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# Polybrominated Diphenyl Ethers in the Sediments of the Great Lakes. 1. Lake Superior

WENLU SONG,† JUSTIN C. FORD,† AN LI,*,† WILLIAM J. MILLS,† DAVE R. BUCKLEY,‡ AND KARL J. ROCKNE‡

*School of Public Health and Department of Civil and Materials Engineering, University of Illinois at Chicago, Chicago, Illinois 60612*

Sediment cores were taken in 2001 and 2002 in Lake Superior at six locations away from lakeshores and segmented at 0.5−5 cm intervals. The year of sediment deposition was estimated for each segment of four cores using the $^{210}$Pb dating technique. Samples were Soxhlet-extracted and cleaned up by silica gel fractionation, and the concentrations of 10 polybrominated diphenyl ethers (PBDEs) and 19 polychlorinated biphenyls (PCBs) were measured by GC-MS in SIM mode. In contrast to recent declining or level-off trends in PCB fluxes, the sedimentary records of PBDEs generally show a significant increase in recent years. The load of total PBDEs to Lake Superior was estimated to be 2−6 metric tons, and the current loading rate was about 80−160 kg yr$^{-1}$. With the exclusion of decabromodiphenyl ether (BDE209), the surficial concentration of ΣPBDE (sum of 9 congeners) ranged from 0.5 to 3 ng g$^{-1}$, and the current ΣPBDEs flux was 8−31 pg cm$^{-2}$ yr$^{-1}$. The concentrations of BDE209 were about an order of magnitude higher than the sum of other congeners, comprising 83−94% of the total PBDE inventory in the sediments. Among the other nine PBDEs detected, congeners 47 and 99 were the most abundant, and congeners 100, 153, 154, and 183 were also detected in all the cores. Congener analysis demonstrated that the pattern of PBDEs in Lake Superior sediments differs from those in air and fish.

## Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of additive flame-retardants that are used in a wide range of consumer products including paints, plastics, textiles, and electronics. They are considered to be environmentally persistent due to their resistance to various degradation, and their high lipophilicity indicates a strong bioaccumulation potential (*1, 2*). Evidence of their toxic, carcinogenic, and hormone-disrupting effects is also mounting rapidly (*3, 4*).

Since first reported in soil and sludge from the United States in 1979 (*5*) and in fish from Sweden in 1981 (*6*), PBDEs have been found in measurable amounts in various samples around the world including air, water, soil, sediment, biota, and human milk, blood, and adipose tissues (*7*). In the Great Lakes region, the concentration of PBDEs in the air at four land locations ranged from 5 pg m$^{-3}$ near Lake Superior to 52 pg m$^{-3}$ in Chicago (*8*). PBDEs were also found in the fish of all the five Great Lakes (*9*−*11*).

Atmospheric deposition has proven to be a major source of many pollutants, including PCBs and dioxins, to the Great Lakes. This has been particularly true in the past decade when emissions from many known point sources have been greatly reduced (*12*). For PBDEs, the major point sources are currently thought to be the incineration of disposed commercial products, sewage and sludge releases, and the leaching from landfills (*4*). Due to their widespread use, volatilization from various products can be a source of PBDEs in the air with even more significant amounts than from the point sources.

Sediments are an important sink and reservoir of persistent pollutants and have a large impact on their distribution, transport, and fate. Sediment profiles from carefully chosen locations may indicate the chronology of a certain pollutant input process. For example, at locations where air deposition is the major pathway of input, chronology of air deposition of persistent pollutants can be directly revealed from data obtained from segmented sediment cores (*13*).

This research project was carried out to investigate the chronology of PBDE air deposition into the Great Lakes as recorded in the sediments. With the hypothesis that atmospheric deposition is a major source of PBDEs in the sediment of the Great Lakes, sedimentary records were retrieved from all five Great Lakes as well as three inland seepage lakes in the region to provide an estimated historical input of PBDEs during the past decades. Through this study, the temporal trend and spatial distribution of PBDEs in the sediments of these lakes will be revealed. To our knowledge, this work is the first comprehensive study examining the long-term history of PBDE pollution in the Great Lakes. The results of this research project will be reported in a series of publications. This paper is the first one of the series, with a focus on Lake Superior.

## Methodology

**Sampling.** Sediment sampling on Lake Superior was conducted in 2001 and 2002 using a 0.084 m$^3$ box corer deployed from the U.S. Environmental Protection Agency (EPA) Research Vessel *Lake Guardian*. Sampling locations are shown in Figure 1, and the geographic coordinates are given in Table 1. Most sampling sites were chosen at locations where the effects of local point sources could be minimized. In summer of 2001, a sediment core was collected at EPA Station SU13 and another one in Thunder Bay (SU-TBay) in order to conduct a preliminary study with the major objective of developing and validating analytical method for PBDEs. In May 2002, samples were collected from four additional locations (Figure 1, Table 1). At each location, 4 or 5 subcores were taken from the box corer using precleaned acrylic tubes (7.0 cm i.d. AIN Plastics, Inc., Bensenville, IL). Individual subcores were extruded using an aluminum foil-covered push plunger and sectioned on the ship, and new hexane rinsed aluminum foil was used for each core. For all cores except the one collected at SU22, sectioning was performed at 1.0 cm intervals for the first 10 cm and then in 5 cm increments for the remainder of the core. For SU22, the cores were sectioned at 0.5 cm intervals down to depth 5 cm and then 1.0 cm intervals for the rest of the core. All sectioning gear was thoroughly cleaned after each slice using three solvent washes in the order of hexane, acetone, and deionized water. The sediment segments at corresponding depth were com-

* Corresponding author phone: (312)996-9597; fax: (312)413-9898; e-mail: anli@uic.edu. Corresponding author address: EOHS, SPH, UIC MC-922, 2121 W. Taylor Street, Chicago, IL 60612.

† School of Public Health.

‡ Department of Civil and Materials Engineering.



