 field-sampling campaign. Water samples were collected at stations located in 15 m, 30 m, and 45 m of water along the C, G, and J transects, to evaluate potential decreases in suspended sediment concentrations with increasing depth, and at the DWS, to evaluate background suspended sediment concentrations. These stations are identified in this paper by the transect's letter and the water depth at that station (e.g., C15).

During the field-sampling campaigns, air samples were collected continuously during all activities of each cruise resulting in samples, representing a region of the atmosphere over southern Lake Michigan rather than at a point (Fig. 1b). Air samples were collected using a modified high-volume (hi-vol) air sampler (Graseby, Cleves, OH) mounted on an extendable boom located on the bow of the *R/V Lake Guardian*.

Analytical methods

The methods by which water and air samples were collected during the eight field-sampling campaigns for this project have been described elsewhere in detail (Bogdan et al., 2002; Crecelius and Lefkovitz, 1997a, b; Miller, 2003). Each water sample was collected from a 2 m depth below the water surface at discrete locations described above. Between 500 L and 1200 L of lake water was first passed through glass fiber filters (GFF) and operationally defined as suspended sediment. The filtrate was operationally defined as dissolved phase, 200 L of which was pumped through XAD-2 resin. Each air sample was collected over the course of 12 to 14 h. Between 130 m^3 and 719 m^3 of air was pumped through a GFF, operationally defined as aerosol phase, in series with XAD-2 resin, operationally defined as gas phase, using a modified hi-vol air sampler.

All water and air samples were analyzed at The University of Iowa for 98 individual polychlorinated biphenyl (PCB) congeners/congener groups, 16 individual polycyclic aromatic hydrocarbon (PAH) compounds, and 25 chlorinated pesticides (including *trans*-nonachlor and dichlorodiphenyltrichloroethane, DDT). Extraction of glass fiber filters and XAD-2 resin included a 24 hour Soxhlet reflux with a 50:50 acetone: hexane mixture. A surrogate solution containing PCB congeners 3,5-dichlorobiphenyl (IUPAC No. 14), 2,3,5,6-tetrachlorobiphenyl (IUPAC No. 65), 2,3,4,4′,5,6-hexachlorobiphenyl (IUPAC No. 166) and the deuterated PAH compounds d_8-napthalene, d_{10}-fluorene, d_{10}-fluoranthene, and d_{12}-perylene was added to every sample prior to Soxhlet extraction. The concentrated extract was passed through a glass column of 3% deactivated silica gel with sequential elutions of hexane (first fraction), 40:60 dichloromethane:hexane mixture (second fraction), and methanol (third fraction) to clean and fractionate each sample by compound. An internal standard solution containing 2,4,6-trichlorobiphenyl (IUPAC No. 30) and 2,2′,3,4,4′,5,6,6′-octachlorobiphenyl (IUPAC No. 204) was added for PCB and pesticide quantification. An internal standard solution containing deuterated PAH compounds d_{10}-acenaphthalene, d_{10}-phenanthrene, d_{10}-pyrene, and d_{12}-benzo[e]pyrene was added to the second fraction for PAH quantification.

A Hewlett Packard 6890 Gas Chromatograph (GC) equipped with a 60 m DB-5 capillary column (J&W Scientific, Inc., Folsom, CA) and a ^{63}Ni micro-electron capture detector (μECD) was used to analyze the first fraction for PCBs. Analysis of the second fraction for PAHs was performed on the same GC equipped with a 30 m DB-5 capillary column (J&W Scientific, Inc., Folsom, CA) and a Hewlett Packard 5973 quadrupole mass selective detector in the electron ionization (MS-EI), select ion mode (SIM). Chlorinated pesticides eluted in the first and second fractions. Analysis of both fractions was performed on the same GC/MS in the negative chemical ionization (MS-NCI), select ion mode (SIM) for chlorinate pesticide quantification. Mass quantitation was accomplished using the relative response factor for each analyte in a daily calibration standard and the internal standard in the samples (Miller, 2003).

Quality assurance

The mean surrogate recoveries (± 95% confidence interval) during PCB detection using GC/μECD were 66 ± 3.6% for congener 14, 73 ± 4.5% for congener 65, and 78 ± 4.2% for congener 166. During chlorinated pesticide detection using GC/MS-NCI, recoveries for congener 166 were 88 ± 5.2%, indicating comparable detector response. Recoveries for d_{10}-fluoranthene were 65 ± 4.1% during PAH detection using GC/MS-EI. All sample concentrations were corrected for surrogate recovery.

During the eight campaigns for this project, 139 water (dissolved phase and suspended sediment) and 118 air (gas phase and aerosol) samples were collected. A total of 36 (25.9%) water and 44 (37.3%) air samples were used for quality assurance (trip and field matrix blanks and replicate samples) purposes (Miller, 2003). The quality of the data set was assessed through matrix blanks (trip and field), quantitation limit studies, and replicate samples. These results are summarized in Table 2.

Trip and field blanks were similar in that pre-cleaned sampling media were brought onto the ship and not actively sampled. Trip blanks remained in either the on-board refrigerator or freezer during the sampling campaign. Field blanks were exposed to the sampling environment and not actively sampled. Because there was no way to passively expose the glass fiber filters used to collect suspended sediment samples, there were no resulting field blanks and are shown in Table 2 as “not applicable”. The mass of each set of compounds found either on the trip or field blanks was low compared to field samples demonstrating the efficiency of media pre-cleaning and conditions in the field. The mass of each set of compounds found in the trip blanks (e.g., suspended sediment) and field blanks (e.g., dissolved phase, gas phase, and aerosol) was used to determine compound-specific quantitation limit (QL).

The QL was calculated as three times the standard deviation of an individual congener or compound in the trip or matrix blank. Individual congener or compound mass in all samples was higher than in their associated matrix blanks except aerosol samples as indicated by the QL (Table 2). This suggests that the mass of individual congener or compound observed in aerosol samples was indistinguishable from background levels, rendering them not reliable; subsequently, they were excluded from any further data analysis.

Replicate sample pairs resulted when two samples for each matrix were collected simultaneously at a select water sampling station or on an air sampling transect. Agreement between samples was determined as the relative percent difference (RPD). The RPD was due to real variability in the matrix between the two samples, the random error in the collection method, and the random error in the sample treatment and analysis.

