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# Soot Deposition in the Great Lakes: Implications for Semi-Volatile Hydrophobic Organic Pollutant Deposition

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Air deposition is a dominant transport mechanism for many hydrophobic organic pollutants (HOCs) to the Great Lakes. Our previous research has shown that soot exhibits large surface areas with high organic carbon contents suggesting the potential for strong HOC partitioning. As yet, however, clear data showing the link between HOCs such as PAHs to the deposition of soot into the Lakes (a proposed transport mechanism) is primarily inferential. We measured soot carbon (SC) and organic carbon (OC) in sediments collected from each of the Laurentian Great Lakes. OC and SC levels collected from locations near urban areas were higher than in sediments collected from distant locations. By far, Lake Superior had the lowest current SC flux of any lake, and Lakes Michigan and Erie had the highest. SC flux for all lakes had the following order: Superior < Huron < Ontario < Michigan < Erie, ranging 0.02–0.89 mg (m<sup>2</sup> yr)<sup>−1</sup>. Differences in lake size resulted in a different order for total SC loading by lake: Superior < Ontario < Huron < Erie < Michigan, ranging 2.3–420 × 10<sup>3</sup> t yr<sup>−1</sup>. SC and PAH accumulation rates reported previously for Lake Michigan sediment were highly correlated; with a SC to PAH mass ratio of 10<sup>4</sup> (0.01%). The importance of soot as a potential sorbent for various classes of airborne HOCs was examined using a simple octanol–air partitioning model together with our previous characterization of soot particles. The results predict that both PAHs and PBDEs should have strong partitioning to soot and suggest the need to further investigate soot as a vector for PBDE transport.

## Introduction

Forms of partially combusted and/or pyrolyzed carbon (which have been variously referred to as charcoal, elemental carbon, black carbon, and soot) are found in air, soils, sediments, and water. There are a variety of environmental sources of black carbon; predominately through combustion of plants, woods, and fossil fuels and as a byproduct of industrial processes such as coke production. Factors affecting the chemical and physical properties of soot carbon (SC) in the environment include the composition of the

materials being combusted, the method of combustion (oxygen-to-carbon ratio), and the transport mechanism from the site of their formation. The determination of the source of SC and the distance traveled have been investigated in detail using three characteristics: their surface morphologies, size distributions, and chemical structure (1, 2). Due to their porous nature (high surface area), high organic carbon contents, and adsorption characteristics, it has been hypothesized that SC particles in the atmosphere have the ability to “scavenge” gas-phase hydrophobic organic contaminants (HOCs) from the air and thus present a potential major vector for transport in the atmosphere (1).

The Laurentian Great Lakes represent the largest source of fresh surface water in the world, and growing urbanization and industrialization has led to the development of large cities along or near the shores. Because of the large surface area-to-volume ratio, the lakes are susceptible to volatile HOC loading from surrounding cities through atmospheric deposition.

In this study, we have measured the concentration of SC, organic matter, and non-soot organic carbon (NSOC) in all of the Laurentian Great Lakes sediments. We investigated correlations between literature-reported octanol–air partitioning coefficients (*K*<sub>OA</sub>) and octanol–water partitioning coefficients (*K*<sub>OW</sub>) for various HOCs including polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and organochlorine pesticides (OCPs) along with their ability to partition to the organic fraction on aerosols such as soot. Results are compared to a previous report of PAH levels at the same sampling sites for correlations between soot and PAH deposition.

## Experimental Methods

**Sediment Collection.** Sediment sampling on all five of the Laurentian Great Lakes was conducted from May through August 2002 using a box corer deployed from the U.S. Environmental Protection Agency R/V *Lake Guardian*. Sampling sites in the Great Lakes (14 total, Figure 1) were chosen based on a review of literature on the geophysics, geography, and limnology of the lakes to be sampled (3–10). Sampling sites were chosen at locations in deep basins dominated by atmospheric deposition with relatively high sedimentation rates, where the effects of local point sources could be minimized. Depositional zones in each lake were targeted. A 0.084 m<sup>3</sup> box corer was deployed from the deck and used to collect a bulk sediment sample maintaining an intact sediment–water interface. The box core was then subcored on deck with precleaned 7.0 cm i.d. acrylic tubes. Five sediment cores were sectioned and composited into precleaned amber glass jars (I-Chem, New Castle, DE) with Teflon-lined caps in order to obtain enough sediment for analysis. The cores were extruded using an aluminum foil-covered push plunger and sectioned on the ship at 1.0-cm intervals for the first 10 cm and then in 5-cm increments for the remainder of the core. The sectioning intervals were targeted to the sediment zones most likely to provide the needed recent time scale of sediment deposition because the important metric in sectioning was not absolute *depth* but *time*. All sectioning gear (and the cores) was thoroughly cleaned before and after each slice using three solvent washes in the following order: hexane, acetone, and deionized water. The extruded and sectioned samples were then frozen onboard the ship (−20 °C) until transport to the laboratory where they were kept frozen (−20 °C) until analysis.

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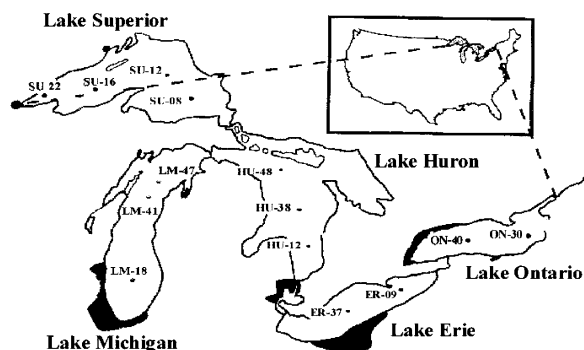


FIGURE 1. Sediment sampling locations in the Great Lakes. Shaded areas represent large metropolitan and industrial areas. Figure adapted from ref 19.

**Sediment Characterization.** Sediment samples were volumetrically sampled from thoroughly mixed composited sample sections using an open-ended 1 or 3 cm<sup>3</sup> syringe (ca. 1.2–3.5 g) as in Rockne et al. (11). Each sample was weighed on tared, clean single-use aluminum trays and dried (105 °C, 48 h). Wet bulk density was determined as a ratio of the wet weight to the sample volume. After being dried, samples were reweighed, and the dry sediment mass, percent moisture, porosity, and percent solids were calculated as in Shor et al. (12).