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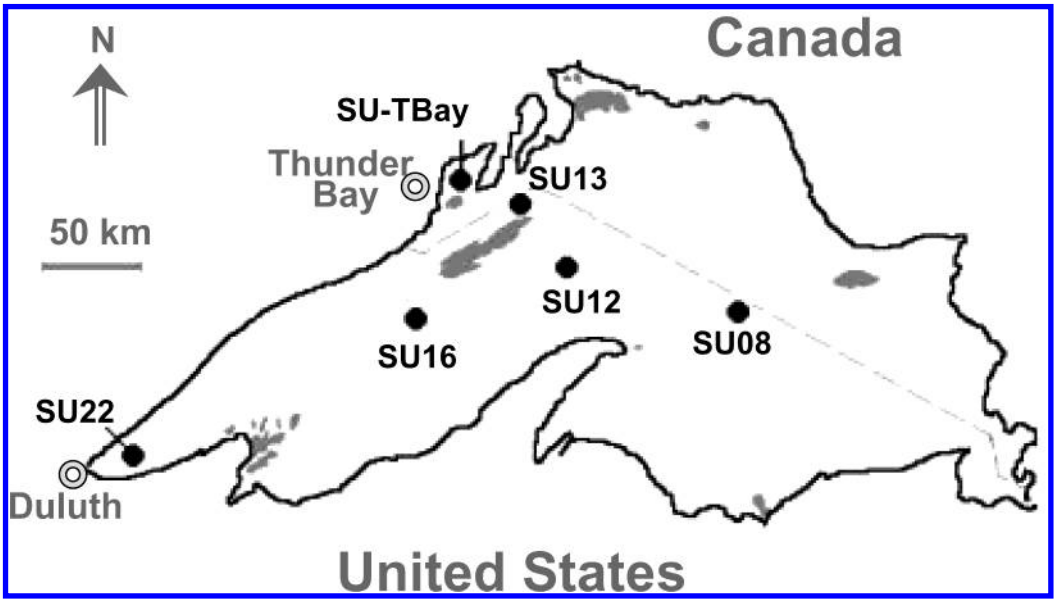


**FIGURE 1. Sampling locations.**

**TABLE 1. Sampling Locations, Sedimentation Rate, and Focusing Factor**

| sampling station | location latitude (N) | location longitude (W) | sedimentation rate ($g\ cm^{-2}\ yr^{-1}$) CIC | CRS | focusing factor |
|---|---|---|---|---|---|
| SU08 | 47°36′21″ | 86°48′57″ | 0.0132 | 0.0151 | 0.89 |
| SU12 | 47°51′22″ | 88°02′31″ | 0.0121 | 0.0133 | 0.73 |
| SU16 | 47°37′17″ | 89°27′47″ | 0.0108 | 0.0111 | 1.25 |
| SU22 | 46°48′05″ | 91°44′59″ | 0.0213 | 0.0210 | 0.58 |
| SU13* | 48°13′46″ | 88°32′43″ | | | |
| SU-TBay[a] | NA | NA | | | |

[a] Sampled in summer 2001. The amounts were not sufficient for sediment characterization and dating. Therefore, the sedimentation rate, inventory, and flux were not determined. Other cores were collected in 2002. (NA = not available).

posited into a precleaned amber glass jar in order to obtain sufficient amount of sample for various laboratory analyses. The extruded and sectioned samples were then refrigerated onboard the ship at 4 °C until transport to the laboratory where they were stored frozen until analysis.

**Sediment Characterization.** Each sediment sample was characterized for percent solids, wet and dry bulk density, particle density, and porosity. The contents of organic matter, organic carbon, soot carbon, nonsoot carbon, nitrogen, and oxygen were also determined. Detailed experimental procedures and results are presented elsewhere (*14, 15*).

**$^{210}$Pb Dating.** The laboratory procedure for sediment core dating was developed based on a $^{210}$Pb radiological method from the University of Wisconsin—Milwaukee (*16*) and a protocol from Argonne National Laboratories (*17*). Briefly, 0.5 or 1.0 g sediment sample was oven-dried at 95 °C overnight. The sample was then ground, weighed, and placed in a 250 mL Erlenmeyer flask, and 1.0 mL $^{209}$Po standard (NIST SRM 4326, diluted to approximately 0.2 Bq $mL^{-1}$) was added. Digestion of the sample was done by adding 25 mL of 6 N hydrochloric acid and heating the flask on a 90—95 °C hot plate for 30 min. Then, 1 mL of 30% hydrogen peroxide and 2 drops of *n*-octanol was added, and the solution was heated for 5 h at 90—95 °C. During the first two and a half hours of heating, the solution was removed from the heat for 5 min, and 1 mL of 30% hydrogen peroxide was added. After heating, the solution sat, covered with a watch glass, overnight. The solution was then filtered using vacuum filtration, and the residue was washed several times with distilled water to keep a quantitative transfer for all the dissolved materials. The solution was then evaporated to approximately 1—2 mL and transferred to a 25 mL scintillation vial keeping the pH between 0.5 and 1.5. Ascorbic acid was added to the vial (0.1—0.2 g), and both $^{209}$Po and $^{210}$Po, granddaughter of $^{210}$Pb, were plated onto a cleaned copper disk for approximately 2 days at room temperature. The disks were then removed, cleaned with distilled water and ethanol, labeled, and counted using a Canberra Alpha Analyst system (Meriden, CT). The $^{210}$Pb activity was calculated from the peak areas of $^{210}$Po, after a correction based on the yield of $^{209}$Po.

The method was initially validated by analyzing a lake sediment sample with known $^{210}$Pb activity, which was previously measured by the Great Lakes Water Institute at the University of Wisconsin—Milwaukee in 1999. The results obtained with our method were within 15% of the results reported from Milwaukee. At least one segment in each sediment core was prepared and dated in duplicates. The average relative standard deviation (RSD) of six duplicated samples was 6.5%. The RSD tends to be lower for sediment segments deposited more recently.

