

**The effect of a large resuspension event in Southern Lake Michigan on
the short-term cycling of organic contaminants**

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ABSTRACT

In March, 1998, an intense, northerly wind-driven storm suspended sediment over the entire coastline of the southern basin of Lake Michigan (~300 km). The effect of this event on the particle settling fluxes and air/water exchange fluxes of persistent organic pollutants (POPs) was investigated. We used a two-pronged sampling strategy of 1) discrete air and water samples collected during intensive campaigns before and after the resuspension event and 2) settling sediment collected using a time-integrated sequencing trap deployed from Dec 1997 through May 1998. The data indicate that concentrations of dissolved phase Σ PCB (sum of 89 congener peaks) and Σ PAHs (sum of 31 compounds) declined significantly ($\alpha = 0.05$) after the event. As a result, potential atmospheric depositional fluxes increase. The potential loading from increased gas-phase deposition due to the resuspension event was 8 kg for Σ PCBs and 2200 kg for Σ PAHs over the 40-day lifetime of the near-shore event. Atmospheric deposition, as induced by the resuspension event, is on the same order of magnitude as event-induced settling fluxes, suggesting a zero net short term change in inputs and losses of POPs to the lake. However, if recycling of POPs at the lake bottom is included there is a large net input of POPs as a result of the event.

INTRODUCTION

Intense springtime episodes of sediment resuspension occur frequently in southern Lake Michigan. The resuspension of sediment material may have an important impact on the cycling of organic contaminants in coastal systems. In the Great Lakes, resuspension may cause release of buried contaminants in older sediments or may cause removal of contaminants through increased particulate fluxes, (1-4). To examine the role of resuspension events on organic contaminants, we have conducted a field study during two resuspension events in the winter/spring of 1998. One resuspension event occurred in mid to late January 1998. A much larger resuspension event, generated by a strong late winter, early-spring storm, initiated in early March and lasted over 40 days.

The turbidity plume event of March 1998 was one of the biggest of recent record. Plume development corresponded with two storm events beginning in early March and reaching a climax on March 9th and 21st. On those two days, strong winds reached 17m/s, primarily from the northerly direction, and wave heights reached 5m in the southern basin. (5). These storms produced the two significant turbidity events on 9-12 March and 20-22 March as observed in satellite imagery. At full development, the plume covered the entire 300 km length of the southern basin and was visible by satellite for six weeks (~40 days) before calming in late April. A spectacular offshore-spiraling eddy was observed on March 12, due to meandering of the strong offshore currents driven by a two-gyre wind-driven circulation pattern (Figure 1). The estimated total mass of suspended sediment in the southern basin of the lake in March 1998 was 7.53×10^6 tonnes (5). For perspective, the United State Geological Survey's Southern Lake Michigan Coastal Erosion Study (1988-1992) reported an average *annual* sediment budget for the southern basin of Lake Michigan from records of the last 100 years to balance at 3×10^6 tonnes (6). Thus, the amount of material comprising the 1998 event represented over twice the 100-year sediment budget for the entire southern basin in a single, large-magnitude event (~40 days in duration).

Conductivity-Temperature-Depth (CTD) profiles, transmissometer readings, and surface water temperature collected by NOAA/GLERL personnel demonstrated nearly constant depth profiles at both nearshore and offshore locations. Thus the plume area was completely mixed in the vertical before and during the March 1998 event. There was low ice cover that year. Counter to the conclusion reached by

Mortimer (7) regarding a May 1981 resuspension event, the initiation of the plume in 1998 did not coincide with the development of thermal stratification or springtime ice-out.

We evaluated the effect of the storm on two contaminant cycling processes. First, we hypothesized that resuspension would cause a change in dissolved / particulate distributions of POPs and this would effect the potential for gas exchange. Second, we hypothesized that downward sediment flux of POPs would increase during the resuspension event. Examination of these two hypotheses results in a picture of short-term net change in the contaminant inputs and losses to the lake after large scale resuspension.

METHODS

Sampling Design and Strategy

The two central hypotheses were addressed using a two-pronged strategy of discrete and time-integrated sampling. First, discrete samples of water and air were collected before and after the resuspension event. The first sampling period (prior to the event) was from January 28 to February 4, 1998, while the second sampling period (after the event) was from March 28 to March 30, 1999. Secondly, settling sediment was collected using an integrated sequencing trap. The sediment trap was deployed over the period during which the resuspension event occurred. While the discrete sampling provides details of the gas, aerosol, dissolved, and particulate phases at one point in time, the sediment trap material provides an integrated view of chemical concentrations that are changing over time. With this strategy, it is possible to assess the effect of sediment resuspension on the cycling of chemical contaminants. Figure 2 illustrates the sampling locations for discrete water samples, the transects over which air samples were collected, and the location of the sequencing sediment trap.

Sampling Procedures

Collection of the discrete water and air samples, collected aboard the U.S. EPA's research vessel *Lake Guardian*, was conducted as described elsewhere (8-11). Water samples consisted of glass fiber filters through which ~500 L of water was passed, and XAD-2 resin through which ~200 L of filtered water was passed. Air samples consisted of quartz fiber filters and XAD-2 resin in series. Air samples were collected from a long pole (yard-arm) that swings out over the water, about 3 m from the ship's bow.

This work was completed in collaboration with the EEGLE study (Episodic Events – Great Lakes Experiment), and all POPs sample collection occurred simultaneous with EEGLE investigators from the Great Lakes Environmental Research Laboratory (GLERL, National Oceanic and Atmospheric Administration). Settling particulate material was collected with a sequencing sediment trap deployed from 11/25/97 - 5/17/98. The trap was deployed, retrieved, and sieved to remove large particles by EEGLE investigators at GLERL. The trap was deployed and retrieved at the 56m isopleth at mid-depth (30m). This location was chosen because of its close proximity both to an offshore transport feature of the plume event that has been observed in satellite imagery by Mortimer (7) as well as to a region of maximum sediment accumulation in Lake Michigan (12). Details of the trap design and operation are provided elsewhere (13). A computer-controlled carousel containing twenty-three 60 mL polyethylene bottles was situated beneath the funnel. At nine-day intervals, an electric motor rotated the carousel to the next collection bottle. The collection bottles were poisoned with 6 mL of chloroform and filled with distilled water prior to deployment. Upon retrieval of the trap, the material collected by each bottle was first screened at 500 μm and then split into two equal fractions. One fraction was subsampled for organic contaminant analysis, while the other fraction was analyzed for total and organic carbon as well as for total and organic nitrogen (M. Lansing – GLERL).

Analytical Procedures

All samples collected were analyzed for a total of 32 individual PAH compounds and 89 individual PCB congeners and/or congener groups. Methods used to extract, cleanup, concentrate, and analyze air samples were consistent with those used during the Lake Michigan Mass Balance Project (14-16). The procedures are described in detail elsewhere(11). The following is a brief description of those procedures.

The analytical quality of the data was determined through recoveries of surrogate compounds, duplicate sampling, detection limit studies, and various blanks. Of the 91 total samples collected and analyzed for this study, 35% were quality control samples, including field blanks, trip blanks, and solvent blanks. Recoveries of PAH surrogates were 69% \pm 25% for d10-fluorene, 80% \pm 17% for d10-fluoranthene, and 88% \pm 21% for d12-perylene (n=88). Recoveries of PCB surrogates were 47% \pm 13% for Congener 14, 60% \pm 16% for Congener 65, and 67% \pm 19% for Congener 166 (n=88). The low

recovery of PCB surrogates is not due to poor sample handling. The lower recoveries are reflective of the removal of extract for the PAH analysis prior to sample cleanup and PCB analysis. The volume of the aliquot removed for PAH analysis was not measured, but this loss is instead quantified by the surrogate analysis. All PAH and PCB concentrations determined in sample extracts were corrected for surrogate recovery. Duplicate sampling was conducted on the January 1998 sampling expedition for air and water samples only. The relative percent difference (RPD) in replicate samples is due to real random error associated with sample collection, handling, extraction, and analysis, as well as to variability in each sample matrix and sampling device. Mean RPD values for dissolved Σ PAHs and Σ PCBs were 60% and 8%, respectively. Mean RPDs for the gaseous phase Σ PAHs and Σ PCBs were 20% and 33%; higher RPD values for water and airborne particulate phases were observed (28.6% - 131.2%), indicative of less precision for sampling of these phases. The percent blank mass (PBM) was calculated for each sample matrix as the mean mass in the field blanks divided by the mean mass in the samples. Dissolved, water particulate, and gas phase samples all had PBM values of <13%. Higher percent blank mass values were found for airborne particulate (42-50%) and sediment trap samples (18-28%).