Following the dry weight measurement, the samples were divided into fractions for organic carbon (OC) and soot carbon (SC) measurements. OC (including both NSOC and SC) content was determined for desiccated (105 °C, 48 h) samples on a Carlo Erba elemental analyzer (Flash EA1112; ThermoQuest/CE Elantech, Lakewood, NJ). Pulverized samples (10–20 mg) were placed in preweighed tin combustion boats supplied by the manufacturer (CE Elantech, Lakewood, NJ), sealed, reweighed, and stored in a desiccator until analysis. Elemental analysis was conducted using automated combustion/reduction (900 °C) followed by molecular sieve gas chromatography (60 °C) and a thermal conductivity detection system. Peak areas for carbon were compared to peak areas using a known standard (desiccated acetanilide) and integrated using the instrument software (EAGER, version 5.0). Standard curves were performed with each run to prevent run-to-run inaccuracies resulting from peak area drift. Only peak areas in unknown samples within the range of standards were used for analysis; samples with peak areas outside the range were re-analyzed.

Realizing that all measurements of soot are necessarily operationally defined, we balanced method ease-of-use with replication and verification steps to ensure accuracy. The pulverized sediment samples for SC analysis were placed in a muffle furnace and combusted in air (375 °C, 24 h) to remove non-soot organic matter through low-temperature oxidation using a modification of the method of Gustafsson et al. (13) as described by Rockne et al. (1). Other studies have generally supported this method of SC determination through measurements of soil matrixes with known compositions (14, 15), although concern has been voiced about potential “condensation” reactions (what we term “pyrolysis”) of non-soot organic molecules during the oxidation step (16). We have previously shown through high-definition thermal gravimetric analysis that this method closely approximates SC using real soot particles (1). In this study, we controlled for the possibility of pyrolysis without having to use the extended HCl and HF extraction followed by the trifluoroacetic acid pretreatment procedure of Gélinas et al. (16) by pulverizing the sediment samples in thin layers (<1 mm) in the combustion boat and placing the boats in a cold muffle furnace to allow a heat gradient to 375 °C to ensure complete oxidation of organic matter without pyrolysis. After removal

of labile fractions in the sample, SC was determined using the same method as described for OC determination. To control for the presence of inorganic carbon in sediment carbonates, samples were kept in an acid fumer and re-analyzed for OC. No significant differences were observed with and without fuming in all lakes studied, thus confirming that no carbonates were present (17).

**Sedimentation Rates and Loading.** The in situ sediment density was calculated from the measured porosity and specific gravity for each core section. Because the sedimentation rates make no correction for sediment compaction, the measured in situ density was used for each core section to compensate. SC and OC accumulations were calculated from the measured sediment parameters using sedimentation rates found in the recent literature for our sample sites or those in close proximity. Table 1 shows the reported sedimentation rates, the calculated sedimentation rates, and the exact locations of sampling used in this study. The calculated sedimentation rates were set equal to reported literature rates if exact site data were available or averaged from reported literature rates for multiple nearby sites if the exact site station data were not available. Sedimentation flux was calculated for the calculated sedimentation rate (g cm<sup>-2</sup> yr<sup>-1</sup>) multiplied by the parameter of interest (OC and SC, in mg g<sup>-1</sup>). Sedimentation rates used in this study were given a range of one standard deviation based on the reported literature values and varied significantly across lakes but generally not within lakes. The maximum relative standard deviation (RSD) with this method was always <36%. Dates for the core layers were estimated based on this calculated sedimentation rate. Flux and loading calculations were corrected for the effects of in-lake sediment transport on sedimentation rates (focusing) using radiodating techniques where these data were available from the literature (see Table 1).

Raw data from a study by Simcik et al. (6) was provided by Matt Simcik at the University of Minnesota for comparisons of soot accumulation data to PAH accumulation data. SC accumulation data in our study were interpolated to match the corresponding dates for the PAH data. Comparisons were made between the accumulation data in both studies under focus-corrected conditions for total PAHs (28 total), LMW PAHs (14 total low molecular weight PAHs and alkylated PAHs with <4 rings), and HMW PAHs (14 total high molecular weight PAHs with >3 rings).

**Quality Control.** Duplicate sediment samples and acetanilide were run as unknowns at least one out of every 10 samples and were used to determine accuracy and precision according to Standard Methods (18). Overall relative precision for analytes is expressed as the square root of the mean of all RSD values squared, where RSD was equal to the absolute difference between duplicates divided by their average for all lakes and was 4.69 ± 0.67% for OC and 6.15 ± 0.85% for SC. Overall accuracy for analytes is expressed as the square root of the mean of the bias squared (keeping the sign) and was -4.27 ± 0.27% for OC, where the relative bias (*B*) among analytes was defined as the difference between the measured and true values of check standards expressed as a percent (retaining the sign). For SC, the bias was set equal to the bias determined for OC during SC analytical runs due to the lack of an authentic SC standard. The overall uncertainty (95% confidence level, CL) combines these two values (18):

$U_{95\%} = \sqrt{2(RSD)^2 + B^2}$ .  $U_{95\%}$  was relatively low in this study: 7.89% for OC and 9.69% for SC.

## Results and Discussion

**Soot and Organic Carbon in Great Lakes Sediments.** SC and OC concentration as a function of time showed great variability between and within the Great Lakes (Figure 2A–E).

TABLE 1. Locations, Sediment Accumulation Rates, Mixing Depths, and Focusing Factors of Sediment Cores in This Study<sup>a</sup>

site	sedimentation rate (g cm <sup>2</sup> yr <sup>-1</sup> )	mixing depth (cm)	focusing factor	latitude	longitude	date	source
Lake Superior							
reported literature values							
NOAA3	0.009 <sup>b</sup>	<1	1.14	47°20'	89°015'	1991	19
LS5	0.011	nr	1.52	na	na	1997	5
LS12	0.016	nr	1.7	na	na	1997	5
LS17	0.006	nr	1	na	na	1997	5
used for sites in this study							
SU-08	0.011			47°36.3'	86°48.9'		
SU-12	0.016			47°51.4'	88°2.5'		
SU-22	0.011 ± 0.004			46°48.1'	91°44.9'		
SU-16	0.006			47°37.3'	89°27.8'		
Lake Michigan							
reported literature values							
LM-68k	0.028	<1	1.27	45°06'	86°23'	1991	19
LM-47s	0.035, 0.016 <sup>c</sup>	<1	1.5	44°42'	86°41'	1991	19
LM-18	0.039, 0.018 <sup>d</sup>	4	2.43	42°45'	87°00'	1991	19
used for sites in this study							
LM-47	0.028			45°10.7'	87°22.5'		
LM-41	0.035, 0.016 <sup>c</sup>			44°44.2'	86°43.3'		
LM-18	0.039, 0.018 <sup>d</sup>			42°43.9'	86°00'		
Lake Huron							
reported literature values							
HU-1	0.02 <sup>e</sup>	nr	2.8	43°30'	81°55'	1975	8
HU-2	0.02 <sup>e</sup>	nr	2.8	43°30'	81°55'	1975	8
HU-3	0.01 <sup>e</sup>	nr	6.4	43°59'	81°59'	1981	8
HU-4	0.03 <sup>e</sup>	nr	5.9	43°59'	82°10'	1981	8
used for sites in this study							
HU-12	0.02 ± 0.007			43°53.5'	82°3.8'		
IU-38	0.02 ± 0.008			44°44.5'	82°3.4'		
IU-48	0.03 ± 0.01			45°16.7'	82°27.2'		
Lake Ontario							
reported literature values							
LO-40	0.064, 0.030 <sup>f</sup>	1.8	1.71	43°35'	78°00'	1991	19
LO-E30	0.067	4.7	2.04	43°32'	76°54'	1991	19
used for sites in this study							
ON-40	0.064, 0.030 <sup>f</sup>			43°35'	78°00'		
ON-30	0.067			43°32'	76°54'		
Lake Erie							
reported literature values							
C-9	0.095	nr	nr	42°11.3'	81°39.0'	1988	9
C-10	0.14	nr	nr	42°5.0'	81°20.8'	1988	9
E-2	0.16	nr	nr	42°31.0'	79°38.0'	1988	9
used for sites in this study							
ER-37	0.12 ± 0.032			42°6.6'	81°34.5'		
ER-9	0.16			42°32.3'	79°36.9'		