**Chemical Analysis.** The PBDE and PCB analytical standards were purchased from Cambridge Isotope Laboratory (Andover, MA) and AccuStanadard (New Haven, CT), respectively. Solvents were purchased from Fisher Scientific (Fair Lawn, NJ). Dichloromethane, hexane, and acetone were GC grade. Silica gel (100—200 mesh, Davisil Grade 644) and anhydrous sodium sulfate were also purchased from Fisher Scientific.

The target PBDE analytes included tri- (BDE28), tetra- (BDE47 and BDE66), penta- (BDE85, BDE99, and BDE100), hexa- (BDE153 and BDE154), hepta- (BDE183), and deca- (BDE209) bromodiphenyl ether congeners. These PBDE congeners were selected on the basis of their relatively high content in the commercial products (*7*) and are the most frequently detected congeners in the environment. For comparison purposes, PCB congeners with IUPAC nos. 8, 18, 28, 52, 44, 66, 101, 77, 118, 153, 105, 137, 126, 187, 128, 180, 170, 195, and 206 were also analyzed for all the sediment samples.

In the laboratory, sediment samples were thawed, homogenized, and subsampled to determine the water content and the concentrations of PBDEs and PCBs. Wet sediment

was ground with anhydrous sodium sulfate. The dried sample was transferred to a Whatman cellulose thimble and spiked with known amounts of PBDE surrogate $^{13}C$ labeled 2,3′,4,4′,5-penta bromodiphenyl ether (BDE118), PCB surrogate 2,3,5,6-tetrachlorobiphenyl (PCB65), and BDE209 surrogate $^{13}C$ labeled BDE209. The sediment was then extracted in a Soxhlet extractor for 20 h with 150 mL 1:1 (v) hexane:acetone mixture. Elemental sulfur was removed by adding activated granular copper (Aldrich, Milwaukee, WI) to the Soxhlet flask during extraction. The extract was then concentrated on a Kuderna-Danish (K−D) concentrator, solvent-exchanged to hexane, and cleaned-up by elution through a glass column (40 cm long × 1.5 cm i.d.) filled with 10 g of fully activated silica gel with 75 mL of a 9:1 (v) hexane:dichloromethane mixture. Afterward, the eluant was again concentrated on the K−D concentrator to about 5 mL. The volumes of samples were further reduced to about 1 mL by a gentle stream of $N_2$ and then brought up to exactly 2.0 mL by adding the solvent that was used to rinse the K−D tube.

Quantitative analyses of PCBs and PBDEs were performed on an Agilent Model 6890 gas chromatograph (GC) coupled with a Model 5973 mass spectrometer (MS). A DB-5MS (30 m × 0.25 mm i.d., 0.25 $\mu$m film thickness; J&W Scientific) capillary column was used for separation, with helium as the carrier gas at flow rate of 1 mL $min^{-1}$. Separate runs were made for PBDEs and PCBs. BDE209 was analyzed separately using a shorter column (see below). An internal standard was added to each sample before GC injection. The internal standard PCB204 was used to normalize the peak areas in PBDE quantification, and PCB30 and PCB204 were used as internal standards for PCBs. For BDE209, BDE190 was chosen as the internal standard. Samples were introduced into GC/MS through a programmable temperature vaporization (PTV) large volume injection port (*18*). A total of 60 $\mu$L was injected in each run, with three injections of 20 $\mu$L each and 10 s intervals to allow complete evaporation of the solvent. The temperature program for the PTV port was from 0 °C (held for 1.5 min) to 300 °C at 600 °C $min^{-1}$. The PTV vent flow was 300 mL $min^{-1}$, and purge flow was 50 mL $min^{-1}$ at run time 2.5 min.

For PBDEs analysis, the initial oven temperature was 140 °C, which lasted for 3 min. It was increased to 200 °C at 15 °C $min^{-1}$, to 220 °C at 2 °C $min^{-1}$, and then to 315 °C at 5 °C $min^{-1}$ and held for 5 min. The oven temperature for PCB analysis started from 100 °C which was held for 10 min. It was then increased to 130 °C at 10 °C $min^{-1}$, to 255 °C at 2 °C $min^{-1}$, and to 285 °C at 10 °C $min^{-1}$ and held for 5 min. For BDE209, a DB-5MS (15 m × 0.25 mm i.d., 0.25 $\mu$m film thickness; J&W Scientific) capillary column was used for GC separation, with helium as carrier gas at constant pressure of 15 psi. The initial oven temperature was 110 °C, which was held for 4 min. It was increased to 310 °C at 15 °C $min^{-1}$ and lasted at this final temperature for 15 min.

While initial analyses were performed using electron-capture negative chemical ionization mass spectrometry (NCI-MS) monitoring the Br ions ($m/z$ 79 and 81), electron impact mass spectrometry (EI-MS) was used to obtain the results reported in this paper for all analytes except BDE209, because EI-MS allowed the molecular ion and additional fragment ions to be monitored, and had higher sensitivity for mono- through tetra-PCBs than the NCI-MS. The MS was operated in selected ion monitoring (SIM) mode. Quantification was performed by external standard calibration, using the primary ion of each compound, on an Agilent ChemStation. The next two most abundant ions were used for confirmation. For BDE209, NCI-MS was used with the fragment ion of $m/z$ 486 for quantitation, and the $m/z$ 485 and 487 ions were used for confirmation. For the BDE209 analytical surrogate ($^{13}C$ labeled BDE209), the $m/z$ 494 ion was used for quantitation and confirmation ions were $m/z$ 495 and 497. A quadratic calibration equation ($R^2 = 0.89$) was obtained and used for quantification of BDE209.

**Quality Control.** Matrix blanks were pre-1850 segments for all dated cores except SU22, for which the last two segments, with dates before 1900, were used as matrix blanks. There were two to six matrix blank samples for different cores. The averages of chemical concentrations in the matrix blanks of each core were subtracted from the results of chemical analysis. Method blanks were also run with the absence of sediment, and the levels of analytes found were comparable to those in the matrix blanks.