The high field blank values observed in the sediment trap samples may be due to absorption of dissolved contaminants by the chloroform in the sediment collection bottles. All sediment trap bottles, including three field blanks, were deployed filled with the chloroform (6mL) and distilled water. During the deployment period, the bottles were open to lake water. As particles fell into the trap bottles, lake water also diffused in and out of bottles, introducing the possibility of extraction of dissolved phase compounds by the liquid organic solvent chloroform. Therefore, the mass of each individual PCB and PAH mass in sediment trap samples was corrected for this contamination by subtracting the average mass found on the field blanks.

RESULTS

Particulate fluxes and concentrations

At the height of the event, a NOAA/GLERL expedition (March 16 – 19, ~one week after the maximum reflectance – Fig 1), measured nearshore total particulate matter concentration (TSM) values ranged from 12 – 34 mg/L, about ten times the normal concentration, and measured during the two cruises

undertaken for this study. The TSM measured during the January (before the March resuspension event) and March (about three weeks after the peak of the resuspension event) cruises were nearly the same (1.38 ± 0.58 mg/L vs. 1.07 ± 0.44 mg/L, respectively). The fraction of organic carbon (f_{oc}) on suspended TSM varied in space (within and outside of the resuspension plume) but were not significantly different when considered as sets during the two cruises, both ~13%.

The trap data provides sediment mass flux over twenty-four, nine-day intervals during the December, 1997 through May, 1998 deployment period. Over this period, mass flux (Table 2) was highest during the January 9 to 18 interval ($24.8 \text{ g m}^{-2} \text{ d}^{-1}$) and during the March 22 to 31 interval ($24.9 \text{ g m}^{-2} \text{ d}^{-1}$). During these intervals, resuspension events occurred in southern Lake Michigan. During other intervals, sediment flux was much less. The flux of sediment, organic carbon, PCBs, and PAHs was at a maxima during the two wind-driven resuspension events transpiring in winter/spring 1998 (Figure 3). Organic carbon undergoes significant diagenesis during settling (17) and did not show any predictable variability over time. The f_{oc} in the trap material ranged from 2.1% to 4.2%, typically low for wintertime and reflective of low productivity and resuspension of bottom sediments.

PCBs and PAHs in dissolved water, suspended particles, and settling sediment

Dissolved-phase concentrations of the organic contaminants decreased by 31% to 70% after the suspension event. This effect was observed for Σ PCBs, Σ PAHs and for most individual compounds when comparing the data from the two cruises as sets and when comparing the measured concentrations at specific sites (Table 1). For points in space sampled in the nearshore region on both cruises, Σ PCB dissolved phase concentrations were significantly lower in March ($128.4 \text{ pg/L} \pm 41.8 \text{ pg/L}$) following the plume event as compared to January levels ($219.3 \text{ pg/L} \pm 54.4 \text{ pg/L}$) ($\alpha=0.05$). Σ PAH concentrations were also less in March ($10.7 \text{ ng/L} \pm 16.7 \text{ ng/L}$) as compared to January ($17.7 \text{ ng/L} \pm 9.5 \text{ ng/L}$). An exception is the Σ PAH dissolved concentrations measured at the St. Joseph 15m site. At the St. Joseph site, a slightly higher dissolved phase Σ PAH concentration was observed in March. In addition to the change in dissolved concentrations over time, we also observe a difference by location. Dissolved phase concentrations are higher near urban/industrial areas. For example, in January 1998, concentrations of Σ PCBs (dissolved and particulate) near Chicago (595.20 pg/L) were nearly double the Σ PCB concentrations found at the St.

Joseph (308.1 pg/L) and Saugatuck (307.1 pg/L) stations. Large Σ PCB concentrations (522.8 pg/L) were also observed near the Milwaukee urban center.

The change in the particulate phase POPs was more complicated than the dissolved phase concentrations. Near urban areas, in the southwest, the concentration of particle bound POPs decreased after the event. In the southeast region, concentrations went up. Particulate phase PCB and PAH concentrations decreased near Chicago and Gary (by 15% to 30%), but increased substantially at the St. Joseph and Saugatuck sites (by 240% to 680%). Because of the small number of samples, this finding cannot be described with a high level of statistical confidence. However, these changes are consistent with a pattern of suspension of clean coastal erosion sediments being transported and mixed with the more contaminated sediments near Chicago and Gary. The storm then moved this mixed suspension into the southeast region of St. Joseph and Saugatuck. In this manner, Chicago and Gary received clean sediment and St. Joseph and Saugatuck received more contaminated sediments.

The settling sediment collected on traps is used to estimate downward contaminant fluxes, and a time series of contaminant in the water column. The flux of Σ PCBs and Σ PAHs ranged from 19.42 to 1052 $\text{ng m}^{-2} \text{d}^{-1}$ and 0.8 to 35.8 $\mu\text{g m}^{-2} \text{d}^{-1}$ respectively (Figure 3). Σ PCB settling fluxes measured in this study were similar to those measured in Lake Superior ($160 \pm 80 \text{ ng m}^{-2} \text{d}^{-1}$) (18); and Lake Ontario (80 – 1900 $\text{ng m}^{-2} \text{d}^{-1}$) (19) during winter unstratified conditions. Similar Σ PCB settling fluxes were determined in Lake Superior ($121 \pm 40 \text{ ng m}^{-2} \text{d}^{-1}$) (20), Esthwaite Water, U.K. ($1270 \text{ ng m}^{-2} \text{d}^{-1}$) (21), West Baltic Sea ($66\text{-}307 \text{ ng m}^{-2} \text{d}^{-1}$), and the southwestern Mediterranean ($15\text{-}625 \text{ ng m}^{-2} \text{d}^{-1}$) (22) over other time periods. The concentrations of PAHs and PCBs exhibited very large variations over the collection period. During periods of known large-scale resuspension (mid January and early March), concentrations of the contaminants on settling particles was very low (Table 2). During periods when there was no evidence, by satellite or by mass particle fluxes, of resuspension, the concentrations of POPs on particles were much higher. PCB concentrations, for example, varied by over three orders of magnitude.

Interestingly, contaminant concentrations on settling particles are comparable to those on suspended particles (Figure 4). Contaminant concentrations on samples collected in January and March are statistically similar to the concentrations on the sediment trap material collected in January and March ($\alpha=0.05$). These findings are markedly different than similar studies in Lake Superior (18) and two lakes in

The Netherlands (23). In those lakes, investigators found that concentrations of PCBs and PAHs on settling particles were enriched 10-100 times relative to suspended particles. Our contradictory findings may be indicative of the source of settling particles collected for this study. In our study, the settling particles are dominated by inorganic material, probably derived from eroded bluffs or exposed glacial clay deposits in shallow waters (24) and therefore they do not reflect preferential decay of the organic carbon that tend to enrich the concentrations of organic contaminants on particles in productive waters (17).