<sup>a</sup> Single values with no SEM were used for sites where literature values for our sample sites are known. Mean and SEM values are used for sites where multiple literature values were used to compute the corresponding deposition rate for our sample sites. nr, not reported in the literature. na, not applicable. Values used in this study were corrected for focusing. <sup>b</sup> Sedimentation rate below 6 cm. <sup>c</sup> Sedimentation rate below 11 cm. <sup>d</sup> Sedimentation rate below 12 cm. <sup>e</sup> Sedimentation rate below 13 cm. <sup>f</sup> Rates are converted to g cm<sup>2</sup> yr<sup>-1</sup> from data in cm yr<sup>-1</sup>.

**Lake Superior.** SC concentrations varied by location in Lake Superior. For example, SC in the core SU-08 was up to four times higher (8.5 mg g<sup>-1</sup>) than in the other three sample sites (Figure 2A). The depositional zone represented by SU-08 is in the deepest part of the central basin and may be within the downwind range of influence of the Chicago, IL, metropolitan area (Figure 1). Work carried out by Hites et al. for the Integrated Atmospheric Deposition Network (IADN) PCB monitoring at Eagle Harbor, Lake Superior, indicates that the impact from the Chicago urban area can be detected here (personal communication). SC at this location peaked near 1950 and has decreased significantly (95% CL) in the last 50 yr. This peak in SC is consistent with literature reports of atmospheric input peaks for HOCs such as dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in Lake Superior (19). PCDD/Fs, like soot, have been shown to originate as byproducts of incineration processes (20).

The relative trend in SC at location SU-22 follows the same trend for SU-08 such that there are two peaks following

the onset of significantly increased SC deposition around 1800 that reached a maximum of 2.0 mg g<sup>-1</sup>, followed by a steady decrease in concentration around 1950. In contrast to SU-08 and SU-22 (SU-22 is closest to Duluth, MN, and Thunder Bay, ON, Canada), the other two sites did not have significant decreases in SC deposition in the last 50–100 yr. These sites also had by far the lowest SC levels in this study. A slight increase in SC in the last 100 yr can be seen in locations SU-12 and SU-16, but the relative concentration of 1 mg g<sup>-1</sup> was not significantly different throughout the core depth at least back to 1750.

OC profiles for all locations with the exception of SU-22 follow a similar downcore decreasing trend from surficial concentrations of 40 mg g<sup>-1</sup> and then steadily decreasing to a relatively constant level of 20 mg g<sup>-1</sup>. Though the mass sedimentation rate at location SU-08 (0.011 g cm<sup>-2</sup> yr<sup>-1</sup>) was approximately twice that of location SU-16 (0.006 g cm<sup>-2</sup> yr<sup>-1</sup>), OC concentrations were not significantly different (95% CL) at the sediment–water interface.



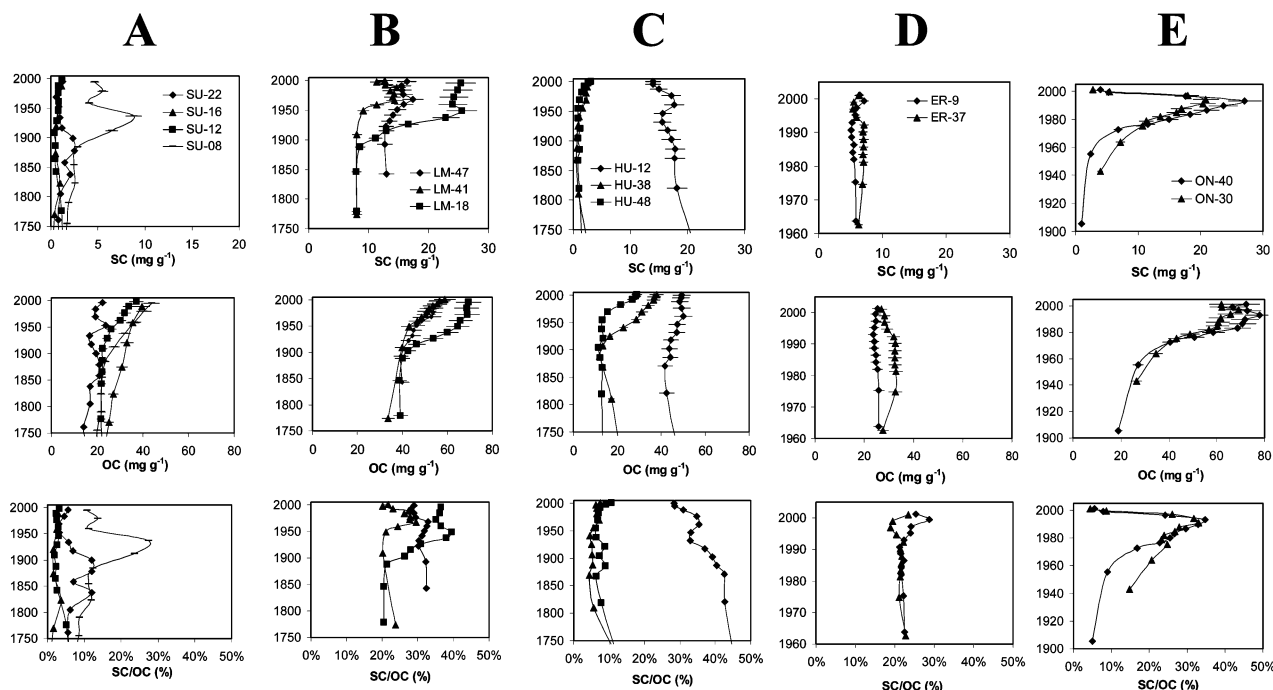


FIGURE 2. SC, OC, and SC/OC ratio in Lake (A) Superior, (B) Michigan, (C) Huron, (D) Erie, and (E) Ontario sediments. Error bars represent total uncertainty (95% CL). Locations are given in Figure 1. Note different time scale for Lakes Erie and Ontario.