The surrogate recoveries for PBDEs were in the range of 60−170%, with a mean of 102%. The mean recovery for PCBs was 87% ranging from 60% to 123%. All but one of the seven samples with recoveries more than 140% for PBDEs were from core SU08, for which the recoveries of PCB surrogate were normal (74−92%). The surrogate recoveries for BDE209 were in the range of 25−97%, with a mean of 58%. The relatively low recovery for BDE209 is similar to those found by Strandberg et al. (*8*) and reflects the difficulties in analyzing this high molecular mass congener. All results reported in this paper are after corrections using surrogate recoveries. NIST Standard Reference Material 1939a (river sediment) was analyzed using the above analytical procedure. Our results were within 70−120% of the certified PCB congener concentrations. Six sediment samples, usually the middle segment of each core, were analyzed in duplicate. The average RSD ranged from 14% to 53% for the nine PBDE congeners and from 5% to 42% for the 19 PCBs. BDE209 was not found in most duplicated samples.

## Results and Discussion

**Sedimentation Rate and Focusing Factor.** Unsupported $^{210}Pb$ activity is plotted against an accumulative mass of sediment in Figure S1 of the Supporting Information for four cores. Cores collected in 2001 at SU13 and SU-TBay were not dated, because of the insufficient amount of sediments in individual segments. Both CIC (constant initial concentration) and CRS (constant rate of sedimentation) models (*19, 20*) were used to determine the year of deposition from the measured $^{210}Pb$ activity. The differences between the results by the two models are minimal for most cores, especially the segments deposited after 1840, indicating steady-state sedimentation and lack of significant mixing.

The sedimentation rate, in g $cm^{-2}$ $yr^{-1}$, is estimated from the slopes of the linear regressions shown in Figure S1. The results for four of the six cores are summarized in Table 1. The average of the four sites is 15 mg $cm^{-2}$ $yr^{-1}$ (0.40 g $m^{-2}$ $d^{-1}$), which agrees well with the average sedimentation rate of 0.43 g $m^{-2}$ $d^{-1}$ suggested for Lake Superior by Jeremiason et al. (*21*). Compared with other locations, a relatively high sedimentation rate was obtained at SU22, which is close to Duluth, MN and Superior, WI, and to the mouth of the St. Louis River. In addition, SU22 showed some mixing at 0.5, 4.5, and 5.5 cm, as can be seen in Figure S1 (Supporting Information).

Sediment focusing factor measures the horizontal movement of sediment particles on the lake bottom due to turbulence and overturns which may cause the settled sediments to redistribute. The focusing factor for each sampling location was calculated as the ratio of the accumulative $^{210}Pb$ activity (unsupported $^{210}Pb$ inventory) to that expected from the regional atmospheric input, which was reported as 15.5 pCi $cm^{-2}$ or 34.4 dpm $cm^{-2}$ for the Great Lakes region (*22*). The calculated focusing factors are given in Table 1. SU16, located in a relatively flat bottom in a deep basin, has a focusing factor greater than unity, indicating sediment accumulation at this spot. All the other locations are subjected to sediment erosion, evidenced by focusing factors < 1. With a focusing factor of only 0.58, location SU22

is believed to be under the impact of the St. Louis River input, which is the largest tributary flow to Lake Superior on the U.S. side, with a mean water flow rate of 5600 $m^3$ $min^{-1}$ (1997 data (*23*)).

**Concentration vs Depth.** Concentrations of PBDEs and PCBs of 48 samples from the 6 cores are quantitatively measured. The concentrations are illustrated in Figure 2 as a function of sediment depth. The surface concentrations at each of the locations are given in Table 2. In the discussion below, "ΣPBDEs" refers to the sum of all PBDE congeners except BDE209, and "ΣPCBs" is the sum of all the 19 PCB congeners.

ΣPBDEs concentrations in surficial sediments are within the range of 0.49−3.1 ng $g^{-1}$ dry weight, with an average of 1.4 ng $g^{-1}$ dry weight. On the basis of organic carbon content (OC), the ΣPBDE concentrations in surface sediments range from 11 to 44 ng $g^{-1}$ OC for the four cores collected in 2002, with an average of 28 ng $g^{-1}$ OC. For each core, the maximum concentrations generally appeared in the top layers of the sediment cores with the exception of SU16, which has the maximum concentration at the second uppermost segment. In the sediment surface layers, the average concentration of BDE47 is 0.44 ng $g^{-1}$ dry weight, which is about one-third of the concentration of PCB153, the most abundant PCB congener. The concentrations of BDE209 in surficial sediment ranged from 4 to 17 ng $g^{-1}$ dry weight or 140−390 ng $g^{-1}$ OC, much higher than those of other individual congeners and even ΣPBDE. At all the sampling locations except SU22, the highest concentration of BDE209 was found in the surficial segment.