Data analysis

In this paper, we examine concentrations of PCBs in water and air. Concentrations of polycylic aromatic hydrocarbons (PAHs), and chlorinated pesticides, such as *trans*-nonachlor, and dichlorodiphenyl trichloroethane (DDT), in water and air for this study have been described elsewhere (Miller, 2003). The foundation of this study was to examine the variability in the POPs concentration with respect to total suspended material (*TSM*) and the sediment-associated, fraction organic carbon (f_{oc}). The main hypothesis of the research presented here is that POPs concentrations in water were higher during sediment resuspension events rather than before or after sediment resuspension events. To examine this hypothesis, concentrations for each cruise and each year were (a) spatially averaged in order to assess any temporal variations due to sediment resuspension, (b) temporally averaged to assess any spatial variations due to sediment resuspension and (c) assessed for any spatial variations as a function of water depth. Temporal variations resulting from spatial averaging are examined first, followed by an examination of spatial variations resulting from temporal averaging and variations as a function of water depth. All mean data values are reported ± 95% confidence interval and a student's *t*-test was evaluated at the 99% confidence interval to determine statistically significant differences, unless noted otherwise. A summary of the data described here may be found in the Supplemental data.

Results and discussion

Suspended sediment concentrations and trends

TSM concentrations were measured in surface waters before, during, and after the sediment resuspension events of 1998, 1999, and 2000 (Fig. 2). First, *TSM* concentrations were highest for the March cruise in 1999 (5.75 ± 4.84 mg/L, $n = 8$) and 2000 (1.88 ± 1.03 mg/L, $n = 11$) than in 1998 (1.26 ± 0.354 mg/L, $n = 5$). Second, maximum resuspension occurred one week after the March 1998 cruise resulting in lower *TSM* concentrations in March 1998 (1.26 ± 0.354 mg/L, $n = 5$) than in January 1998 (1.82 ± 1.21 mg/L, $n = 5$) (Bogdan, 1999). Third, *TSM* concentrations measured during the 1999 field-sampling year (3.16 ± 1.87 mg/L, $n = 23$) were higher than either the 1998 (1.54 ± 0.624 mg/L, $n = 10$) or the 2000 (1.71 ± 0.619 mg/L, $n = 19$) field-sampling years. Spatially averaged f_{oc} did not vary significantly inter-annually. The f_{oc} measured during the June 1999 sampling cruise (0.302 ± 0.093, $n = 5$) was higher than the other seven sampling cruises (0.155 ± 0.028, $n = 47$), a difference most likely due to the onset of thermal stratification and increased primary productivity associated with higher surface water temperatures. Overall, we observed no significant changes in suspended sediment concentrations that can be attributed only to the resuspension events, despite clear evidence in satellite images of elevated suspended sediment concentrations (Eadie et al., 2008).

TSM concentrations were averaged in space (Fig. 3). First, *TSM* concentration measured at the DWS was lower (0.64 ± 0.23 mg/L, $n = 7$) than at any of the other six stations at which samples were collected (3.04 ± 1.35 mg/L, $n = 32$). Clearly, the DWS was located well outside the influence of near-shore sediment resuspension exhibiting lower *TSM* concentrations. This result supports using the DWS as an indicator of concentrations less affected by episodic sediment resuspension. Second, *TSM* concentrations measured at C15

(4.11 ± 5.57 mg/L, *n* = 7) were similar to the other six stations (2.28 ± 0.756 mg/L, *n* = 32). This was attributed to the variability caused by including the high *TSM* concentration (21.1 mg/L) measured at the C15 station during the March 1999 cruise in the average. Third, *TSM* concentrations measured at R15 (4.46 ± 3.01, mg/L, *n* = 4) were similar to the other six stations (2.28 ± 1.22 mg/L, *n* = 35). Temporally averaged f_{oc} did not vary significantly (Fig. 3). The f_{oc} measured at the DWS (0.302 ± 0.098, *n* = 7) was higher than what was measured at any of the other six stations (0.134 ± 0.030, *n* = 32).

TSM concentrations and f_{oc} were examined as a function of water depth (Fig. 4). First, *TSM* concentrations along the C, G, and J transects decreased with increasing water depth (from 15 m to 45 m). Second, *TSM* concentrations at the DWS were lower than at any of the near-shore sites. Third, f_{oc} increased with increasing water depth along the C, G, and J transects.

ΣPCB water concentrations and trends

Total ΣPCB concentrations ($\Sigma PCB_T = \Sigma PCB_d + \Sigma PCB_s$, ng/L) did not vary significantly between cruises in a field-sampling year when averaged over the entire sampling region (Fig. 2). ΣPCB_T concentrations were similar before, during, and after sediment resuspension in each of the three field-sampling years. ΣPCB_T concentrations measured in 1998 (0.348 ± 0.104 ng/L, *n* = 10) were (1) similar to those measured in 1999 (0.265 ± 0.052 ng/L, *n* = 23) and (2) higher than those measured in 2000 (0.165 ± 0.029 ng/L, *n* = 19). ΣPCB_T concentrations measured in 1999 were higher than those measured in 2000. The average suspended sediment fraction (ΣPCB_s, %) was similar before, during, and after sediment resuspension in each of the field-sampling years and the highest ΣPCB_s occurred during the period of sediment resuspension in each field-sampling year. The ΣPCB_s measured in 1998 (43.0 ± 13.3%, *n* = 10) were higher than those measured in 1999 (19.9 ± 5.1%, *n* = 23) and 2000 (17.4 ± 3.4%, *n* = 19). The ΣPCB_s measured in 1999 were similar to those measured in 2000.

ΣPCB_T concentrations and ΣPCB_s averaged over time were similar (Fig. 3). First, concentrations were lower at the DWS (0.162 ± 0.045 ng/L, *n* = 7) than at any of the other six stations (0.291 ± 0.047 ng/L, *n* = 32). Second, concentrations were higher at R15 (0.473 ± 0.074, ng/L, *n* = 4) than at any of the other six stations (0.245 ± 0.039 ng/L, *n* = 35). The average ΣPCB_s were similar at all seven sampling stations.

ΣPCB_T concentrations and ΣPCB_s varied as a function of water depth (Fig. 4). First, ΣPCB_T concentrations along the C, G, and J transects decreased with increasing water depth (from 15 m to 45 m). Second, ΣPCB_T concentrations and ΣPCB_s at the DWS were lower than at any of the near-shore sites. Third, ΣPCB_s decreased with increasing water depth along the G and J transects. This effect is opposite for the C transect, where ΣPCB_s increased with increasing depth.

The U.S. Environmental Protection Agency (U.S. EPA) also measured PCBs in water at sites located throughout all of Lake Michigan. A subset of those data from sites located only in southern Lake Michigan was compiled and compared to the results of this study. Dissolved phase ΣPCB concentrations measured for this study (0.177 ± 0.024 ng/L, *n* = 52) were higher than concentrations measured for the Lake Michigan Mass Balance (LMMB)

(0.120 ± 0.024 ng/L, $n = 23$, U.S. Environmental Protection Agency, 2004). There was no significant difference between suspended sediment ΣPCB concentrations measured for this study (0.067 ± 0.023 ng/L, $n = 53$) and the LMMB (0.078 ± 0.016 ng/L, $n = 23$, U.S. Environmental Protection Agency, 2004).