DISCUSSION

Partitioning of PCBs and PAHs in water

Particles control cycling of persistent organic pollutants in two ways. First, POPs associated with particles can be removed from the water column by sedimentation. Second, POPs *not* sorbed to particles can be removed from the water column by volatilization. Large resuspension events, combined with heavy atmospheric contamination in the southern basin could cause important changes in the relative magnitude of HOC fluxes to the sediment and to the air. We have examined the distribution of POPs before and after the resuspension event in order to determine the likely fate of POPs.

Congener/compound-specific, organic carbon normalized distribution coefficients, K_{oc} 's ($L\ kg^{-1}\ OC$), were determined for each discrete sampling site. These partition coefficients are defined as the particulate POP concentration ($pg\ kg^{-1}$) divided by the concentration in the dissolved phase ($pg\ L^{-1}$) and the fraction of organic carbon on the collected particles. The partitioning of PCBs and PAHs to aquatic particles is expected to increase as the hydrophobicity (K_{ow}) increases (25-28). This was affirmed in all calculated K_{oc} s for the PAH compounds. In fact, regressions for $\log K_{oc}$ vs. $\log K_{ow}$ for PAHs have slopes (mean slope = 1.1) and R^2 values close to unity during both cruises (Table 3). Interestingly, the intercept increases for the K_{oc} s calculated for the March cruise. For that dataset, there are more PAHs on particles (relative to the dissolved phase) than in January and more than predicted by equilibrium studies (27). PCB partitioning, on the other hand, is poorly correlated to K_{ow} . The lack of correlation of $\log K_{oc}$ with $\log K_{ow}$ for PCBs were also observed in previous studies focused upon the distribution of HOCs in water column of the Great Lakes (10, 29).

It is surprising that PAHs appear to be at equilibrium but PCBs are not. This may be a result of different immediate sources of the chemical. PCBs are known to have important gas-phase atmospheric sources in southern Lake Michigan. PAHs, on the other hand, may enter the water column already attached to particles. Gustafsson *et al.* (30) have suggested that PAHs tend to remain sorbed to particles long after re-equilibration with cleaner water. They have found evidence for a significant non-exchangeable fraction of PAHs on aquatic particles due to incorporation of PAHs on soot particles. Other studies have also reported this for PAHs on atmospheric particles (31-34).

We suspect that there are two sources of particles resuspended after the storm events. The first and largest source of particles appears to be contaminant-free, inorganic particles that were eroded from the bluffs of the western shore. This clean material tends to dilute particulate concentrations and scour the dissolved phase. It is low in organic carbon and settles quickly. This material makes up the bulk of the settling particles in the sediment trap in January and March. The second, smaller source of particles may be heavily contaminated with soot particles bound with PAHs. It originated in rivers, embayments, or sedimentary zones near industrial areas. When resuspended, POPs sorbed to this material do not desorb rapidly. We propose this possibility to explain: 1) why PAHs are linear with K_{ow} , have a slope near unity for $\log K_{oc}$ vs $\log K_{ow}$, but a larger intercept after the event and; 2) why contaminants on particles are diluted by the resuspension event at sites 'downstream' of the Chicago/Gary urban industrial complex.

Figure 5 illustrates the change in K_{oc} s for individual PCB congeners before and after the event. In all cases, the plotted data for the correlation was biased *above* the 1:1 line. The same phenomena occurred for PAH compounds, listed in Table 3. This suggests that the plume event not only affected partitioning status of POPs, but also that the particles suspended in the water column became enriched with a larger amount of particulate phase POPs.

Air/Water Exchange of PCBs and PAHs

Instantaneous net PAH and PCB fluxes were calculated for simultaneous air-water sampling sites both before and after the resuspension event in March 1998. Net fluxes were determined on a congener/compound-specific basis (35). This model has been applied a number of times in the Great Lakes and not reviewed here (8, 9, 36, 37). Flux determinations are based on dissolved (Table 1) and gaseous (Table 4) phase PCB and PAH concentrations as well as on Henry's Law constant (38-40). The Henry's

constants were corrected for measured surface water temperatures. The effect of wind speed on the mass transfer coefficients were estimated using a two parameter Weibull distribution function (41, 42). Net gas phase deposition (air-to-water) of contaminants was calculated for individual PCB congeners and PAHs for all discrete sites sampled for this study. The depositional flux of Σ PAHs varied from -2.3 to $-66 \mu\text{g m}^{-2}\text{d}^{-1}$, while that of Σ PCBs varied from -58 to $-259 \text{ ng m}^{-2}\text{d}^{-1}$ (Table 5).

Atmospheric (gas) deposition of PCBs and PAHs increased after the resuspension event at most sites that were measured before and after the event. The increase in atmospheric deposition is a result of the re-distribution of these compounds in the water column, and not due to changes in air concentrations or meteorology. The gas phase concentrations of PCBs and PAHs measured in this study were similar to those recently measured during other studies in southern Lake Michigan (33, 42, 43). Gas phase concentrations of Σ PCBs did not vary significantly between January and March in this study and in the LMMB (43). Meteorological parameters such as air temperature, water temperature, and wind speed also did not vary significantly over the two-month interval of this study.

The observed increase in gas phase deposition of PCBs and PAHs over the short time scale (January to March) is a result of the drop in dissolved phase contaminants after the event. Thus, the sediment resuspension event, thought initially to cleanse the water column via scouring of dissolved phase contaminants by suspended and settling particulate matter, represents a natural event that may bring about a *short-term increased input of SOCs* to the lake via gas phase deposition. This differential increase in atmospheric deposition is as much as $130 \text{ ng m}^{-2} \text{ d}^{-1}$ for Σ PCBs near Chicago and $36 \text{ mg m}^{-2} \text{ d}^{-1}$ for Σ PAHs (Table 5).

Coupled Air/Water and Sediment/Water Exchange Near Chicago

The largest increase in gas phase deposition of PCBs and PAHs was observed for discrete sampling locations near the Chicago/Gary urban center, a highly populated and industrialized region adjacent to the southern basin of Lake Michigan (Figure 6). Higher gas phase deposition of SOCs at these locations suggests that the sediment resuspension event may be acting together with the “urban plume” of air possessing elevated levels of gas phase PCBs and PAHs from the Chicago urban region to bring about an increased short-term loading of PCBs and PAHs through enhanced gas phase deposition. That is, the *proximity* of the air pollution source to the resuspension region greatly increases the potential for induced

atmospheric deposition fluxes to the lake. We have estimated the loading of POPs within a zone 30 km from Chicago (33, 42, 44), predicting that the combined (or synergistic) effect of the urban air plume and sediment resuspension plume is greatest in this region. We estimated the magnitude of the combined effect on increased contaminant depositional flux by multiplying the surface area of the annual average urban air plume influence zone (1575 km²)(44) by the approximate duration of the sediment resuspension event in the nearshore region (~40 days) and the average increase in gas depositional flux of PCBs (122 ng m⁻²d⁻¹) and PAHs (35 µg m⁻²d⁻¹) observed after the sediment resuspension event. The estimated mass of gas phase PCBs and PAHs absorbed by the lake over the 40 day time scale of the resuspension event due to the air-water-sediment couple between the Chicago urban air plume and the sediment resuspension event is 8 kg and 2200 kg respectively. The additional loading of PCBs and PAHs due to this coupled process represents a previously unknown load of POPs to Lake Michigan.