The ratio of SC to OC shows that SC constituted a larger fraction of the OC (28%) for site SU-08. The high percentage of OC as soot was not seen at cores SU-12 and SU-16 (typically 2% of OC). SU-22 was intermediate, with 10% of the OC comprised of SC. Peaks for SC fractions in SU-08 and SU-22 were seen at approximately the same time period (1900s) and follow an overall downcore decrease in SC fractions of OC. Previous reports that measured toxaphene in air (5) have shown that the potential air mass trajectory would pass over the Chicago metropolitan area and influence atmospheric deposition to site SU-08 in Lake Superior, in support of the findings here.

**Lake Michigan.** In all three Lake Michigan sample sites, the SC profile was very similar in shape, and the SC concentration was not significantly (95% CL) different for the past 50 yr, after peaking near 1950 (Figure 2B). Prior to 1950, SC decreased significantly (95% CL) to approximately 1900 and then was relatively constant to the bottom of the core. These trends are consistent with literature reports of PAH deposition trends at the same locations (6). The constant trend and variance in magnitude among the locations may be explained through sediment mixing and focusing. Sediment mixing depths and focusing factors at these locations are reported in Table 1. For site LM-18, the top three or four data points correspond to the reported mixing depth (4 cm) for this site, as far back as 1950. Site LM-18 had the highest surface SC concentration ( $25 \text{ mg g}^{-1}$ ) and is the closest site to the Chicago metropolitan area. The two northern basin cores (LM-47 and LM-41) had fairly similar surface concentrations of SC to each other; approximately half that of the southern basin site.

SC and OC in Lake Michigan were much higher (three times) than Lake Superior. At the sediment–water interface, OC (LM-18) was  $70 \text{ mg g}^{-1}$  down to core depths corresponding to 1950. At deeper core depths, the OC decreased to approximately  $40 \text{ mg g}^{-1}$ . This decrease was likely the result of degradation of the OC downcore. This diagenetic alteration proceeded with a relatively linear temporal decrease in concentration to the mid-1800s.

**Lake Huron.** Because literature values of sedimentation rates at the specific Lake Huron sample sites in our study

were unavailable, the mass sedimentation rate used for the three locations in Lake Huron was taken as an average of several reported rates in close proximity to our sample sites (Table 1). SC concentrations in cores collected from the northern (HU-48) and central (HU-38) basins of Lake Huron were not significantly different (95% CL),  $2 \text{ mg g}^{-1}$  at the surface, and were similar in magnitude to samples collected from Lake Superior (Figure 2C). Site HU-12, which is located in the southern basin, had much higher SC ( $14 \text{ mg g}^{-1}$ ). Like the southern basin site in Lake Michigan (LM-18), HU-12 is the closest site in Lake Huron to a major metropolitan area (Detroit, MI), and the elevated SC levels may be a signature of releases from the area. SC to OC ratios in this site were also comparable to LM-18 and show that SC comprised more than 30% of the OC at the sediment–water interface.

The Lake Huron sediments revealed diagenetic alteration of OC as a linear decrease in concentrations of OC in the past 20 yr. OC concentrations at the sediment–water interface ( $35\text{--}50 \text{ mg g}^{-1}$ ) were similar to Lake Superior samples, although the rate of diagenesis appears to be more rapid. The SC to OC ratio was high (SC comprised up to 40% of the OC) at site HU-12 (nearest Detroit, MI) and was similar to site LM-18 (nearest Chicago, IL), reflecting the influence of the nearby upwind metropolitan areas.

**Lake Erie.** Sampling site ER-37 represents the zone of deposition in the central Erie basin, and site ER-9 represents the corresponding zone in the eastern basin. SC concentrations for both cores at the sediment–water interface were  $6\text{--}7 \text{ mg g}^{-1}$ , and SC accounted for 25% of the total organic carbon fraction at the surface (Figure 2D). By comparison, Kralovec et al. (7) reported soot particle mass of  $0.5\text{--}1.0 \text{ mg g}^{-1}$  for both wood and oil soot and  $5\text{--}6 \text{ mg g}^{-1}$  for coal soot, for a combined range of  $6\text{--}8 \text{ mg g}^{-1}$ . Assuming that SC accounts for 40–90% of soot mass (1), this would be very similar to the values that we found at these two sites in the same time frame. The Lake Erie sediment cores stood in marked contrast to the others in this study. For both SC and OC, no significant trend was seen to the bottom of the core (ca. 1960). This may suggest mixing throughout the core. Mixing can occur not only from convective currents and other sediment bed movement processes but also through bio-

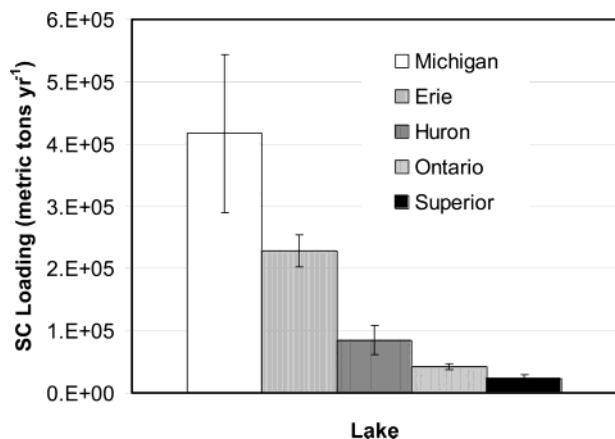


FIGURE 3. Total SC loading to each Great Lake. Error bars represent the SEM of loading from all lake segments within each lake. Lake area for loading from ref 32.

turbation. During sampling, there was a notable abundance of *Dreissena polymorpha* at the sediment–water interface and continued through approximately the top 10 cm of the core. Given the high reported mass sedimentation rates in these locations (up to 10 times that of the Lake Superior), this mixing coupled with the short depositional history did not allow resolution of long-term trends.