On a study-average basis, between 4% and 72% (23 ± 4%, $n = 52$) of the ΣPCB_T concentrations were associated with suspended sediment. This is less than the subset of LMMB water data from sampling sites located only in southern Lake Michigan (20% to 68%, 40 ± 5%, $n = 23$, U.S. Environmental Protection Agency, 2004). The difference between data from this study and LMMB data may be attributed to differences in sampling strategy. Samples were specifically collected for this study to examine the effects of near-shore sediment resuspension on POPs concentrations in water. In contrast, the subset of water samples for the LMMB (U.S. Environmental Protection Agency, 2004) was collected to assess POPs concentrations within Lake Michigan. On a study-average basis, more than half of the ΣPCB_T concentrations were associated with the dissolved phase creating a concentration gradient of preferential partitioning to suspended sediment.

Overall, we observed no significant changes in total (dissolved phase + suspended sediment) water concentrations and suspended sediment fraction of ΣPCBs that can be attributed only to the resuspension events. There were significant, inter-annual variations in ΣPCBs. Variations in ΣPCB total water concentrations and fraction suspended sediment were subtle. These subtle variations were further examined using the distribution shifts between the dissolved phase and suspended sediment, the discussion of which follows in the next section.

Distribution shifts in PCBs

The distribution of POPs between the dissolved phase and suspended sediment changes as a function of sediment resuspension (i.e., ΔK_{oc}). Zhang et al. (2008) modeled 54 PCB congeners in Lake Michigan using 1994 and 1995 LMMB field data. They used constant congener-specific values of K_{oc} for each of the 54 PCB congeners modeled and did not account for variations in K_{oc} due to sediment resuspension. Similarly, Swackhamer et al. (1999) used constant, isomer-specific values for K_{oc} to model annual toxaphane concentrations in Lake Superior. The goal of each of these modeling efforts was to analyze annual variations in either PCBs or toxaphane. Modeled results reported by Zhang et al. (2008) did not capture the increased suspended sediment ΣPCB observed in the Mar/Apr-95 LMMB field data. It is suggested from the results presented here that it is necessary to use several, congener-specific K_{oc} values to effectively model short-term cycling of PCBs with respect to sediment resuspension.

For this study, subtle variations in PCBs on an individual congener basis were examined using study-averaged congener profiles for the gas phase, dissolved phase and suspended sediment. Individual congener concentrations in a sample were normalized to its ΣPCB concentration and reported as a fraction (Fig. 5). On average, gas phase samples were enriched in lighter congeners; dissolved phase samples were enriched in light to mid-weight congeners; and suspended sediment was enriched in heavier congeners. These differences in congener profiles suggest the potential for shifts in distribution, specifically, between the dissolved phase and suspended sediment.

The extent of distribution between PCBs in the dissolved phase and on suspended sediment were examined using congener-specific, organic carbon-normalized partition coefficients (K_{oc}, L/mg) as defined in Eq. (1). The calculated K_{oc} for each individual congener is a function of the congener's concentration in the dissolved phase (C_d, ng/L) and on suspended sediment (C_s, ng/mg), normalized to the f_{oc}. Congener-specific K_{oc} values were determined for data collected at all water sampling stations, for all three sampling years. On a site-specific basis, those congeners, either in the dissolved phase or on suspended sediment, below the limit of detection, were eliminated from further calculations. This resulted in a different number of congeners evaluated at each station.

$$K_{oc}=\frac{C_s}{C_d f_{oc}} \quad (1)$$

where

K_{oc} organic carbon-normalized distribution coefficient (L/mg)

Cs suspended sediment concentration (ng/mg)

Cd dissolved phase concentration (ng/L)

foc fraction organic carbon, = $\frac{POC}{TSM}$

POC particulate organic carbon (mg/L)

TSM total suspended material (mg/L)

The formulation of K_{oc} in Eq. (1) describes PCB partitioning between two phases, dissolved and suspended sediment. A third phase, dissolved organic carbon (*DOC*), has been shown to play an important role in water column PCB distribution (Pedersen et al., 1999). Sorption experiments have shown weaker equilibrium partitioning to the presence of *DOC* potentially causing competition with dissolved PCBs for sorption sites on suspended sediment (Jonker et al., 2004). Dissolved phase, as operationally defined for this study, includes both truly dissolved PCBs and PCBs sorbed to the *DOC* fraction, which can lead to overestimation of PCBs in the truly dissolved phase (Gerofke et al., 2004). Algae are the largest producers of *DOC* in natural waters and because field sampling for this study was conduction during low primary productivity, we assumed the influence of *DOC* in water column PCB distribution would be minimized. Subsequently, we did not measure *DOC* in any of our samples for this study. We used the formulation of K_{oc} in Eq. (1) as a means to assess subtle differences in the distribution operationally defined dissolved phase and suspended sediment PCBs before, during, and after sediment resuspension.

Figures were constructed where the congener-specific log K_{oc} for data collected during sediment resuspension (Mar-98, Mar-99, and Mar-00) were plotted versus the congener-specific log K_{oc} for data collected before sediment resuspension (Jan-98 and Feb-99) or after sediment resuspension (Apr-99 and Jun-99) to evaluate changes in distribution. Shown in

Fig. 6 are log–log correlations between measured organic carbon-normalized distribution coefficients for stations at which samples were collected before, during, and after sediment resuspension, through which a linear regression was performed. These regressions were expected to yield a result of unity (i.e., 1 to 1 slope) for distributions that did not change because of sediment resuspension.

Three observations may be made about this analysis. First, a slope of unity occurred only at the DWS where suspended sediment concentrations were invariant to sediment resuspension. Second, the slope of the linear regression for the G15 station was biased above the line of unity. This suggests the suspended sediment at this station was enriched in all PCB congeners during resuspension. Third, the slope of the linear regression for C15 and M15 straddle the reference line of unity near the origin of the axes. This suggests the suspended sediment becomes enriched in heavier congeners and deficient in lighter congeners during sediment resuspension. At all four stations where these observations were made, K_{oc} shifted from the right (lower hydrophobicity, more volatile, before sediment resuspension versus during sediment resuspension) to the left (higher hydrophobicity, less volatile, after sediment resuspension versus during sediment resuspension).