The additional load of PCBs is significant when compared to both previous estimates of the gas phase deposition and other depositional inputs to the lake. Zhang *et al.* (1999) estimated, through similar sampling and modeling procedures, that the annual net air-water absorptive flux of gas phase PCBs to the southern basin of Lake Michigan (south of the 45° latitude) is -8.6 µg m⁻²d⁻¹, or -140 kg yr⁻¹. If the net annual absorptive flux of -8.6 µg m⁻²d⁻¹ is instead applied to the surface area of zone of influence of the Chicago air plume proposed by Green *et al.* (In review), the estimated net annual air-water absorptive flux due to the contribution of the high gas phase concentrations from Chicago becomes -14 kg yr⁻¹. The predicted load of 8 kg of PCBs during the brief 40 day period of the sediment resuspension plume represents a significant portion (~57%) of the estimated entire *annual* gas phase deposition load to proximate waters of the urban complex on the southwestern shore of the lake. The additional load of gas phase PAHs during the sediment resuspension event is also significant. The estimated 2200 kg load of gas phase PAHs deposited to the southern basin of the lake due to the synergistic relationship proposed in this study is a large portion (55 – 610%) of previous whole-lake annual PAH loading estimates. PAH dry deposition estimates to the whole lake have ranged from 360 kg yr⁻¹ (45) to 4000 kg yr⁻¹ (46), while the wet depositional loading of PAHs to the entire lake have been estimated to be ~1600 kg yr⁻¹ (45).

A comparison between air/water and settling particle fluxes

Settling fluxes after the resuspension event are similar in magnitude to the potential atmospheric deposition fluxes resulting from the scouring of dissolved phase compounds by the resuspended sediments. PCB settling fluxes are as high as $1000 \text{ ng m}^{-2} \text{ day}^{-1}$ while potential PCB deposition from the atmosphere is $\sim 760 \text{ ng m}^{-2} \text{ day}^{-1}$. The same is true for PAHs: settling fluxes are as high as $36 \text{ ug m}^{-2} \text{ day}^{-1}$ while PAH gas depositional fluxes are up to $260 \text{ ug m}^{-2} \text{ day}^{-1}$. Because calculated and measured fluxes are similar in magnitude, we suggest that there appears to be no net change in the input or loss of persistent organic contaminants as a result of the resuspension event. Two issues preclude our ability to address this conclusion satisfactorily, however. First, we expect that there is large spatial and temporal variability in the fluxes of contaminants induced by resuspension. Further field and computational research is ongoing to evaluate the spatial and temporal variability of the effect. Secondly, this study has not addressed the ultimate fate of the contaminants, only the short term changes in fluxes. It is well known that a large portion of the settling contaminants do not subsequently accumulate in the bottom sediments, and are in fact recycled back into the water column (18, 20, 21, 47-50). It is therefore likely that the effect of large scale resuspension, such as described here, is to increase atmospheric deposition, especially when the resuspension event occurs near areas heavily impacted by urban and industrial air pollution.

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REFERENCES

1. Bierman, V.J., DePinto J.V., Young T.C., Rodgers P.W., Martin S.C., Raghunathan R. *Final Report: Development and Validation of an Integrated Exposure Model for Toxic Chemicals in Green Bay, Lake Michigan*. USEPA, Environmental Research Laboratory - Large Lakes Research Station, Grosse Ile, Michigan September, 1992.
2. Cheng, C.Y., Atkinson J.F., Depinto J.V. *Marine & Freshwater Research* **1995**, *46*, 251-256.
3. Nelson, E.D., McConnell L.L., Baker J.E. *Environ. Sci. Technol.* **1998**, *32*, 912-919.
4. Bamford, H.A., Offenbergh J.H., Larsen R.K., Ko F., Baker J.E. *Environ. Sci. Technol.* **1999**, *33*, 2138-2144.
5. Schwab, D.J., Beletsky D., Lou J. *Estuarine, Coastal, and Shelf Science* **In Press**.
6. Folger, D.W., Colman S.M., Barnes P.W. *J. Great Lakes Res.* **1994**, *20*, 2-8.
7. Mortimer, C.H. *Limnol.Oceanogr.* **1988**, *33*, 203-226.
8. Hornbuckle, K.C., Achman D.R., Eisenreich S.J. *Environ. Sci. Technol.* **1993**, *27*, 87-98.
9. Hornbuckle, K.C., Sweet C.W., Eisenreich S.J. *Environ. Sci. Technol.* **1994**, *28*, 1491-501.
10. Pearson, R.F., Hornbuckle K.C., Eisenreich S.J., Swackhamer D.L. *Environ. Sci. Technol.* **1996**, *30*, 1429-1436.
11. Bogdan, J.J. M.S. Thesis, State University of New York at Buffalo, 1999.
12. Lineback, J.A., Gross D.L. *Depositional patterns, facies, and trace element accumulation in the Waukegan member of the late-Pleistocene Lake Michigan formation in southern Lake Michigan*. EGN-58. Illinois State Geological Survey, Urbana, Illinois.
13. Eadie, B.J. *Water Air and Soil Pollution* **1997**, *99*, 133-139.
14. Basu, I. (*IADN*) *Analysis of PCBs and Pesticides in Air and Precipitation Samples: IADN Project Standard Operating Procedure*. Indiana University, Bloomington, IN.
15. Basu, I. (*IADN*) *Quality Control Report 1994-1995, Integrated Atmospheric Deposition Network*. Indiana University, Bloomington, IN 1996.
16. Cortes, D., Brubaker W. In *Lake Michigan Mass Balance Study Methods Compendium*; USEPA,1996; Vol. 2, pp 4-22.
17. Meyers, P.A., Eadie B.J. *Org. Geochem.* **1993**, *20*, 47-56.

18. Baker, J.E., Eisenreich S.J., Eadie B.J. *Environ. Sci. Technol.* **1991**, 25, 500-509.
19. Oliver, B.G., Charlton M.N., Durham R.W. *Environ. Sci. Technol.* **1989**, 23, 200-208.
20. Jeremiason, J.D., Eisenreich S.J., Baker J.E., Eadie B.J. *Environ. Sci. Technol.* **1998**, 32, 3249-3256.
21. Sanders, G., HamiltonTaylor J., Jones K.C. *Environ. Sci. Technol.* **1996**, 30, 2958-2966.
22. Dachs, J., Bayona J.M., Fowler S.W., Miquel J.C., Albaiges J. *Marine Chemistry* **1996**, 52, 75-86.
23. Koelmans, A.A., Gillissen F., Makatita W., VandenBerg M. *Water Res.* **1997**, 31, 461-470.
24. Eadie, B.J., Schwab D.J., Assel R.A., Hawley N., Lansing M.B., Miller G.S., Morehead N.R., Robbins J.A. *Eos, Transactions, American Geophysical Union* **1996**, 77, 337-338.
25. Karickhoff, S., Brown D., Scott T. *Water Res.* **1979**, 13, 241-248.
26. Elzerman, A.W., Coates J.T. In *Sources and Fates of Aquatic Pollutants*, 1987;.
27. Schwarzenbach, R.P., Gschwend P.M., Imboden D.M. *Environmental Organic Chemistry*. New York, NY, Wiley Interscience., New York, NY, 1993., pp.
28. Achman, D.R., Brownawell B.J., Zhang L.C. *Estuaries* **1996**, 19, 950-965.
29. Baker, J.E., Eisenreich S.J., Swackhamer D.L. In *Organic Substances and Sediments in Water*; Baker RA, ed; Lewis Publishers: Chelsea, MI, 1991; Vol. 2, pp 79-90.
30. Gustafsson, O., Haghseta F., Chan C., MacFarlane J., Gschwend P.M. *Environmental Science & Technology*. **1997**, 31, 203-209.
31. Cotham, W.E., Bidleman T.F. *Environ. Sci. Technol.* **1995**, 29, 2782-2789.
32. Pankow, J.F., Bidleman T.F. *Atmospheric Environment Part a-General Topics* **1992**, 26, 1071-1080.
33. Simcik, M.F., Zhang H.X., Eisenreich S.J., Franz T.P. *Environ. Sci. Technol.* **1997**, 31, 2141-2147.
34. Simcik, M.F., Golden K.A., Liu S.P., Eisenreich S.J., Lippiatou E., Swackhamer D.L., Long D.T. *Environ. Sci. Technol.* **1996**, 30, 3039-3046.
35. Whitman, W.G. *Chem. Metall. Eng.* **1923**, 29, 146-148.
36. Achman, D.R., Hornbuckle K.C., Eisenreich S.J. *Environ. Sci. Technol.* **1993**, 27, 75-87.
37. Hornbuckle, K.C., Sweet C.W., Pearson R.F. *Environ. Sci. Technol.* **1995**, 29, 869-77.
38. Brunner, S., Hornung E., Santl H., Wolff E., Piringer O.G., Altschuh J., Bruggemann R. *Environ. Sci. Technol.* **1990**, 24, 1751-1754.
39. Hulscher, T.E.M.t., Velde L.E.v.d., Bruggeman W.A. *Environ. Toxicol. Chem.* **1992**, 11, 1595-1603.