**Lake Ontario.** Lake Ontario was sampled in the central (ON-40) and the eastern basin (ON-30), the latter representing the deepest part of the lake. Both sites exhibited remarkably similar trends in SC and OC (Figure 2E). SC in both cores sharply peaked in the last 20 yr with a maximum concentration of 20–25 mg g<sup>-1</sup>. There was a relatively linear temporal decrease in both analytes in the preceding 50 yr where SC concentrations in both sediment cores reached surface values of 2–3 mg g<sup>-1</sup>. The presence of large peaks in SC during this time may suggest that bulk sediment mixing did not occur at these sites to the extent seen in Lakes Michigan and Erie.

OC followed the same trend as SC, with peak values around 1990 at 70 mg g<sup>-1</sup>. Lake Ontario together with LM-18 had the highest OC concentrations of the Great Lakes sample sites with SC making up more than 35% of the total organic carbon. The high percentage of SC in the OC again reflects the proximity of large metropolitan areas (Hamilton and Toronto, ON, Canada) to these sample sites.

**Total SC Loading Was Dependent on Proximity to Urban Areas.** In a comparison of whole-lake SC loading (Figure 3), the highest loadings were seen in lakes that were in close proximity to large urban areas: Chicago (Lake Michigan), Toronto and Hamilton (Lake Ontario), and Detroit/Cleveland (Lake Erie). Of the Great Lakes, Lake Superior received by far the smallest SC loading,  $12 \pm 3.3 \times 10^3$  t yr<sup>-1</sup>; this despite being the largest lake by area. The highest calculated SC mass loading ( $4.2 \pm 1.3 \times 10^5$  t yr<sup>-1</sup>) was observed in Lake Michigan; nearly 20 times that of Lake Superior. This large difference clearly resulted from the proximity to important contaminant sources (relative to prevailing atmospheric transport pathways). Lake Superior is not in close proximity to major cities as is Lake Michigan, resulting in much lower soot loading to Lake Superior. Griffin and Goldberg (21) proposed that amounts of SC found in the sedimentary record reflect the intensity of combustion of fossil fuels during industrial activities and also mark the onset of improved controls of emissions from the stacks of power plants and other industrial facilities. Our results agree with this hypothesis.

An analysis of deposition by lake segment within Lakes Michigan and Huron demonstrates the importance of spatial proximity to urban areas. Both lakes were sampled in the

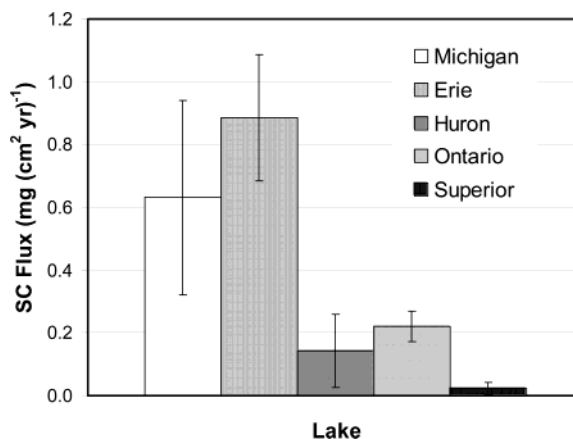


FIGURE 4. SC flux to Great Lakes surficial sediments. Rate represents current inputs to each lake. Error bars represent the SEM for sites within each lake.

major depositional basins at three locations in north to south transects (Figure 1). In both lakes, the highest soot loading occurred at the lake segment closest to urban areas; Chicago (site LM-18 in Lake Michigan) and Detroit (site HU-12 in Lake Huron). Site HU-12 is located in the southern basin of Lake Huron, and the lake segment encompassing HU-12 comprised 65% of the SC loading. Similarly, the LM-18 lake segment comprised more than half (52%) of the SC loading to Lake Michigan. In contrast, large significant differences did not exist between sampling locations within the other lakes. This was likely due to their smaller basin size and diversity of SC sources (particularly for Lake Erie) relative to prevailing atmospheric transport pathways. The difference in pre-1900 SC data between Lake Ontario and Lake Michigan and site HU-12 in Lake Huron likely reflects the differences in both industrial activity (Detroit and Chicago had more extensive industrial activity prior to 1900) and, potentially, natural sources of SC (such as forest fires) in the areas contributing to airborne deposition to the corresponding lakes.

**Lake Erie Had the Highest SC Deposition Flux.** To determine current SC flux, sediment–water interface SC levels in each depositional zone were used to calculate an overall SC flux for each lake using the mean for all lake segments within each lake (Figure 4). The results show a change in ranking from highest to lowest in the SC flux as compared to whole lake SC loading. Lake Erie had the highest current deposition rate of  $0.89 \pm 0.2$  mg cm<sup>2</sup> yr<sup>-1</sup> among the Great Lakes. Though the flux of soot was higher for Lake Erie than Lake Michigan (but not significant at 95% CL), the overall SC loading was higher in Lake Michigan because of the larger surface area. The larger relative standard deviation (Figure 4) seen in Lakes Michigan and Huron are attributed to the greater differences in SC flux between sites LM-18 and HU-12 and the other sites as discussed in the previous section. The SC depositional flux for Lake Superior (0.023 mg cm<sup>2</sup> yr<sup>-1</sup>) was significantly lower than all other lakes (up to 30 times lower).

**Implications of Soot Deposition on the Transport of HOCs to the Great Lakes.** The extent of gas–aerosol partitioning of HOCs in the atmosphere greatly affects wet and dry deposition rates and atmospheric residence time (2). The equilibrium octanol–air partition coefficient ( $K_{OA}$ ) is a useful descriptor of the partitioning of HOCs between atmosphere and organic phases found on aerosols (22). At equilibrium, the  $K_{OA}$  value for specific compounds can be used to predict the concentration in gas and aerosol phases provided that the nature of the particulate matter (i.e., fraction organic carbon) is known.