This suggests the sediment resuspension results in a preferential uptake of heavier, more chlorinated PCB congeners. Because the slope of these data does not change due to sediment resuspension, the lighter, less chlorinated PCB congeners do not desorb from suspended sediment during their residence time in the water column. The formulation of K_{oc} in Eq. (1) describes PCB partitioning under conditions of equilibrium. Our analysis suggests changes in the apparent distribution of PCBs are the result of sediment resuspension (e.g., increased TSM and/or f_{oc}), not a state of equilibrium.

A student's t-test was performed to determine if the change in K_{oc} due to sediment resuspension was significant to further evaluate the effect of sediment resuspension on the distribution behavior of PCBs. First, the congener-specific change in log K_{oc} was determined and then it was evaluated if the change was different from zero. A change that was not different from zero suggests the distribution behavior was unaffected by sediment resuspension. These data are illustrated in Fig. 7. Despite there being no predictable temporal variation in f_{oc}, there were significant variations in the distribution behavior between phases as a result of sediment resuspension.

In general, sorption to suspended sediment increased during sediment resuspension. An increase in the suspended sediment to dissolved phase PCB ratio (i.e., log K_{oc}) implies that the PCBs associated with suspended sediment increased because of sediment resuspension. In 1998, log K_{oc} increased from January (before sediment resuspension) to March (during sediment resuspension) at four stations: C15, G15, J15, and S15 stations. PCBs were likely distributed from the dissolved phase to suspended sediment (i.e., sorption) in 1998. In 1999, log K_{oc} increased from February (before sediment resuspension) to March (during sediment resuspension) only at the G15 station. This station was within the area most affected by increased TSM, whereas the other five stations (i.e., R15, C15, J15, M15, and DWS stations) were not (see Fig. 7).

In general, sorption to suspended sediment decreased after sediment resuspension. A decrease in the suspended sediment to dissolved phase PCB ratio (i.e., log K_{oc}) implies the PCBs associated with suspended sediment decreased because of sediment resuspension. In 1999, log K_{oc} decreased from March (during sediment resuspension) to April (after sediment resuspension) at three stations: R15, G15, and M15 stations. PCBs were likely redistributed from the suspended sediment back to the dissolved phase in 1999. This effect may be kinetically limited and sediment-associated PCBs may actually be lost due to gravitational settling rather than desorption. A similar effect was observed in 2000 when log K_{oc} decreased from March (during sediment resuspension) to May (after sediment resuspension). At the G30, G45, and J45 stations, log K_{oc} increased because there was still a region of increased *TSM* (see Fig. 7). Increased *TSM* concentrations were the result of resuspended surficial sediments rather than algae, which have different characteristics, such as *POC*, because sampling occurred when primary productivity was low (i.e., late winter, early spring).

Finally, sorption to suspended sediment continues to decrease as the water warms and thermal stratification begins. In 1999, the suspended sediment to dissolved phase PCB ratio (i.e., log K_{oc}) decreased from April (after sediment resuspension) to June (after sediment resuspension) at three stations: C15 and J15 stations and the DWS. This implies the PCBs associated with sediment decreased long after the sediment resuspension event. It is likely that this effect is a function of increased primary productivity and is an indication of dilution due to algal growth.

Atmospheric concentrations

Aerosol samples were excluded from further data analysis because the masses measured in samples were less than the quantitation limits (QL). Based on the predominant location of the *R/V Lake Guardian* over the duration of atmospheric sampling, the resulting gas phase concentrations were categorized into regions (i.e., west, south, east, or central).

Gas phase ΣPCB concentrations demonstrated no consistent temporal variation. Spatially, gas phase ΣPCB concentrations were higher in the west (0.436 ± 0.200 ng/m^3, $n = 11$) and south (0.408 ± 0.286 ng/m^3, $n = 5$) than the east (0.214 ± 0.082 ng/m^3, $n = 10$) and central (0.253 ± 0.145 ng/m^3, $n = 8$) regions of southern Lake Michigan.

Gas phase ΣPCB concentrations from three separate studies are compared here to demonstrate how results from this study, which was designed to not specifically examine gas phase concentrations, compare with those studies that did examine the effects of spatial and temporal variations. Air samples were collected as part of the LMMB in 1994 and 1995 at sites located on the shore and over water of Lake Michigan and summarized by Green et al. (2000) and Miller et al. (2001). The highest gas phase ΣPCB concentrations were observed at a site located in Chicago, Illinois. Air sampling was not conducted in Milwaukee, Wisconsin, a city with a similar industrial history.

While docked in Milwaukee Harbor at the Great Lakes Wisconsin Aquatic Technology and Environmental Research (WATER) Institute prior to commencement of sampling cruises for this study in February and June of 1999, air samples were collected using the modified hi-vol samplers aboard the *R/V Lake Guardian* for this study. In a study to specifically measure PCB concentrations in Milwaukee, Wisconsin, Wethington and Hornbuckle (2005) collected air samples for five days in June 2001 using hi-vol air samplers mounted on the roof of the WATER Institute.

First, ΣPCB concentrations observed at the WATER Institute in Milwaukee were similar to those observed by Green et al. (2000) and Miller et al. (2001) in Chicago during the LMMB. For example, concentrations measured in Milwaukee, Wisconsin during February 1999 were 0.555 ng/m^3 compared to 0.473 ng/m^3 measured in Chicago, Illinois during February 1995. Concentrations measured in Milwaukee, Wisconsin were 0.995 ng/m^3 in June 1999 and 1.94 ± 0.284 ng/m^3 (n = 26) in June 2001 compared to 2.63 ng/m^3 for June 1994 and 2.68 ng/m^3 for June 1995 in Chicago, Illinois. Second, ΣPCB concentrations measured over water during this study (0.295 ± 0.084 ng/m^3, n = 32) were similar to those measured over water in the spring of 1995 as reported by Green et al. (2000) and Miller et al. (2001) for the LMMB (0.393 ± 0.239 ng/m^3, n = 14).

Atmospheric concentration analysis

Meteorological data (i.e., air temperature, wind speed, and wind direction) were recorded on an hourly basis during the collection of all air samples. While temperature was arithmetically averaged over the period of sampling, an arithmetic vector average was used to determine the wind speed weighted average wind direction. Each hourly wind speed and wind direction was transformed into their corresponding vectors u and v as defined in Eq. (2).

$$u=-f\sin(d) \qquad \nu=-f\cos(d) \qquad (2)$$

where

f measured wind speed (m/s)

d measured wind direction (decimal degrees)

An arithmetic average of each u and v vector was used to determine the weighted average, wind direction of each period of sampling as defined in Eq. (3).

$$\bar{d}=\arctan\left(\frac{u}{\nu}\right)+\theta \qquad (3)$$

where:

- $\bar{d}$ weighted average wind direction (decimal degrees)

$\theta = 180°$	if $\nu>0$
$\theta = 0°$	if $\nu<0$ and $u<0$
$\theta = 360°$	if $\nu<0$ and $u>0$

These quantitative, wind speed weighted average wind directions were qualitatively classified into four zones that correspond with cardinal directions (i.e., north, east, south, and west). The north (N) zone ranged from 315° to 045°; the east (E) zone ranged from 045° to 135°; the south (S) zone ranged from 135° to 225°; and the west (W) zone ranged 225° to 315°. Depending on the region in which the air sample was collected, these wind direction zones may have been either land based or water based. Gas phase ΣPCB concentrations from each of the four southern Lake Michigan regions sampled are shown in Fig. 8. The highest and lowest observed gas phase ΣPCB concentrations are indicated by bubble size and are plotted according to the sampling period averaged wind direction with corresponding sampling period averaged temperature and concentration.