40. Bamford, H.A. Master's of Science Thesis, University of Maryland, 1998.
41. Livingstone, D.M., Imboden D.M. *Tellus* **1993**, *45B*, 275-295.
42. Zhang, H., Eisenreich S.J., Franz T.R., Baker J.E., Offenbergl J.H. *Environ. Sci. Technol.* **1999**.
43. Miller, S.M. Master's of Science Thesis, SUNY Buffalo, 1999.
44. Green, M.L., Depinto J.V., Sweet C., Hornbuckle K.C. *Environ. Sci. Technol.* **2000**, *34*, 1833-1841.
45. Eisenreich, S.J., Strachan W.M.J. *Estimating Atmospheric Deposition of Toxic Substances to the Great Lakes, an Update*. Environment Canada, Canada Centre for Inland Waters, Burlington, Ontario
January 31-February 2, 1992. p60.
46. Franz, T.P., Eisenreich S.J., Holsen T.M. *Environ. Sci. Technol.* **1998**, *32*, 3681-3688.
47. Baker, J.E., Eisenreich S.J., Eadie B.J. *Abstracts of Papers of the American Chemical Society* **1988**,
195, 119-ENVR.
48. Lipiatou, E., Marty J.C., Saliot A. *Marine Chemistry* **1993**, *44*, 43-54.
49. Gevao, B., Jones K.C., Hamilton-Taylor J. *Sci. Tot. Environ.* **1998**, *215*, 231-242.
50. Jeremiason, J.D., Eisenreich S.J., Paterson M.J. *Canadian Journal of Fisheries and Aquatic Sciences*
1999, *56*, 650-660.

Table 1. Volume-based dissolved (d) and suspended particulate (p) phase Σ PCB and Σ PAH concentrations for surface water samples obtained during January and March 1998. Σ PCB concentrations represents 87 separate congeners or co-eluting congener groups and Σ PAH levels represents 31 separate compounds or co-quantified compounds. The ‘*’ denotes water sampling sites that were sampled as part of both sampling campaigns. TSM and f_{oc} data was collected by collaborative scientists (EPA, GLERL).

| <i>January Sampling Campaign</i> | | | | | | |
|---|--------------------------|--------------------------|--------------------------|--------------------------|---------------|----------|
| Sampling Location | Σ_d PCB [pg/L] | Σ_p PCB [pg/L] | Σ_d PAH [ng/L] | Σ_p PAH [ng/L] | TSM [mg/L] | f_{oc} |
| Racine 15m | 286.17 | 236.58 | 22.55 | 15.17 | 4.15 | 0.04 |
| Chicago 15m* | 246.08 | 349.20 | 20.89 | 21.69 | - | - |
| Gary Dup1 15m* | 166.04 | 44.21 | 16.01 | 3.62 | 0.82 | 0.21 |
| Gary Dup2 15m* | 156.96 | 102.35 | 19.59 | 3.26 | 0.82 | 0.21 |
| St. Joseph 15m* | 248.42 | 60.49 | 11.68 | 2.92 | 1.35 | 0.15 |
| Saugatuck 15m* | 278.79 | 28.32 | 14.26 | 1.06 | 1.97 | 0.10 |
| <i>March Sampling Campaign</i> | | | | | | |
| Chicago 15m* | 169.51 | 300.74 | 14.93 | 18.41 | 1.02 | 0.15 |
| Gary 15m* | 102.57 | 63.01 | 6.78 | 2.45 | 1.54 | 0.10 |
| St. Joseph 15m* | 158.01 | 413.73 | 16.96 | LOST | - | - |
| Saugatuck 15m* | 83.49 | 138.97 | 10.41 | 5.65 | - | - |
| Basin 150m | 95.63 | 68.42 | LOST | 5.60 | 0.66 | 0.16 |

Table 2 Sediment fluxes and chemical characteristics of settling solids collected by the sequencing sediment trap deployed for this study. The dashed cells denote Σ PCB and Σ PAH fluxes that were negative following field blank correction. Each trap sample collected settling material for nine days, with the exception of T2661, which had a two-day collection period.

| Name | Start Date | Sed. Flux [g m ⁻² d ⁻¹] | SPCB Flux [ng m ⁻² d ⁻¹] | SPCB Conc. [ng/g] | SPA H Flux [mg m ⁻² d ⁻¹] | SPA H Conc. [mg g ⁻¹] |
|-------|------------|---|--|----------------------|---|--------------------------------------|
| T2642 | 11/25/97 | 1.15 | - | 2.70 | - | 0.49 |
| T2643 | 12/4/97 | 8.08 | 1050 | 148 | 19.4 | 2.79 |
| T2644 | 12/13/97 | 6.61 | - | 8.0 | 5.0 | 1.23 |
| T2645 | 12/22/97 | 0.87 | - | 1.3 | - | 0.45 |
| T2646 | 12/31/97 | 6.72 | 728 | 130 | 3.2 | 0.94 |
| T2647 | 1/9/98 | 24.8 | 439 | 23.6 | 24.7 | 1.12 |
| T2648 | 1/18/98 | 1.14 | 19.4 | 147 | - | 2.56 |
| T2649 | 1/27/98 | 0.30 | - | 102.0 | - | 3.04 |
| T2650 | 2/5/98 | 0.12 | 264 | 3530 | 3.0 | 53.2 |
| T2651 | 2/14/98 | 0.09 | 188 | 3680 | 3.5 | 73.3 |
| T2652 | 2/23/98 | 4.47 | 129 | 61.9 | 4.6 | 1.74 |
| T2653 | 3/4/98 | 14.5 | 608 | 51.9 | 30.0 | 2.28 |
| T2654 | 3/13/98 | 13.4 | 427 | 43.0 | 14.6 | 1.33 |
| T2655 | 3/22/98 | 24.9 | 759 | 36.5 | 35.8 | 1.57 |
| T2656 | 3/31/98 | 0.83 | 412 | 673 | 1.7 | 5.91 |
| T2657 | 4/9/98 | 0.33 | - | 376 | - | 5.13 |
| T2658 | 4/18/98 | 1.36 | - | 100 | - | 1.70 |
| T2659 | 4/27/98 | 0.12 | - | 72.5 | - | 0.37 |
| T2660 | 5/6/98 | 0.03 | - | 2710 | 0.8 | 112 |
| T2661 | 5/15/98 | 0.63 | 472 | 1810 | - | 7.57 |

Table 3. Summary of linear regression statistics for log K_{oc} vs. log K_{ow} correlations for PCBs and PAHs for surface water samples for this study.