TABLE 2.  $K_{OA}$  and  $K_{OW}$  for Different Classes of Hydrophobic Organic Contaminants (25 °C)

HOC	$\log K_{OA}^a$	$\log K_{OW}^b$	HOC	$\log K_{OA}^a$	$\log K_{OW}^b$
PBDEs <sup>c</sup>					
17	9.30	5.74	85	11.66	7.37
28	9.50	5.94	153	11.82	7.37
47	10.53	6.81	154	11.92	7.37
100	11.13	7.24	183	11.96	7.37
99	11.31	7.32			
PCBs <sup>c</sup>					
49	7.92	6.10	138	9.06	6.70
101	8.24	6.40	170	9.19	7.08
66	8.29	6.31	128	9.32	7.00
153	9.03	6.90			
PAHs					
fluorene	6.68	4.18	benz[a]anthracene	9.54	5.91
phenanthrene	7.45	4.57	chrysene	10.44	5.86
anthracene	7.34	4.54	benzo[a]pyrene	10.77	6.40
fluoranthrene	8.60	5.22	benzo[k]fluoranthene	11.19	6.20
pyrene	8.61	5.18			
OCPs					
$\alpha$ -hexachlorohexane	7.26	3.81	<i>p,p'</i> -DDE	9.45	6.96
$\gamma$ -hexachlorohexane	8.08	3.80	<i>p,p'</i> -DDD	9.81	6.22
hexachlorobenzene	8.54	6.00	<i>p,p'</i> -DDT	9.93	6.91

<sup>a</sup>  $K_{OA}$  values for PBDEs are from ref 22; values for PCBs, PAHs, and OCPs are from ref 23. <sup>b</sup>  $K_{OW}$  values for PBDEs are from ref 24; values for PCBs and PAHs are from ref 25; and values for OCPs are from ref 23. <sup>c</sup> Selected congener numbers for PBDEs are from ref 22, and PCBs are from ref 23.

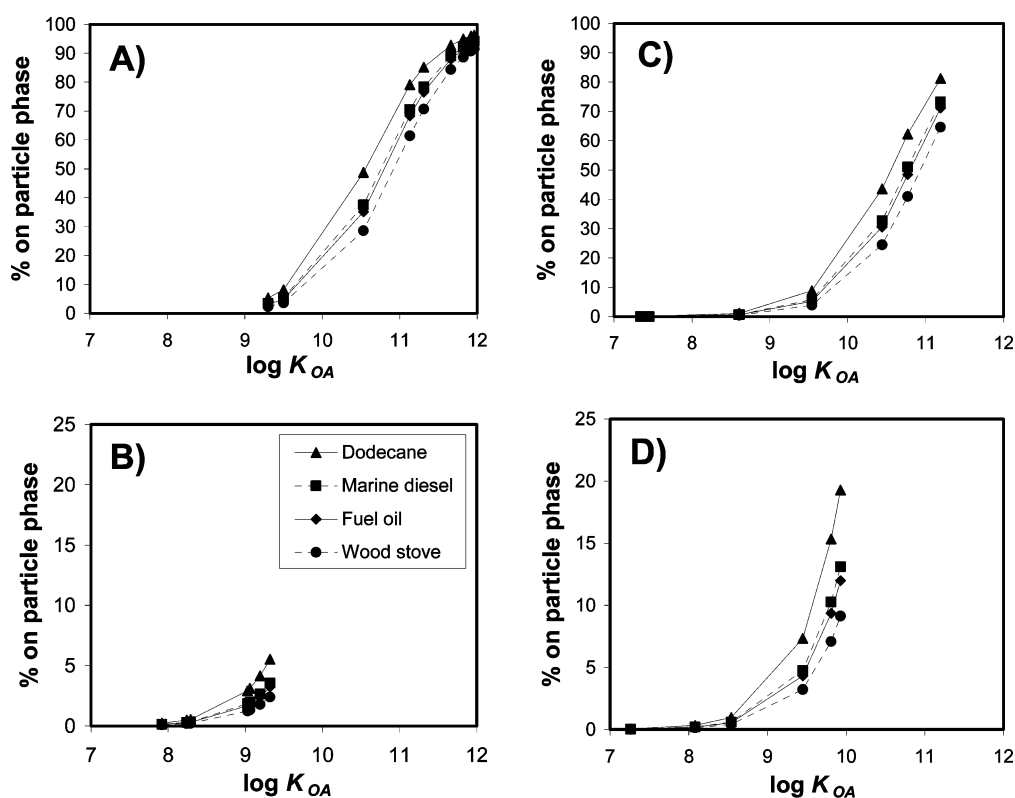


FIGURE 5. Predicted  $\phi$  values of selected (A) PBDEs, (B) PCBs, (C) PAHs, and (D) OCPs for different soot types. Calculated using parameters in Table 2, assuming that all carbon was free to exchange. Note that all figures describe the same equation with different HOC classes and y axis scales for panels B and D for clarity.

**Predicted Partitioning from Gas Phase to Soot Was Highest for PAHs and PBDEs.** Reported  $K_{OA}$  values for PBDEs, PCBs, PAHs, and OCPs were used to calculate the particle-bound mass fraction ( $\phi$ ) using eqs 4 and 5 in Harner and Shoeib (22) as developed by Finizio et al. (23) for each HOC (22–25) using four different types of soot with variable organic carbon fractions from our previous work (1). Four different types of soot were used for this analysis: dodecane ( $f_{oc} = 0.91 \pm 0.059$ ), marine diesel ( $f_{oc} = 0.58 \pm 0.037$ ), fuel oil

( $f_{oc} = 0.52 \pm 0.032$ ), and wood stove ( $f_{oc} = 0.38 \pm 0.025$ ). HOCs used in the analysis comprise a large range of volatility ( $K_{OA}$ ) and hydrophobicity ( $K_{OW}$ ), including Great Lakes relevant tetra- through hepta-chlorinated PBDEs and PCBs, three- to five-ring PAHs, and various OCPs (Table 2). The masspercentage on the particle phase ( $\phi$ ) revealed high variability between the HOC classes (Figure 5A–D). The model predicted an increase in  $\phi$  as the affinity for octanol ( $K_{OA}$ ) increases for all classes of compounds, as expected

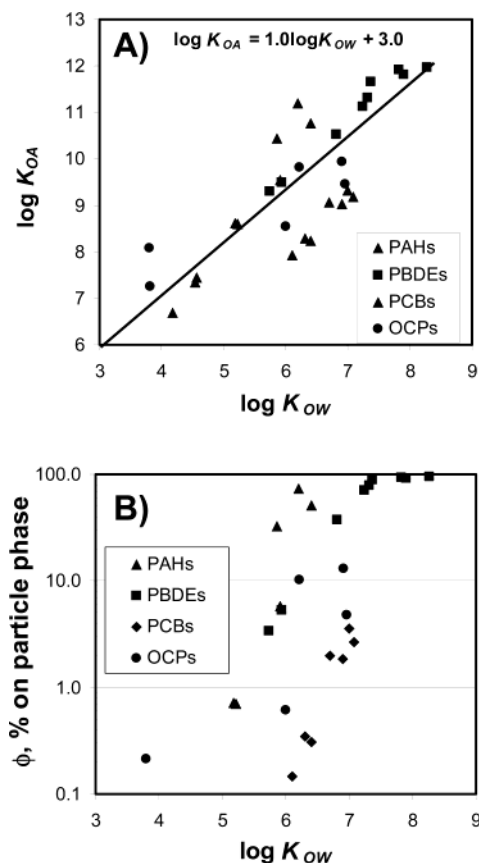


FIGURE 6. (A) Correlation of  $\log K_{OA}$  with  $\log K_{OW}$  values for HOCs listed in Table 2. The standard error of slope is  $1.0 \pm 0.14$ , and the intercept is  $3.0 \pm 0.88$ . (B) Fraction of total HOCs on marine diesel soot as a function of  $K_{OW}$ . Note log scale for  $\phi$ .

based on the model formulation. In addition, the increase in  $f_{oc}$  of the soot particle resulted in an increase in  $\phi$ .