There are two patterns that emerge. First, in all four regions, the highest gas phase ΣPCB concentrations correspond with elevated air temperature (i.e., >8 °C) and prevailing wind direction from either the west or the south. Second, in all four lake regions, the lowest gas phase ΣPCB concentrations correspond with lower air temperature (i.e., <8 °C) and prevailing wind direction from either the east or the north. Green et al. (2000) showed for Chicago that when the prevailing wind direction was land based (i.e., west or south), gas phase ΣPCB concentrations were higher than when the prevailing wind direction was water based (i.e., east or north). Concentrations reported here for this study agree with their finding for the LMMB.

Conclusions

Lake Michigan continues to be affected by the input of PCBs and other POPs, decades after their use was banned. The resuspension of contaminated sediment may act either as a sink from or a source to the water column of these potentially toxic compounds. The difficulty lies in controlling this source, a task that which is further clouded by an incomplete understanding of its magnitude. The primary purpose of the work described here was to assess the magnitude and variability of this mechanism for elimination and uptake of PCBs and other POPs in southern Lake Michigan. In particular, this work evaluated event driven sediment resuspension processes that control the short- and long-term cycling of POPs in southern Lake Michigan.

Overall, total (dissolved phase + suspended sediment) water concentrations and the suspended sediment fraction of ΣPCBs did not vary spatially or temporally because of sediment resuspension. There were significant, inter-annual variations in ΣPCBs although variations in ΣPCB total water concentrations and fraction suspended sediment were subtle.

Variations in ΣPCB total water concentrations were examined by congener-specific distribution shifts between field-sampling campaigns. Sediment resuspension disrupts the cycling of PCBs in Lake Michigan. Specifically, sediment resuspension results in a short-term enrichment of sediment-associated PCBs. This results in proportionately higher PCBs in the dissolved phase.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.jglr.2010.02.009.

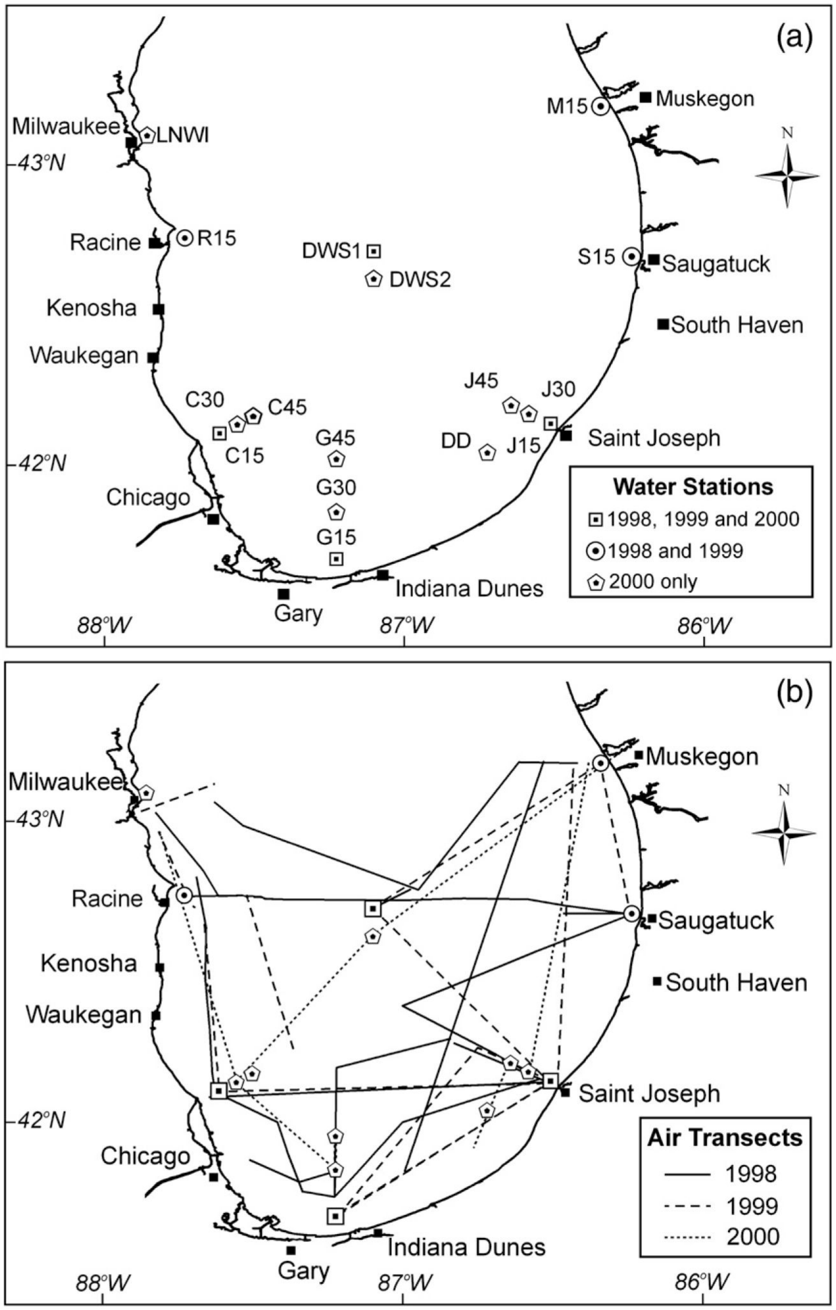

Fig. 1.

(a) Water sampling stations and (b) air sampling transects.