| <i>January 1998 PAHs</i> | | | |
|---------------------------------|--------------|------------------|-------------------------|
| Station Name | Slope | Intercept | r^2 |
| Gary Dup1 15m | 1.11 | 0.84 | 0.80 |
| St. Joseph 15m | 0.94 | 1.48 | 0.84 |
| Saugatuck 15m | 0.63 | 2.34 | 0.90 |
| Gary Dup2 15m | 1.34 | -0.61 | 0.93 |
| Racine 15m | 1.31 | 0.08 | 0.88 |
| Chicago 15m | 1.41 | -0.33 | 0.91 |
| <i>March 1998 PAHs</i> | | | |
| Gary 15m | 0.81 | 2.60 | 0.94 |
| Chicago 15m | 1.21 | 1.07 | 0.95 |
| Saugatuck 15m | 0.92 | 2.03 | 0.93 |
| <i>January 1998 PCBs</i> | | | |
| Saugatuck 15m | 0.27 | 4.03 | 0.31 |
| Racine 15m | 0.26 | 4.98 | 0.23 |
| St. Joseph 15m | 0.20 | 4.87 | 0.08 |
| Chicago 15m | 0.31 | 4.97 | 0.22 |
| Gary Dup2 15m | 0.24 | 5.01 | 0.14 |
| Gary Dup1 15m | 0.37 | 3.80 | 0.50 |
| <i>March 1998 PCBs</i> | | | |
| Basin 150m | 0.16 | 5.76 | 0.19 |
| Saugatuck 15m | 0.21 | 5.66 | 0.19 |
| Chicago 15m | 0.33 | 4.93 | 0.42 |
| St. Joseph 15m | 0.17 | 6.09 | 0.12 |
| Gary 15m | 0.34 | 4.39 | 0.51 |

Table 4. Volume-based gaseous (d) and airborne particulate (p) phase Σ PCB and Σ PAH concentrations and ancillary measurements for air samples obtained in January and March 1998. Σ PCB concentrations represent 87 separate congeners or co-eluting congener groups and Σ PAH levels represents 31 separate compounds or co-quantified compounds. The wind direction data is expressed in degrees from north (D. Schwab – NOAA/GLERL).

| January Sampling Campaign | | | | | | |
|---------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-----------------------|---------------------------|
| Sampling Location | Σ_g PAH [ng/m ³] | Σ_p PAH [ng/m ³] | Σ_g PCB [ng/m ³] | Σ_p PCB [pg/m ³] | Mean Wind Speed [m/s] | Mean Wind Direction (deg) |
| Milwaukee/Racine | 78.7 | 1.8 | 0.90 | 51.9 | 7.8 | 106.0 |
| Chicago/Gary Dup1 | 152.0 | 18.7 | 0.66 | 39.6 | 5.9 | 243.0 |
| Chicago/Gary Dup2 | 122.3 | 3.9 | 0.65 | 31.8 | 5.9 | 243.0 |
| Saugatuck | 52.0 | 2.3 | 0.33 | 24.0 | 11.6 | 158.4 |
| St. Joseph | 45.5 | 1.4 | 0.41 | 20.7 | 8.3 | 55.6 |
| Basin | 53.2 | 0.8 | 0.38 | 53.2 | 9.1 | 94.0 |
| March Sampling Campaign | | | | | | |
| Chicago | 94.0 | 2.0 | 0.66 | 13.5 | 8.3 | 218.1 |
| Gary | 222.2 | 3.6 | 0.85 | 30.3 | 7.2 | 179.2 |
| St. Joseph | 23.8 | 5.5 | 0.38 | 13.9 | 7.2 | 179.2 |
| Basin | 72.7 | 4.2 | 0.68 | 15.1 | 9.2 | 177.0 |

Table 5. Net Σ PCB and Σ PAH air-water fluxes for discrete points in January and March 1998. “NA” denotes that either an air or water sample was not taken at the specified location for that particular sampling expedition. Net fluxes with negative values are depositional fluxes. In the ‘Differential’ Column, a positive value (**bold**) indicates an *increased gas phase deposition*, while a negative value denotes *decreased gas phase deposition*.

| <i>PCBs</i> | | | |
|-------------------|--|--|--------------|
| Sampling Location | Net Σ PCB Flux [ng/m ² d] | Net Σ PCB Flux [ng/m ² d] | Differential |
| | Jan. | Mar. | |
| Racine 15m | -257 | NA | - |
| Chicago 15m | -128 | -259 | +131 |
| Gary Dup1 15m | -130 | -245 | +112 |
| Gary Dup2 15m | -137 | NA | - |
| St. Joseph 15m | -75 | -76 | +1 |
| Saugatuck 15m | -58 | -103 | +45 |
| Basin 150m | NA | -257 | - |
| <i>PAHs</i> | | | |
| Sampling Location | Net Σ PAH Flux [μ g/m ² d] | Net Σ PAH Flux [μ g/m ² d] | Differential |
| | Jan. | Mar. | |
| Racine 15m | -16.1 | NA | - |
| Chicago 15m | -26.9 | -24.3 | -2.6 |
| Gary Dup1 15m | -30.0 | -65.8 | +35.8 |
| Gary Dup2 15m | -20.0 | NA | - |
| St. Joseph 15m | -7.6 | -2.3 | -5.3 |
| Saugatuck 15m | -15.9 | -3.0 | -12.9 |
| Basin 150m | NA | LOST | - |

FIGURE CAPTIONS

Figure 1. Satellite images of reflectance on January 31, March 12, and March 29, 1998. (images left to right). The scale is from 0% reflectance (dark blue) to 6% reflectance (red). The images on the left and right are days that the discrete air and water sampling took place aboard the R.V Lake Guardian. Sampling locations are noted as white circles. The triangle notes the location of the sequencing sediment trap collector. The center image shows the date of maximum reflectance due to March 1998 resuspension event.

Figure 2. Sampling locations for the spring 1998 sampling cruises. The solid line indicates the collection transect for the January air sampling, the dotted line is the transect for the March air sampling. January water sampling sites are indicated by solid circles. March water sampling sites are indicated by open squares. The sediment trap deployment site (97-T24A) is indicated by a triangle. Cities are noted for reference with solid squares.

Figure 3. Results from the sequencing sediment trap, starting at top plot: Sediment flux ($\text{g m}^{-2} \text{d}^{-1}$), ΣPAH settling flux ($\text{ng m}^{-2} \text{d}^{-1}$), ΣPCB settling flux ($\text{ng m}^{-2} \text{d}^{-1}$), ΣPAH concentration on settling particles (ng g^{-1}), ΣPCB concentration on settling particles (ng g^{-1}), and organic carbon flux ($\text{mg m}^{-2} \text{d}^{-1}$). Each vertical black bar represents a nine-day sequential collection period beginning on November 25, 1997. The gray areas through each plot identifies the two plume events transpiring in January and March 1998 as observed in the temporal profile of sediment flux.

Figure 4. Concentrations of ΣPCB (top, in $\text{ng g}^{-1} \text{OC}$) and ΣPAH (bottom, in $\text{mg g}^{-1} \text{OC}$) on sediment normalized to organic carbon. The bars represent the concentrations on settling sediment. The solid points represent the concentrations measured in suspended sediment. The dates on the x-axis are the first day of the sediment trap collection periods. The discrete samples of suspended sediment were collected on Jan 29-Feb 1, and on Mar 29-31.

Figure 5. $\log K_{oc} - \text{March}$ vs. $\log K_{oc} - \text{January}$ plots and linear regression statistics for PCB congeners for locations that were sampled before and after the large resuspension event in 1998. The lighter diagonal line represents a slope of unity.

Figure 6. Potential gas exchange fluxes of ΣPAHs (plot a.) and ΣPCB (plot b.). Only fluxes calculated for air and water pair collected at the same site in January and March are illustrated. The black bars are the net fluxes calculated from the January samples, the gray bars are the net fluxes calculated from the March samples.