The largest predicted percentage on the particle phase was seen for the PBDEs (Figure 5A), where congeners with  $\log K_{OA}$  values  $> 11.0$  yielded more than 60% on the particle phase for all types of soot. The PBDE congeners of known environmental significance (BDE 47, 99, 100, and 183) all have  $\log K_{OA}$  values from 11 to 12 (Table 2). A similar trend to that of PBDEs was predicted for PAHs (Figure 5C). PAHs with five rings and relatively higher  $\log K_{OA}$  values ( $> 10.5$ ) were predicted to have more than 40% on the particle phase. Again, soot particles with a larger organic carbon content were predicted to have a larger  $\phi$  for all  $K_{OA}$  values.  $\log K_{OA}$  values in the range of 10–11 had the greatest predicted dependence on  $f_{oc}$ . At  $\log K_{OA}$  values less than 10 and greater than 11.5, large differences in  $f_{oc}$  were not predicted to result in large differences in  $\phi$ .

In marked contrast to PBDEs and PAHs, PCBs and OCPs were predicted to have less particle-phase partitioning (Figure 5B,D). For example, the PCB with the largest  $K_{OA}$  value reported here (PCB-128) yielded only 2–6% on the particle phase. The OCP with the highest  $K_{OA}$  (dichlorodiphenyl trichloroethane, DDT), was predicted to partition only 10–20% on the particle phase. These predictions suggest strongly that PAHs and PBDEs are much more likely to partition onto soot at equilibrium whereas PCBs and OCPs are not. Interestingly, this does not seem to be the case in the aqueous phase (26).

The contrast in predicted aerosol partitioning between PCBs/OCPs and PBDEs/PAHs is not immediately predictable based upon typical thermodynamic correlations with hydrophobicity (Figure 6A). Although there is a significant linear

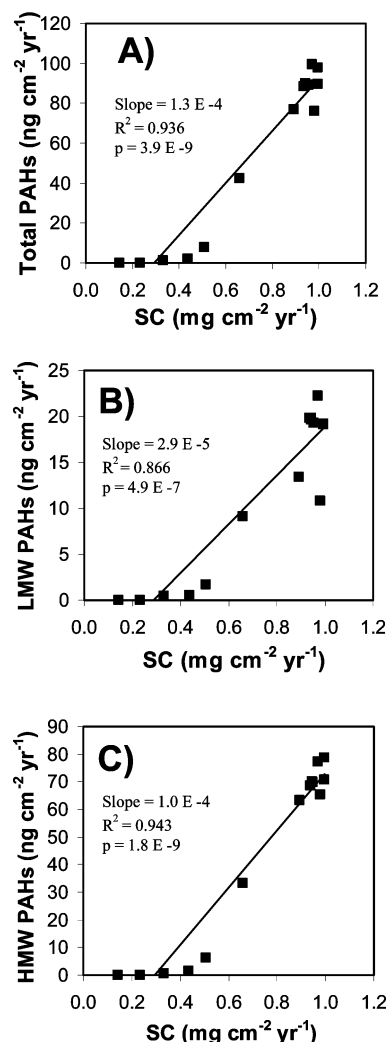


FIGURE 7. Correlation between accumulation of (A) total PAHs, (B) PAHs with  $< 4$  rings, or (C) PAHs with  $> 3$  rings and soot accumulation in sediments at site LM-18 in Lake Michigan. PAH data (28 total, alkylated, and nonalkylated) from ref 6. Shown are slope, Pearson coefficient, and significance. Note different scale of y axes.

correlation between  $\log K_{OA}$  and  $\log K_{OW}$  ( $\log K_{OA} = 1.0 \log K_{OW} + 3.0$ ,  $p = 0.0019$ ,  $R^2 = 0.66$ ), there is not a corresponding clear correlation between  $\phi$  and  $\log K_{OW}$  for all HOCs (Figure 6B). This is due to the nonlinear relationship between  $\phi$  and  $\log K_{OA}$ . For example, within the  $\log K_{OW}$  range of 6–7,  $\phi$  values range by 3 orders of magnitude. There are, however, prediction clusters on a plot of  $\phi$  versus  $\log K_{OW}$  (Figure 6B). PBDEs with  $\log K_{OW}$  ranging from 7 to 8.5 (including BDE 47, 99, 100, and 183) have a much higher predicted affinity ( $> 2$  orders of magnitude) for the particle phase and form a distinct cluster (note log scale for  $\phi$ ). Similarly PAHs, PCBs, and OCPs appear to have prediction clusters.

**Soot and PAH Deposition in Southern Lake Michigan Were Highly Correlated.** There have been numerous studies that suggest soot contains relatively high levels of PAHs and may control the distribution and bioavailability of PAHs in the sediment environment (13, 15, 26–31). Direct ties between the two are often inferential however based on historical coal usage and/or combustion data. Simcik et al. (6) proposed that soot from coal combustion was the main source of PAHs to Lake Michigan sediments. Although they did not measure soot levels in the sediment, they showed a correlation between historic records of coal usage and their measured PAH accumulation rates. Evidence was also provided that PAH species in Lake Michigan sediments were



correlated to PM<sub>10</sub> (particles <10 µm in diameter) data collected from Chicago metropolitan air.

Using our Lake Michigan sample data from the same southern Lake Michigan sampling location as the Simcik et al. study, we compared their reported sediment accumulation data for 28 PAHs to our SC data to provide support for the proposed source pathway. A strong and highly significant correlation was found between SC and PAH accumulation rates (Figure 7A–C). Regression of the PAH and SC data sets had *p* values of 3.9E–9, 4.9E–7, and 1.8E–9 for total PAHs, LMW PAHs, and HMW PAHs, respectively. Furthermore, although these correlations were all highly significant as expected (based on the predictions of Figure 5C), the least highly significant correlation was seen for the PAHs with the lowest *K*<sub>OA</sub> values (LMW PAHs, which also include several alkylated PAHs generally not associated with combustion, Figure 7B), and the most highly significant correlation was seen for the HMW PAHs (Figure 7C), which have the highest *K*<sub>OA</sub> values. These strong correlations (and their relative pattern) are highly suggestive of a connection between soot and PAH deposition at this Lake Michigan site. The slopes for these regressions suggest that the total PAH to SC ratio was on the order of 10<sup>–4</sup> or 0.01% of the SC (Figure 7A).