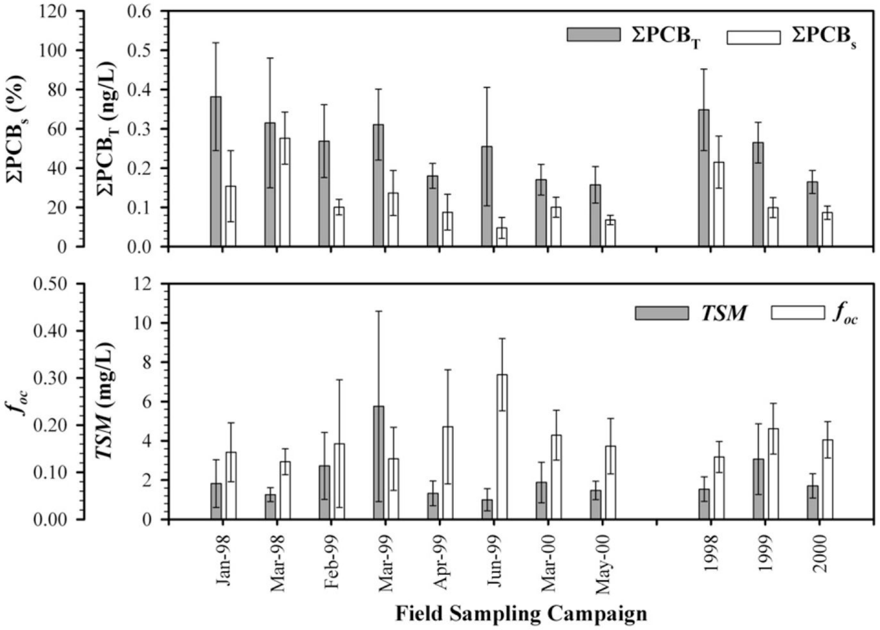

Fig. 2.

Averaged total suspended material concentrations (*TSM*, mg/L), fraction particulate organic carbon (f_{oc}) and total ΣPCB concentrations ($\Sigma PCB_T = \Sigma PCB_d + \Sigma PCB_s$, ng/L) with corresponding fraction suspended sediment (ΣPCB_s, %) at all stations where samples were collected during each cruise.

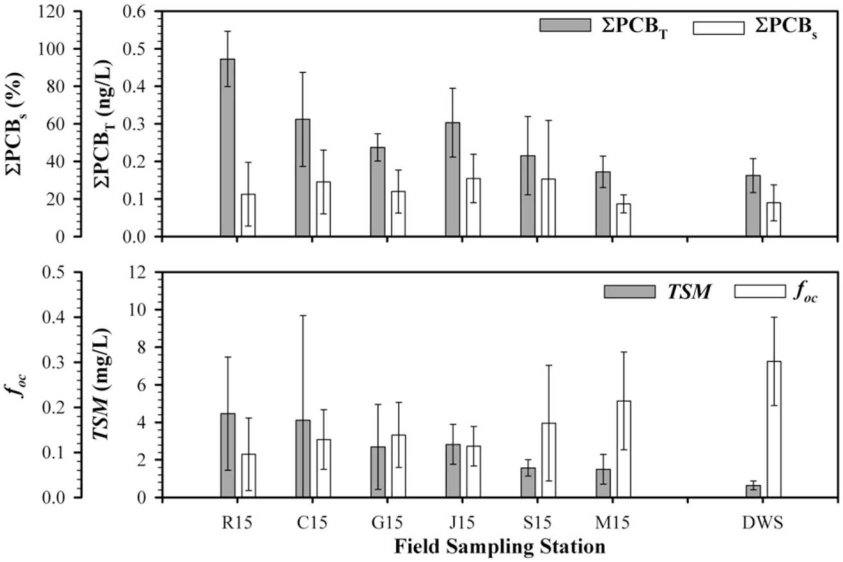

Fig. 3.

Averaged total suspended material concentrations (*TSM*, mg/L), fraction particulate organic carbon (f_{oc}) and total ΣPCB concentrations ($\Sigma PCB_T = \Sigma PCB_d + \Sigma PCB_s$, ng/L) with corresponding fraction suspended sediment (ΣPCB_s, %) at each station where samples were collected during all three field-sampling years.

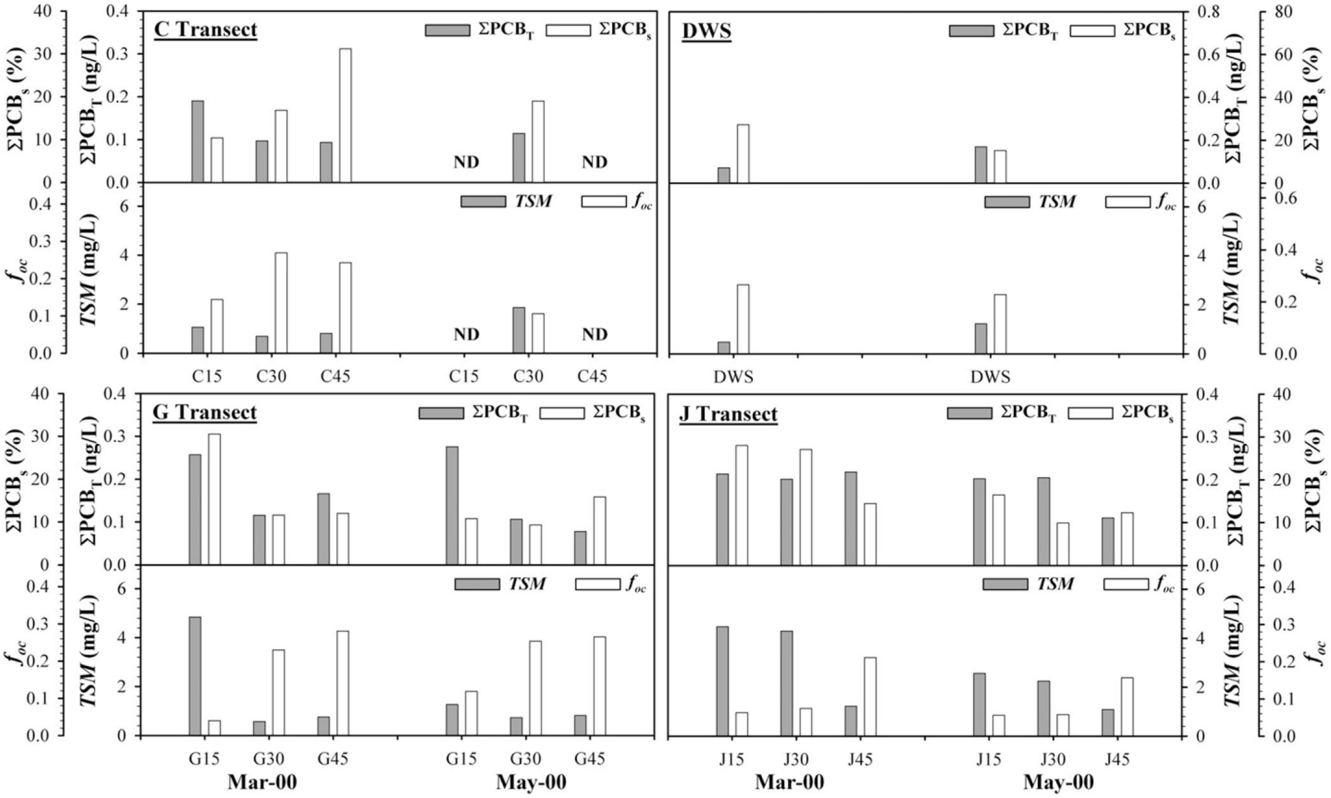

Fig. 4.