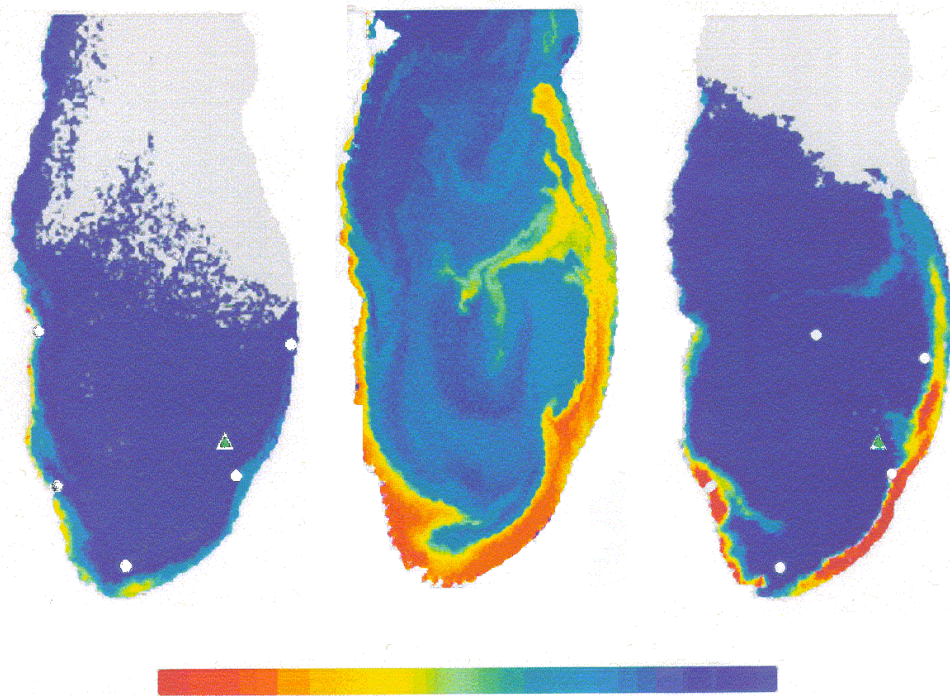


Figure 1. Satellite images of reflectance on January 31, March 12, and March 29, 1998. (images left to right). The scale is from 0% reflectance (dark blue) to 6% reflectance (red). The images on the left and right are days that the discrete air and water sampling took place aboard the R.V Lake Guardian. Sampling locations are noted as white circles. The triangle notes the location of the sequencing sediment trap collector. The center image shows the date of maximum reflectance due to March 1998 resuspension event.

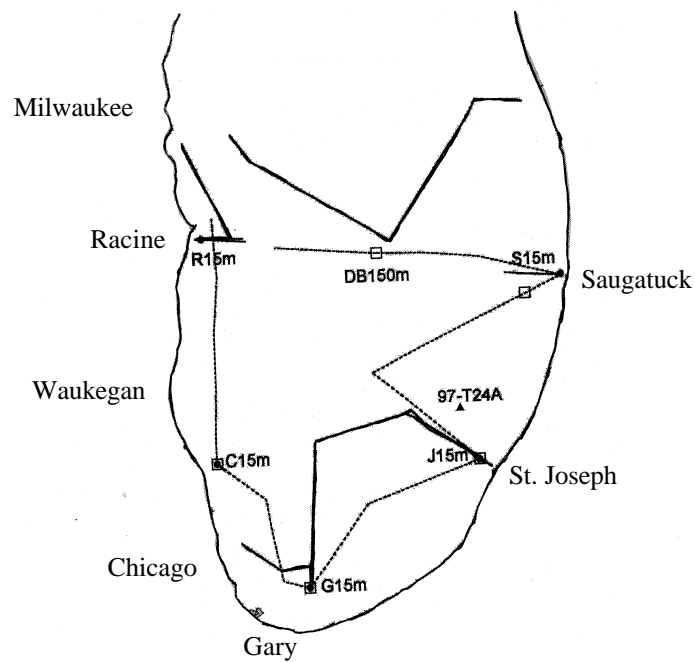


Figure 2. Sampling locations for the spring 1998 sampling cruises. The solid line indicates the collection transect for the January air sampling, the dotted line is the transect for the March air sampling. January water sampling sites are indicated by solid circles. March water sampling sites are indicated by open squares. The sediment trap deployment site (97-T24A) is indicated by a triangle. Cities are noted for reference with solid squares.

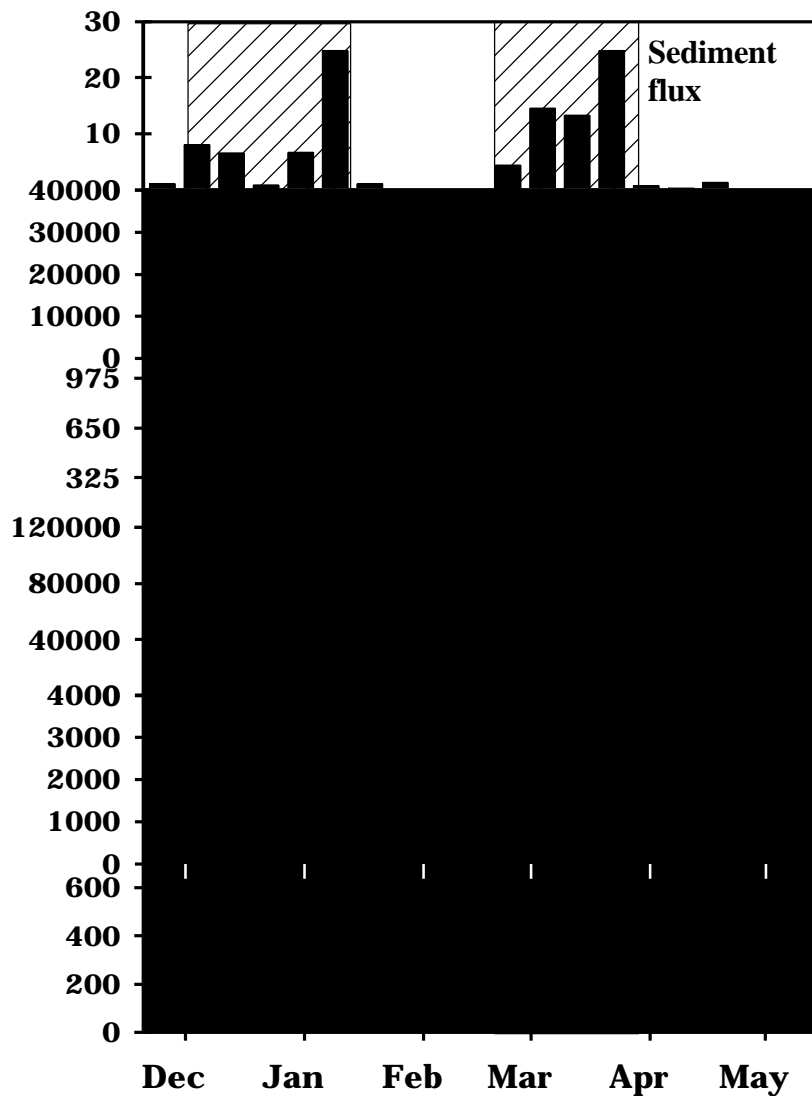


Figure 3. Results from the sequencing sediment trap, starting at top plot: Sediment flux ($g\ m^{-2}\ d^{-1}$), Σ PAH settling flux ($ng\ m^{-2}\ d^{-1}$), Σ PCB settling flux ($ng\ m^{-2}\ d^{-1}$), Σ PAH concentration on settling particles ($ng\ g^{-1}$), Σ PCB concentration on settling particles ($ng\ g^{-1}$), and organic carbon flux ($mg\ m^{-2}\ d^{-1}$). Each vertical black bar represents a nine-day sequential collection period beginning on November 25, 1997. The hatched areas through each plot identifies the two plume events transpiring in January and March 1998 as observed in the temporal profile of sediment flux.