PBDE concentrations in sediments have been reported for various regions of the world. At Hadley Lake, IN, only 1.3 km away from the research and development facility of a PBDE producing manufacturer, the sum of tetra- through hexa-BDEs in surface sediments averaged 103 ± 16 ng $g^{-1}$ OC (*24*), about a factor of 4 higher than the average found in this work for Lake Superior. In the Columbia river, Canada, and its major tributary, the surficial sediments contain 2.7−91 ng $g^{-1}$ OC of nine PBDEs (*25*). The highest concentration reported in the United States was seen in the surficial sediments from two Virginia watersheds, the total tetra- to hexa-PBDE concentrations ranged from nondetectable to 52.3 ng $g^{-1}$ dry weight or 1210 ng $g^{-1}$ OC (*26*). In Western Europe, PBDE concentrations in surficial sediments of Drammenfjord (Norway), the western Wadden Sea (Netherland), and freshwater Lake Woserin (Germany) were reported to be 20, 27, and 18 ng $g^{-1}$ OC, respectively, excluding BDE209 (*27*). Coastal and river sediments in Portugal contained 0.5−20 ng $g^{-1}$ of 40 PBDE congeners (*28*). In Eastern Asia, PBDE concentrations of five PBDE congeners in marine sediment samples from two coastal locations in Korea were in the ranges of 0.05−6.37 ng $g^{-1}$ and 1.1−33.8 ng $g^{-1}$ dry weight, respectively (*29, 30*). In Osaka Bay, Japan, PBDE concentrations in sediments were found to be 8 and 352 ng $g^{-1}$ (*31*). Sediment concentrations of BDE209 as high as 1700 ng $g^{-1}$ were reported in a river in the United Kingdom (*32*) and 16 000 ng $g^{-1}$ ignition loss in Sweden (*33*). In The Netherlands, BDE209 in sediment samples was more than an order of magnitude higher than the sum of BDE47 and BDE99 (*32*). Similar ratios were found at the three locations in Western Europe mentioned above (*27*).

The ΣPCB concentrations in surficial sediments of Lake Superior ranged from 2 to 27 ng $g^{-1}$ dry weight, with an average of 3.6 ng $g^{-1}$ dry weight. For the four cores taken in 2002, the average PCB concentration in surficial segments ranged from 50 to 148 ng $g^{-1}$ OC, averaged 102 ng $g^{-1}$ OC. Two SU08 samples, with depth about 2−4 cm, had unusually high concentrations of PCBs for reasons that are unclear at this time and are to be investigated further. The results of these two samples are not included in Figure 2 and were not used in computing inventories and fluxes. Compared with the results of Eisenreich and co-workers (*34*) from the 1970s, significant reduction of PCB concentration in the sediments has been observed. Possible recycling of previously settled PCBs back to the water column in Lake Superior has been reported (*21*). PCB concentration in the Great Lakes sediments and biota may respond more slowly to reduction in external PCB loading than those in the water column (*35*). Decreases in PCB concentrations in the air and water of Lake Superior in recent years have also been reported (*21*), although an increase in air concentration was observed for a short period of time in the late 1990s (*36*).

PBDEs and PCBs were detected in several sediment segments deposited before their respective commercial productions began. Although the natural production of halogenated organics in oceans were reported (*37*), bioturbation, mixing, and selective downward migration of pollutants may occur after burial. The "background" levels could also result from sampling and analytical artifacts such as smearing during core extrusion. The resolution regarding depth might be partially compromised from combining segment layers, which might not have exactly equal in situ depth, from the several subcores collected at the same location. Considering the very low sedimentation rates in Lake Superior, these artifacts were difficult to avoid and could affect the accuracy in sediment dating and the resolution of the chronological profiles of these compounds due to the large differences in the concentrations of $^{210}Pb$ and the chemical analytes between the surface and pre-1970 sediment samples.

**Inventories and Fluxes.** Inventories of the contaminants represent the total integrated mass of the compound of interest per unit area. It was calculated for individual PBDE and PCB congeners using eq 1

$$\text{inventory} = \Sigma C_i \rho_b d_i \qquad (1)$$

where $C_i$ is the concentration in sediment segment i (ng $g^{-1}$ dry weight), $\rho_b$ is the dry mass bulk density (g $cm^{-3}$), and $d_i$ is the thickness of segment i.

The inventories of PBDEs and PCBs at four sampling locations are summarized in Table 2. Sampling site SU08, far from any large urban area and having a focusing factor less than 1, has the lowest accumulations. SU16, with a focusing factor of 1.25, has accumulated more PBDEs and PCBs than other sampling locations, due probably to the migration of sediment to this site. Using the inventory values at the four locations sampled in 2002, we estimate that the load of the ΣPBDEs in the sediment of Lake Superior, which has a water surface area of 82 100 $km^2$, would be in the range of 130 to 1000 kg. When BDE209 is included, the total load of PBDEs is estimated to range from 2 to 6 metric tons.

The flux of chemicals into the sediment segment i was calculated using eq 2

$$\text{flux}_i = C_i \times R_i/\text{FF} \qquad (2)$$

where FF is the focusing factor of the location, and $R_i$ is the sedimentation rate in g $cm^{-2}$ $yr^{-1}$, for which the average of CIC and CRS derived values were used. The fluxes of ΣPBDEs and BDE209 are plotted against deposition year in Figure 3. The fluxes of ΣPCBs are also included for comparison.

Although the resolution of the chronological profiles as shown in Figure 3 may have been compromised due to the low sedimentation rates and the possible artifacts in sample handling as discussed in the previous section, the PBDE fluxes at all locations were, as expected, generally in continuous and obvious increase since the 1970s when PBDE commercial production began. The temporal pattern coincides well with the increasing production and use patterns. The ratio of