Total suspended material (*TSM*, mg/L), fraction particulate organic carbon (f_{oc}) and total ΣPCB concentrations ($\Sigma PCB_T = \Sigma PCB_d + \Sigma PCB_s$, ng/L) with corresponding fraction suspended sediment (ΣPCB_s, %) during the Mar-00 and May-00 sampling cruises at stations located in 15 m, 30 m, and 45 m of water.

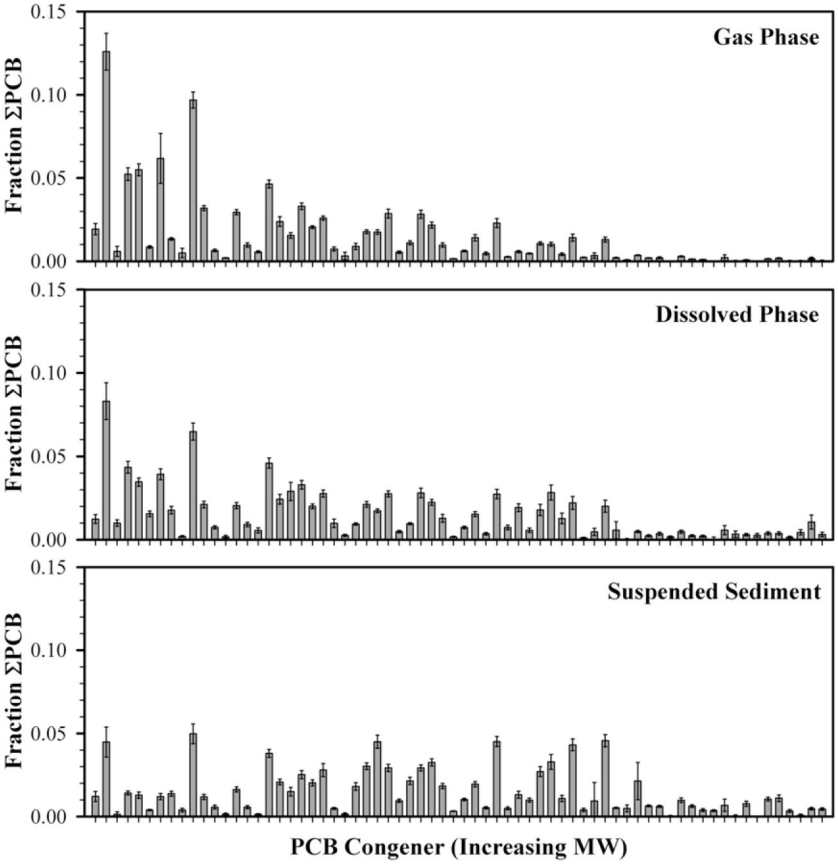

Fig. 5.

Comparison of study-average congener distribution for gas phase, dissolved phase, and suspended sediment. Each congener was normalized to ΣPCBs and is reported as a fraction.

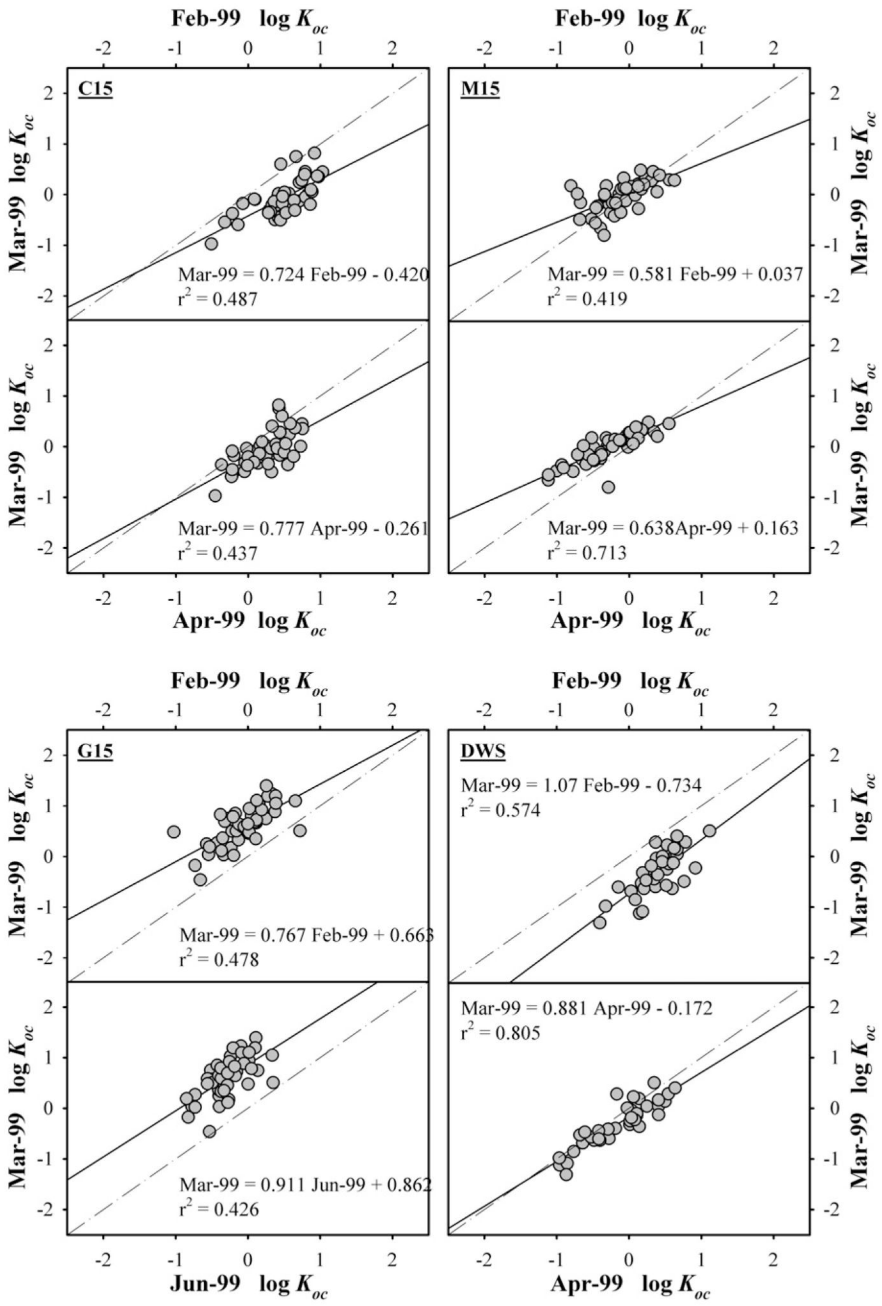

Fig. 6.