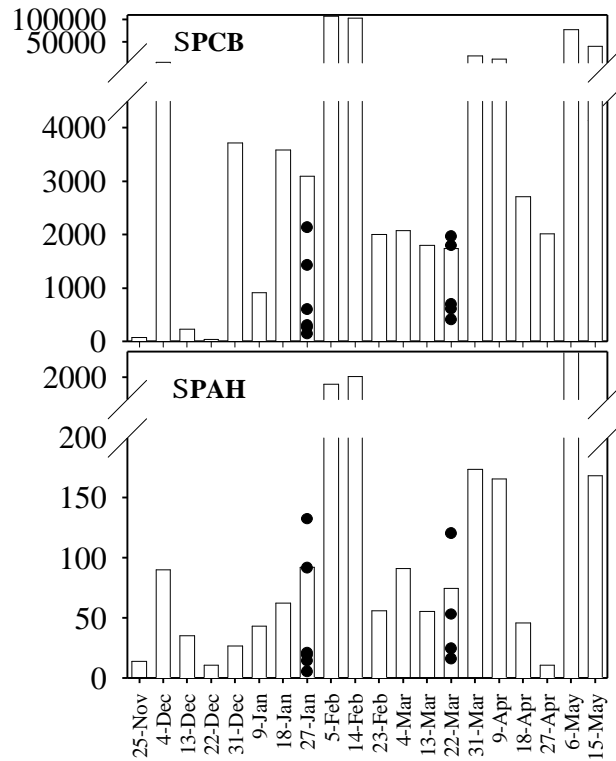


Figure 4. Concentrations of Σ PCB (top, in ng g^{-1} OC) and Σ PAH (bottom, in mg g^{-1} OC) on sediment normalized to organic carbon. The bars represent the concentrations on settling sediment. The solid points represent the concentrations measured in suspended sediment. The dates on the x-axis are the first day of the sediment trap collection periods. The discrete samples of suspended sediment were collected on Jan 29-Feb 1, and on Mar 29-31.

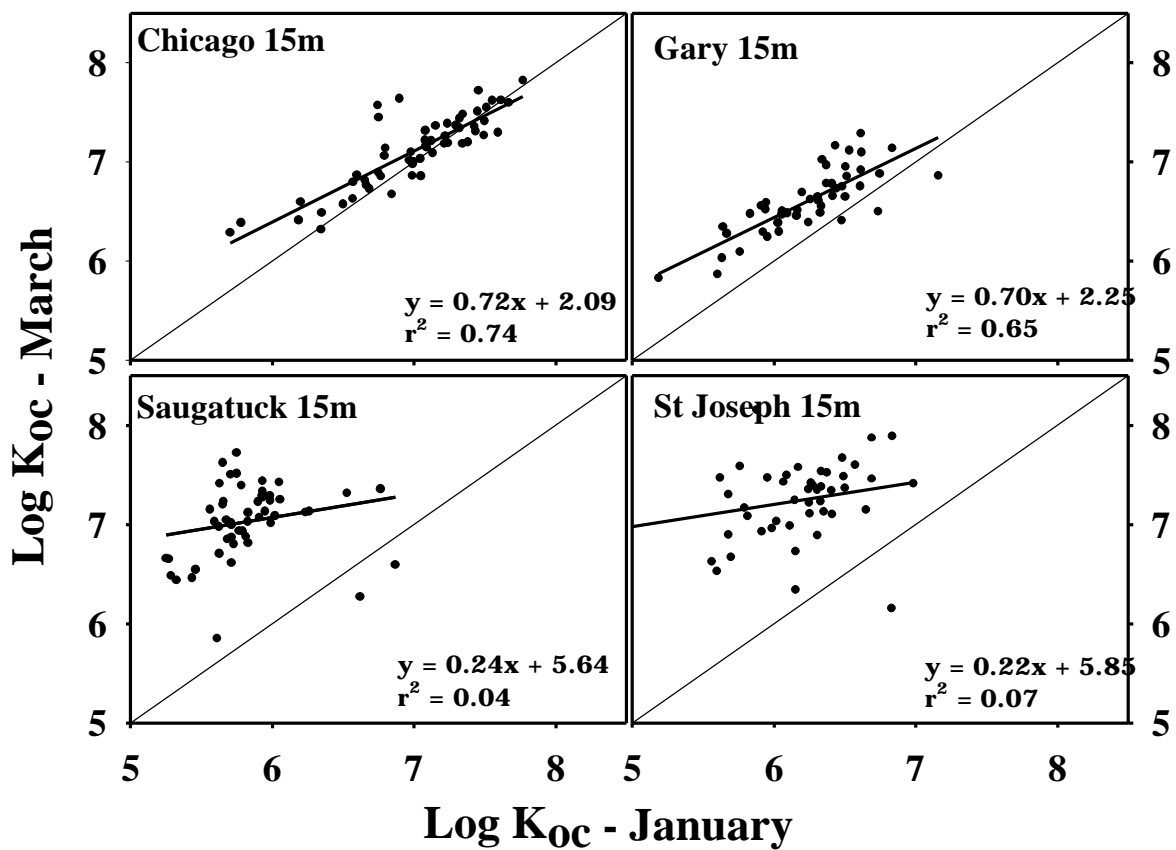


Figure 5. Log K_{oc} – March vs. log K_{oc} – January plots and linear regression statistics for PCBs for locations that were sampled before and after the large resuspension event in 1998. The lighter diagonal line represents a slope of unity.

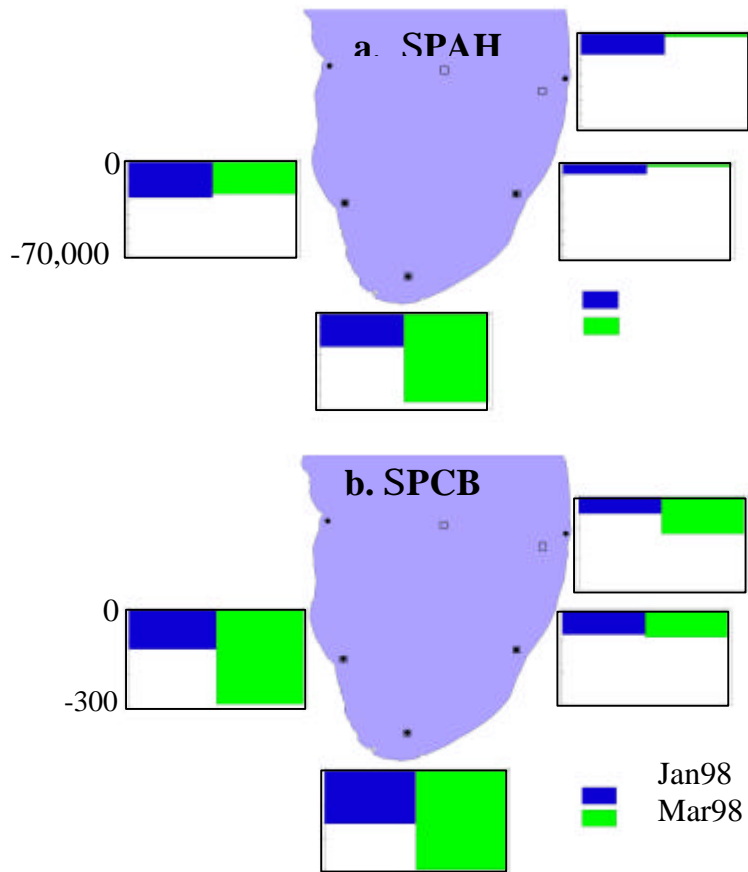


Figure 6. Potential gas exchange fluxes of Σ PAHs (plot a.) and Σ PCB (plot b.). Only fluxes calculated for air and water pair collected at the same site in January and March are illustrated. The black bars are the net fluxes calculated from the January samples, the gray bars are the net fluxes calculated from the March samples.