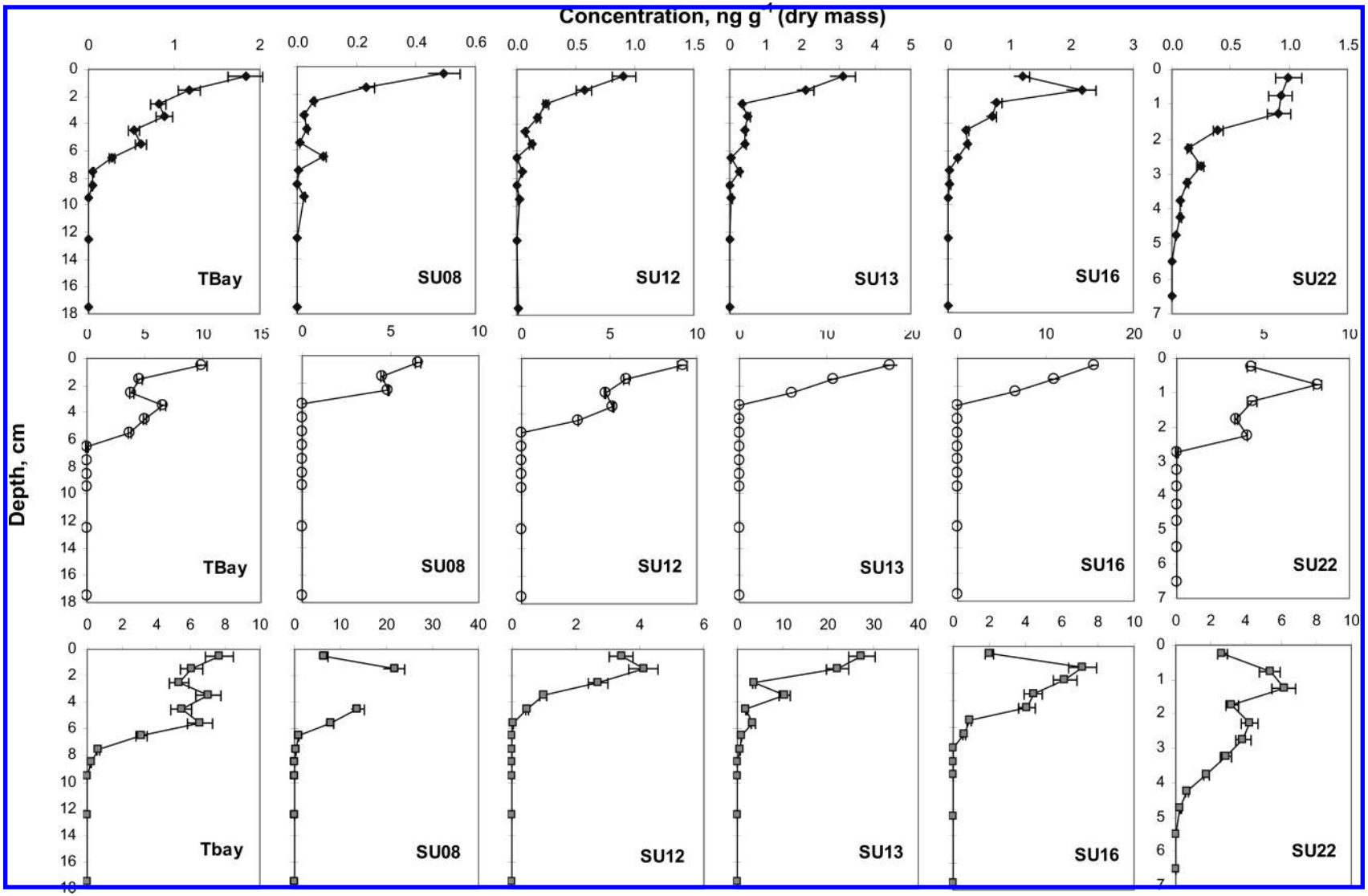


**FIGURE 2. Total concentrations of (a) 9 PBDEs and (b) 19 PCBs versus depth in Lake Superior. Note that the y-scale for SU22 is different from others. Filled diamond — ΣPBDEs; empty circle — BDE209; grayed square — ΣPCBs.**

**TABLE 2. Surface Concentration, Surface Flux, and Inventory of PBDEs and PCBs in the Sediments of Lake Superior**

| | ΣPBDEs | | | BDE209 | | | ΣPCBs | | |
|---|---|---|---|---|---|---|---|---|---|
| sampling station | surface concn (ng $g^{-1}$) | inventory (ng $cm^{-2}$) | surface flux (ng $cm^{-2}$ $yr^{-1}$) | surface concn (ng $g^{-1}$) | inventory (ng $cm^{-2}$) | surface flux (ng $cm^{-2}$ $yr^{-1}$) | surface concn (ng $g^{-1}$) | inventory (ng $cm^{-2}$) | surface flux (ng $cm^{-2}$ $yr^{-1}$) |
| SU08 | 0.49 | 0.15 | 0.008 | 6.6 | 3.1 | 0.10 | 6.50 | 12.18[a] | 0.106 |
| SU12 | 0.91 | 0.37 | 0.013 | 9.2 | 5.4 | 0.16 | 3.42 | 2.14 | 0.049 |
| SU16 | 1.20 | 1.26 | 0.009 | 15.5 | 6.4 | 0.14 | 1.99 | 6.50 | 0.015 |
| SU22 | 1.00 | 0.57 | 0.031 | 4.3 | 4.1 | 0.16 | 2.65 | 5.58 | 0.082 |
| SU13 | 3.14 | | | 17.5 | | | 27.48 | | |
| SU-TBay | 1.83 | | | 9.9 | | | 7.65 | | |

[a] The accumulation of PCBs in two sediment segments in the core collected at SU08 was excluded in inventory calculation.