Comparison of log K_{oc} for PCB congeners measured at stations where samples were collected prior to, during, and after sediment resuspension in 1999. Each point represents congener for which the concentration was greater than zero in both the dissolved phase and suspended sediment. The solid line represents the linear fit through the data. The dashed line represents a line of unity for comparison only.

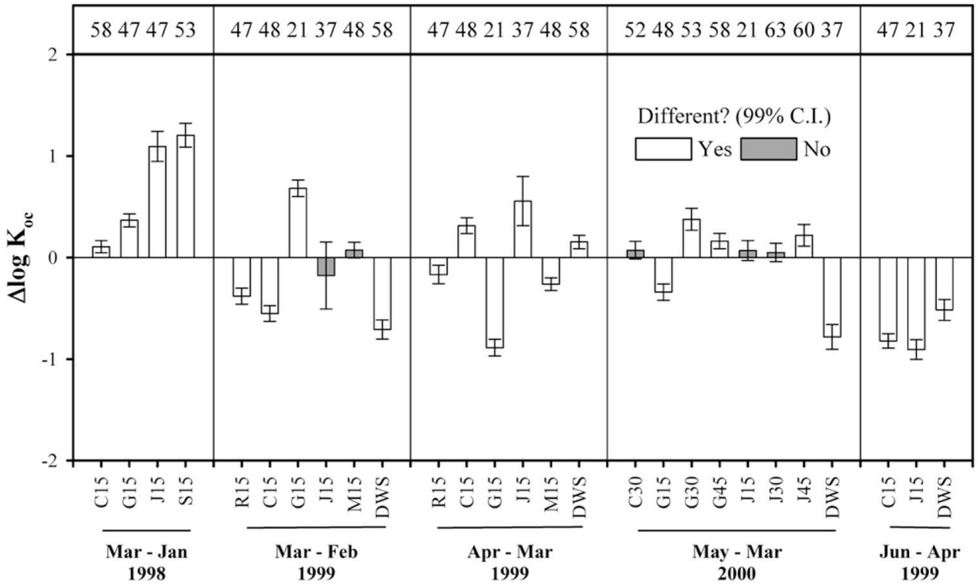

Fig. 7.

Change in log K_{oc} because of sediment resuspension. Bars indicate the average congener-specific change in log K_{oc} with the error bars ± 95% C.I. The number of congeners evaluated for each sample is indicated by the top row of numbers. The shading indicates whether the change is different from zero (at the 99% C.I.).

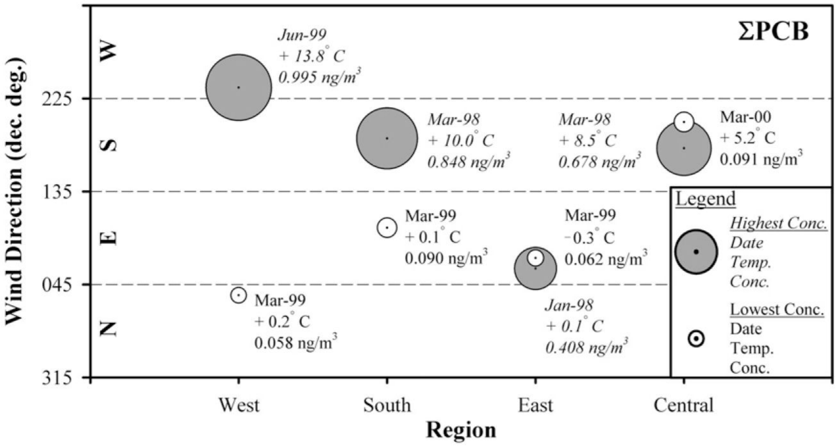

Fig. 8.

Highest and lowest ΣPCB gas phase concentrations (ΣPCB_g) measured in each of the four regions of southern Lake Michigan. Bubble size indicates the relative concentration magnitude. Each bubble is centered within the range of prevailing cardinal wind direction (decimal degrees) measured during sampling. Corresponding air sample averaged air temperature (°C) and concentration (ng/m^3) are indicated next to each bubble.

Table 1

Field-sampling cruise dates.

	1998	**1999**	**2000**
Before sediment resuspension	28-Jan-98 to 04-Feb-98	14-Feb-99 to 20-Feb-99	
During sediment resuspension	28-Mar-98 to 30-Mar-98	07-Mar-99 to 16-Mar-99	10-Mar-00 to 15-Mar-00
After sediment resuspension		04-Apr-99 to 09-Apr-99	14-May-00 to 20-May-00
After sediment resuspension		03-Jun-99 to 08-Jun-99	

Table 2

Summary of trip blanks, field blanks, quantitation limits (QL), and replicate sample pairs (RPD).

Compound	Dissolved phase	Suspended sediment	Gas phase	Aerosol
ΣPCBs				
Trip blanks (ng)	5.66 ± 2.95 (*n* = 6)	1.16 ± 0.82 (*n* = 5)	1.88 ± 1.03 (*n* = 6)	1.16 ± 0.85 (*n* = 6)
Field blanks (ng)	5.31 ± 1.41 (*n* = 6)	Not applicable	2.99 ± 1.73 (*n* = 6)	0.94 ± 0.26 (*n* = 6)
QL (ng)	5.30	2.80	6.49	0.98
RPD	40.4 ± 26.2% (*n* = 6)	14.8 ± 11.2% (*n* = 6)	20.8 ± 16.3% (*n* = 6)	58.3 ± 34.7% (*n* = 6)
ΣPAHs				
Trip blanks (ng)	not detected (*n* = 6)	442.6 ± 110.0 (*n* = 5)	2.34 ± 2.93 (*n* = 6)	Not detected (*n* = 4)
Field blanks (ng)	13.8 ± 11.1 (*n* = 6)	Not applicable	Not detected (*n* = 5)	2.52 ± 4.94 (*n* = 5)
QL (ng)	41.7	376.5	32.8	80.5
RPD	76.6 ± 47.4% (*n* = 5)	34.7 ± 29.6% (*n* = 6)	30.2 ± 12.7% (*n* = 6)	56.0 ± 49.5% (*n* = 6)