To our knowledge, there has been no recent complete quantification of soot carbon deposition to the sediments of all the Laurentian Great Lakes. While other studies have correlated fuel consumption in the region with soot and PAH loadings in Lakes Erie (7) and Michigan (6), findings here were conducted on a larger scale that included all of the Great Lakes. The data provided here quantitatively demonstrate the importance of large industrial/metropolitan areas on the soot flux to the lakes. We found that SC makes up more than 20% of the OC in both sites sampled in Lakes Erie and Ontario and more than 40% in sites LM-18 and HU-12 in southern Lakes Michigan and Huron.

Our previous characterization of soot (1), combined with an expression defining partitioning of HOCs to aerosols (22), predicts that soot could be a major vector for long-range (allowing equilibrium) PAH and PBDE transport, whereas PCBs and OCPs are not as likely to partition to soot in the atmosphere. Our data showing that higher soot levels occurred in locations close to large metropolitan areas were well correlated to a recent report on PAH deposition to Lake Michigan and are consistent with the hypothesis that soot and PAHs co-occur in the environment.

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## Literature Cited

- (1) Rockne, K. J.; Taghon, G. L.; Kosson, D. S. *Chemosphere* **2000**, *41*, 1125–1135.
- (2) Goldberg, E. D. *Black Carbon in the Environment*; Wiley-Interscience: New York, 1985.
- (3) Ostrom, N. E.; Long, D. T.; Bell, E. M.; Beals, T. *Chem. Geol.* **1998**, *152*, 13–28.
- (4) Meyers, P. A.; Ishiwatari, R. *Org. Geochem.* **1993**, *20*, 867–900.
- (5) James, R. R.; McDonald, J. G.; Symonik, D. M.; Swackhamer, D. L.; Hites, R. A. *Environ. Sci. Technol.* **2001**, *35*, 3653–3660.
- (6) Simcik, M. F.; Eisenreich, S. J.; Golden, K. A.; Liu, S.; Lipiatou, E.; Swackhamer, D. L.; Long, D. T. *Environ. Sci. Technol.* **1996**, *30*, 3039–3046.
- (7) Kralovec, A. C.; Christensen, E. R.; Van Camp, R. P. *Environ. Sci. Technol.* **2002**, *36*, 1405–1413.
- (8) Czuczwa, J. M.; Hites, R. A. *Environ. Sci. Technol.* **1986**, *20*, 195–200.
- (9) Carter, D. S.; Hites, R. A. *Environ. Sci. Technol.* **1992**, *26*, 1333–1341.
- (10) Pearson, R. F.; Swackhamer, D. L.; Eisenreich, S. T.; Long, D. T. *Environ. Sci. Technol.* **1997**, *31*, 3523–3529.
- (11) Rockne, K. J.; Shor, L. M.; Y., Y. L.; Taghon, G. L.; Kosson, D. S. *Environ. Sci. Technol.* **2002**, *36*, 2636–2644.
- (12) Shor, L. M.; Liang, W.; Rockne, K. J.; Young, L. Y.; Taghon, G. L.; Kosson, D. S. *Environ. Sci. Technol.* **2003**, *37*, 1545–1552.
- (13) Gustafsson, O.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. *Environ. Sci. Technol.* **1997**, *31*, 203–209.
- (14) Accardi-Dey, A.; Gschwend, P. M. *Environ. Sci. Technol.* **2002**, *36*, 21–29.
- (15) Gustafsson, O.; Gschwend, P. M. *Geochim. Cosmochim. Acta* **1998**, *62*, 465–472.
- (16) Gélinas, Y.; Prentice, K.; Baldock, J. A.; Hedges, J. I. *Environ. Sci. Technol.* **2001**, *35*, 3519–3525.
- (17) Buckley, D. R. Soot and organic carbon flux to the Great Lakes sediment: Links to atmospheric transport of toxic pollutants. M.S. Thesis, University of Illinois at Chicago, Chicago, IL, 2003.
- (18) APHA; AWWA; WEF. *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; APHA, AWWA, WEF: Washington, DC, 1998.
- (19) Pearson, R. F.; Swackhamer, D. L.; Eisenreich, S. T.; Long, D. T. *Environ. Sci. Technol.* **1997**, *31*, 2903–2909.
- (20) Bruzy, L. P.; Hites, R. A. *Environ. Sci. Technol.* **1996**, *30*, 1797–1803.
- (21) Griffin, J. J.; Goldberg, E. D. *Environ. Sci. Technol.* **1983**, *17*, 244–245.
- (22) Harner, T.; Shoeib, M. *J. Chem. Eng. Data* **2002**, *47*, 228–232.
- (23) Finizio, A.; Mackay, D.; Bidleman, T.; Harner, T. *Atmos. Environ.* **1997**, *31*, 2289–2296.
- (24) Braekvelt, E.; Tittlemier, S. A.; Tomy, G. T. *Chemosphere* **2003**, *51*, 563–567.
- (25) Palm, A.; Cousins, I. T.; Mackay, D.; Tysklind, M.; Metcalfe, C.; Alae, M. *Environ. Pollut.* **2002**, *117*, 195–213.
- (26) Jonker, M. T. O.; Koelmans, A. A. *Environ. Sci. Technol.* **2002**, *36*, 4107–4113.
- (27) Ghosh, U.; Gillette, J. S.; Luthy, R. G.; Zare, R. N. *Environ. Sci. Technol.* **2000**, *34*, 1729–1736.
- (28) Jonker, M. T. O.; Koelmans, A. A. *Environ. Sci. Technol.* **2001**, *35*, 3742–3748.
- (29) Lima, A. L. C.; Eglinton, T. I.; Reddy, C. M. *Environ. Sci. Technol.* **2003**, *37*, 53–61.
- (30) Fernandez, P.; Carrera, G.; Grimalt, J. O.; Ventura, M.; Camarero, L.; Catalan, J.; Nickus, U.; Thies, H.; Psenner, R. *Environ. Sci. Technol.* **2003**, *37*, 3261–3267.
- (31) Ribes, S.; Van Drooge, B.; Dachs, J.; Gustafsson, O.; Grimalt, J. O. *Environ. Sci. Technol.* **2003**, *37*, 2675–2680.
- (32) U.S. EPA. *The Great Lakes: An Environmental Atlas and Resource Book*, 3rd ed.; United States Environmental Protection Agency: Chicago, IL, 1995.

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