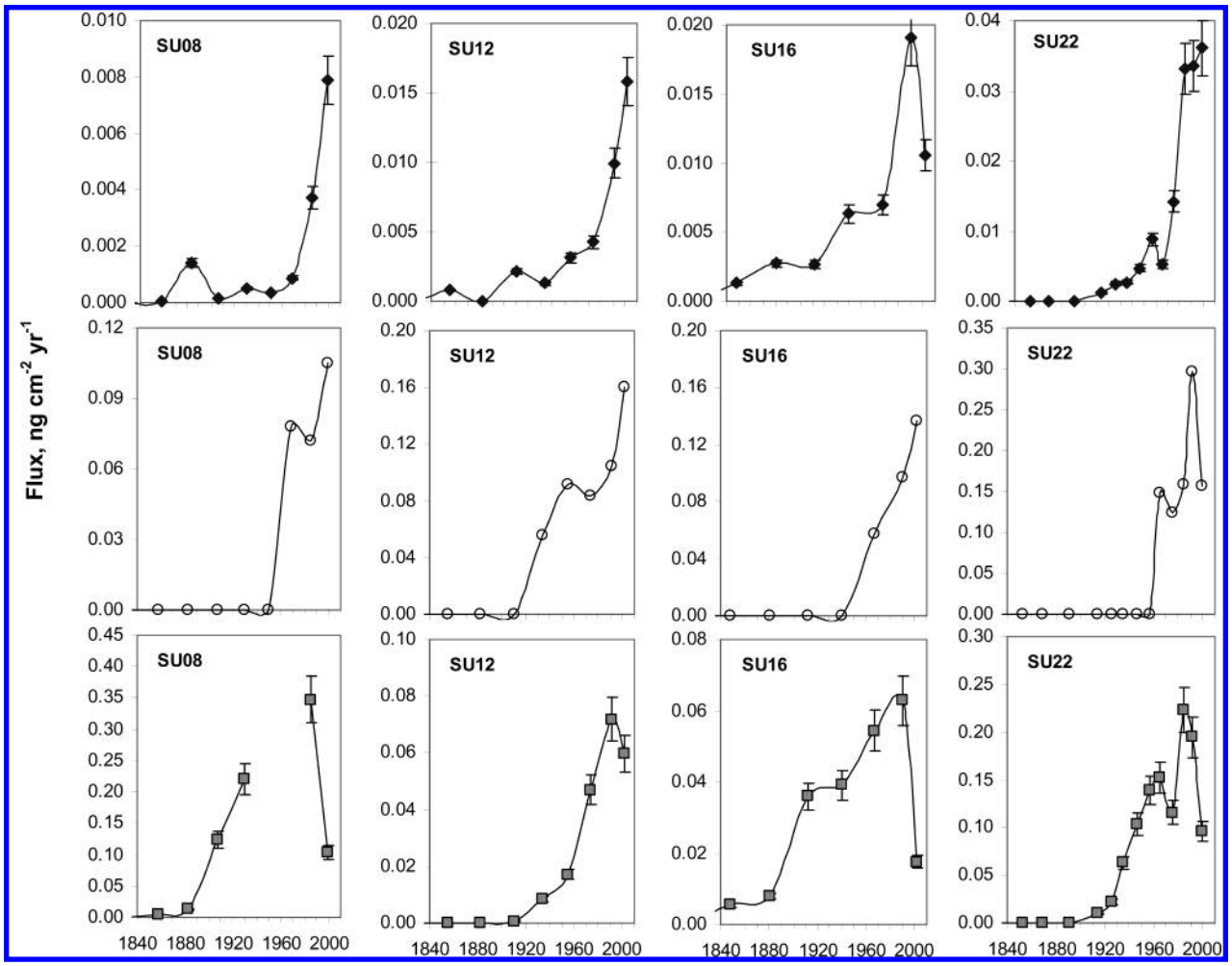


**FIGURE 3. Fluxes of PBDEs and PCBs to the sediment of Lake Superior. Filled diamond − ΣPBDEs; empty circle − BDE209; grayed square − ΣPCBs.**

ΣPBDEs fluxes in recent years to those in the 1970s ranged from 1.5 at SU16 to 7.0 at SU22. However, a trend of level-off since the 1990s was observed at SU22, which is close to Duluth, MN. The flux of BDE209 ranges from 0.10 to 0.16 ng $cm^{-2}$ $yr^{-1}$ in the sediment surface at the four locations and shows sharp increases in the last three decades. Muir et al. have found that the flux of BDE209 declines with latitude in North America (*38*). In Lake Openogo, Canada (45°N), the flux in 1997 was found to be 0.11 ng $cm^{-2}$ $yr^{-1}$, similar to those found in this study for the most recent sediments in Lake Superior (Table 2).

The current ΣPBDE fluxes, as observed at the sediment surface for the four locations sampled in 2002, are in the range of 8−31 pg $cm^{-2}$ $yr^{-1}$, with an average of 18 ± 5 pg $cm^{-2}$ $yr^{-1}$. Based on this range, we estimate that the current loading of ΣPBDEs to Lake Superior sediments is at a rate of 7−25 kg $yr^{-1}$. If BDE209 is included, the loading rate estimates are from 80 to 160 kg $yr^{-1}$. These estimates may be a fraction of what Lake Superior receives from atmospheric deposition and other sources. The amount of PBDEs in the water column and the food web currently remain unknown.

An apparent difference between PCBs and PBDEs is that, for PCBs, there is an obvious decrease in the influx toward the sediment surface, where PBDE flux continues to increase at most locations. For most of the cores, the peaks of PCB flux are around 1985, followed by a decrease in recent years. It seems that, after the ban of production and usage of PCBs in the late 1970s, an increasing trend had continued for less than a decade before PCB flux to the sediments of Lake Superior began to show a noticeable decrease. The surface

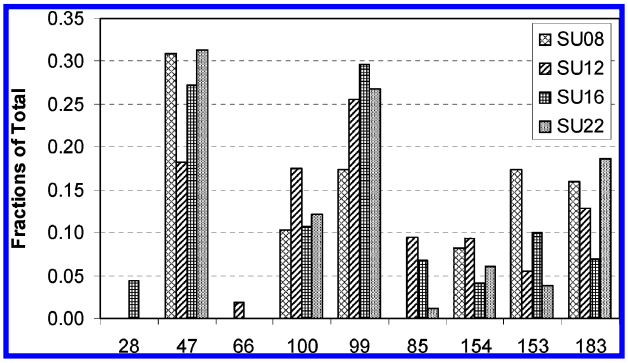


**FIGURE 4. Comparison of PBDE congener patterns in the sediments at different locations.**

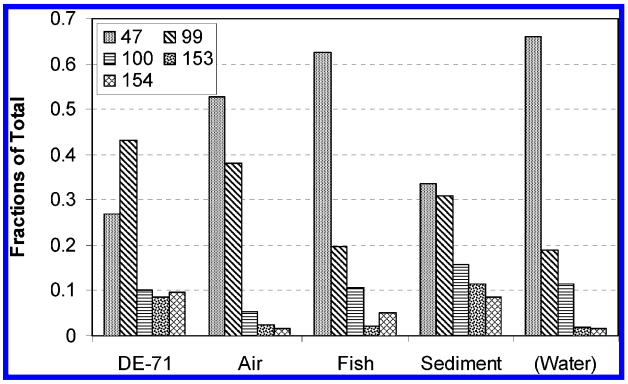


**FIGURE 5. Comparison of PBDE congener patterns in technical mixture DE-71 (*24*), air in Eagle Harbor, MI (*8*), fish in Lake Superior (smelt (*24*)), and the sediments (average of SU08, SU12, SU16, and SU22, this study). The pattern for water was estimated (see text). For each category, the sum of the five fractions is 1.**

flux for PCBs ranged from 15 to >100 pg $cm^{-2}$ $yr^{-1}$, with an average of 60 pg $cm^{-2}$ $yr^{-1}$. Recently, Simcik et al. reported PCB distributions in sediments of western Lake Superior collected in 1990 (*39*). The surface fluxes of 109 PCB congeners were in the range of 90−370 pg $cm^{-2}$ $yr^{-1}$. It also showed that PCBs accumulated at a higher rate in the western arm of Lake Superior closest to the Duluth/Superior area. This finding agrees with our observation that the flux at location SU22 is significantly higher than that at SU16.

**Congener Distribution Patterns.** The dominance of BDE209, the fully brominated congener, in the total PBDEs is unquestionable (Table 2). The inventory of BDE209 at the four locations ranges from 83% to 94% on a mass basis, and from 73% to 90% on molar basis, of the sum of the 10 congeners. The surface concentration and flux of BDE209 range from 79% to 98% and from 69% to 96% of the total PBDEs on mass and molar bases, respectively. The ratio of BDE209 to ΣPBDEs averages 12±10, with a median of 9. This finding agrees with the fact that BDE209 counts for >70% of the total PBDE production in North America (*40*).

A comparison among the inventories of individual PBDE congeners is shown in Figure 4, with BDE209 excluded. Among the nine PBDE congeners, BDE47 and BDE99 are apparently more abundant than the others and were detected in 98% and 83% of the samples, respectively. These two congeners constitute 50−83% of ΣPBDE inventories over all locations. Congeners 100, 153, 154, and 183 were also found in all the cores. The other congeners, BDE28, BDE66, and BDE85, were detected in less than 25% of the samples. For the 19 PCB congeners, PCBs 101, 153, and 180 generally have higher abundance than other PCB congeners.

Noticeable differences exist in congener distribution patterns among the sediment samples collected in different regions of the world. For example, our results show that the ratio of BDE47 to BDE99 is >1 in 62% of the samples, with an average of 1.5 and a median of 1.1, in Lake Superior sediments. However, this ratio for Hadley Lake, IN, is only about 0.5 (estimated from Figure 3 of ref *24*). Such difference may reflect the differences in volatilization and long-range transport behavior of these two congeners, because Lake Superior is remote while Hadley Lake is close to potential PBDE sources. Another remarkable difference is that BDE183 constituted 7−20% of the inventories in Lake Superior, while it was reported as "never detected" in the three Western European sediment cores (*27*) as well as in fish that feed on benthic invertebrates in Belgium (*41*). However, it is interesting to see that BDE183 is the predominant (33−52%) congener in marine sediment samples, although the sampling location is not given (*42*). Because DBE-183 is the marker congener for commercial mixtures of octa-BDE (*27*), its presence in the Great Lakes reflects the history of its manufacturing in North America.

In Figure 5, the average PBDE congener pattern in the sediments is compared with the U.S. commercial product DE-71 as well as the air and fish samples collected in Lake Superior. BDE183 is not included because it is not reported for air and fish samples, and no reliable congener-specific composition information is found for DE-79, the commercial octa-BDE product. The sediment pattern resembles the commercial penta mixtures fairly well, showing evidence that the observed PBDEs in the environment are originated from the commercial product.

When compared with air and fish, an obvious difference is the enhanced fractions of heavier congeners in the sediments. This was well expected, recognizing the fact that heavier congeners have higher sediment−water distribution ratio $K_d$, which depends heavily on the hydrophobicity of the chemicals as well as the organic matter content of the soil or sediment (*43*). Using published experimental $K_{ow}$ values (*44*) and assuming equilibrium between sediment and water, the relative abundance of the five congeners in water was estimated from that in sediment and is included in Figure 5. The pattern resembles that in fish, implying the importance of bioconcentration as a mechanism of PBDE accumulation in biota. Compared with other mechanisms of removal such as volatilization, sediment burial may be a more important sink for heavier congeners.

It is well established that air deposition is the major pathway for persistent organic pollutants such as PCBs to enter Lake Superior (*45*). This study shows evidence that this is also true for PBDEs. Compared with the commercial mixture DE-71, the higher fractions of BDE47 in the air, water, and fish of Lake Superior may attribute to the stronger "grasshopper effect" for BDE47 (*46, 47*) than others. That is, more of BDE47 can be atmospherically transported to remote areas through a series of deposition/volatilization hops than heavier congeners can. To confirm this hypothesis, congener-specific air concentration data at the source regions and along the transport paths are needed. In addition, data regarding PBDE concentrations in the water column, both dissolved and particle-bound, must be obtained in order to estimate what is the percentage of the total atmospheric deposition that ends up in sediments. A preliminary equilibrium calculation, using both experimental and estimated physicochemical properties, seems to indicate that the direction and the extent of air−water exchange may differ among different PBDE congeners. It is possible that equilibria have been established or are being approached for less brominated congeners such as BDE28 and BDE47, while significant input from air into Lake Superior continues for heavier congeners. However, a reliable estimation cannot be made before more process parameters become available. The possibility of PBDE transformation during their transport cannot be excluded by the results of this work.

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## Supporting Information Available

Results of $^{210}$Pb dating for the four sediment cores collected in 2002 (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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