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Polybrominated Diphenyl Ethers in the Sediments of the Great Lakes. 2. Lakes Michigan and Huron

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

School of Public Health and Departments of Earth and Environmental Sciences and of Civil and Materials Engineering, University of Illinois at Chicago, Chicago, Illinois 60612

Sediment cores were taken in 2002 in Lakes Michigan and Huron at six locations. A total of 75 samples were characterized, dated using ^{210}Pb, and analyzed for 10 congeners of polybromodiphenyl ether (PBDE) including BDE209, as well as 39 congeners of polychlorinated biphenyls (PCBs). The concentrations of nine tri- through hepta-BDE congeners ($\sum_9$PBDE) in the surficial sediments range from 1.7 to 4 ng g^{-1} for Lake Michigan and from 1.0 to 1.9 ng g^{-1} for Lake Huron, on the basis of the dry sediment weight. The $\sum_9$PBDEs fluxes to the sediment around the year 2002 are from 36 to 109 pg cm^{-2} yr^{-1} in Lake Michigan and from 30 to 73 pg cm^{-2} yr^{-1} in Lake Huron, with spatial variations in both lakes. The flux of BDE209 ranges from 0.64 to 2.04 ng cm^{-2} yr^{-1} and from 0.67 to 1.41 ng cm^{-2} yr^{-1} in Lake Michigan and Lake Huron, respectively. Dramatic increases in PBDE concentrations and fluxes upward toward the sediment surface and the present time are evident at all locations. The inventory of PBDEs in both lakes appears to be dependent upon latitude and the proximity to populated areas, implying that north-bound air plumes from urban areas are the major sources of PBDEs found in the lake sediments at locations away from the shores. Heavier congeners are more abundant in the sediments than in air and fish samples in the region. BDE209 is about 96% and 91% of the total PBDEs on a mass basis in Lake Michigan and Lake Huron, respectively; both are higher than the 89% found in Lake Superior, although a *t* test shows that the value for Lake Huron is not statistically different from that for Lake Superior at the 95% confidence level.

Introduction

Due to the widespread use of polybrominated diphenyl ethers (PBDEs) since the 1970s, they are now found in measurable amounts throughout the environment. To assess the extent of PBDE pollution in the Great Lakes and provide evidence of their long-range transport via the atmosphere, a total of eight lakes, including the five Great Lakes and three inland seepage lakes in the States of Illinois, Wisconsin, and Michigan, have been investigated for PBDE contamination of the lake sediments. Following our previous report on Lake Superior (*1*), in this paper we present the results on the spatial distribution and input chronology of PBDEs in the sediments of Lakes Michigan and Huron.

Lake Michigan and Lake Huron have many things in common. They rank as the second and third largest among the Great Lakes, are located at the same elevation and similar latitudes, with almost the same land drainage and water areas. Both lakes stretch south to north, with the southern parts being warmer and more densely inhabited than the northern parts. The Chicago−Milwaukee metropolitan area on the southwest shore of Lake Michigan is the most urbanized area in the region, with about 8 million people or about one-fifth of the total population of the Great Lakes region. Discharges of PCBs to Lake Michigan from the eight areas of concern (AOCs), including the Fox River/Green Bay, WI, the Waukegan Harbor in Illinois, and the Grand Calumet River and Indiana Harbor in northern Indiana, are well documented (*2*). Lake Huron receives PCBs and pesticides from the intensively farmed Saginaw River basin and Bay City (*3*).

With about 40% of the world total consumption of PBDEs occurring in North America (*4*), it is not surprising that PBDEs have been found in the fish of all the Great Lakes (*5*, *6*). Lake Michigan fish contain 6 times more PBDEs than Baltic salmon (*7*), and their concentration is the highest among all the Great Lakes (*5*). In addition, the correlation of PBDE tissue concentration with age in Lake Michigan salmon implies that PBDEs have been in the lake for many years (*4*). The increasing trend in concentration in fish of the Great Lakes from 1980 to 2000 has been confirmed by analyzing archived fish samples (*5*). Compared with fish, PBDE contamination of the sediments is less investigated. In a study of the southeastern area of Lake Michigan, PBDEs in sediments were found to have increased since the 1980s, while PCB contents decreased during the same time period (*8*). No previous research on PBDEs in the sediments of Lake Huron has been reported.

In this study, a total of 75 samples from 6 sediment cores collected in Lakes Michigan and Huron were analyzed for 10 PBDE congeners as well as 39 PCBs. For each sampling location, a concentration profile was constructed against sediment depth. Inventory was calculated to assess the chemical accumulation. The temporal trend of chemical loading rate, or flux, to the sediments was demonstrated.

Experimental Section

Sampling and Sample Characterization. Sediment sampling was conducted on Lake Michigan in May and Lake Huron in August 2002 on board the EPA R/V *Lake Guardian*. Sampling and sample storage procedures as described in ref *1* were followed. The sampling locations are shown in Figure 1, and the geographic coordinates are given in Table 1. At each sampling location, four or five subcores were taken using the box corer of the ship. They were extruded and sectioned immediately after the sample collection. For the cores collected in Lake Michigan, 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. The cores collected in Lake Huron were sectioned at 0.5 cm intervals down to a depth of 1 cm, 1.0 cm intervals to 10 cm, and then 5 cm increments for the rest of the core. The segments in all the subcores with the same depth at the same site were combined into a precleaned amber glass jar. All samples were refriger-

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[*] Corresponding author phone: (312) 996-9597; fax: (312) 413-9898; e-mail: anli@uic.edu.

[†] School of Public Health.

[‡] Department of Earth and Environmental Sciences.

[§] Department of Civil and Materials Engineering.

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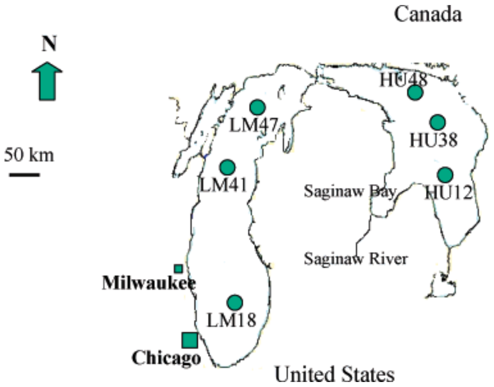

FIGURE 1. Sampling locations.

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	sedimentation rate ($g\ cm^{-2}\ yr^{-1}$) CRS	focusing factor
LM18	42°43′00″	87°00′00″	0.0370	0.0362	2.86
LM41	44°44′12″	86°43′14″	0.0362	0.0457	1.49
LM47	45°10′42″	86°22′58″	0.0265	0.0353	1.45
HU12	43°53′24″	82°03′24″	0.1000	0.0913	2.44
HU38	44°44′30″	82°03′15″	0.0226	0.0242	0.76
HU48	45°16′42″	82°27′06″	0.0225	0.0295	0.88

ated at 4 °C on the ship, and transported in coolers to the laboratory, where they were frozen until analysis.

Contents of the organic matter, organic carbon, soot carbon, nonsoot carbon, nitrogen, and oxygen, as well as solid content, wet and dry bulk density, particle density, and porosity, were measured for each sample with methods described elsewhere (*9*).

^{210}Pb Dating. Each segment of the sediment core was dated by the ^{210}Pb method, using a ^{209}Po tracer. Detailed procedures can be found in ref *1*. Briefly, the sample was dried, ground, and weighed before digestion with HCl and H_2O_2. The solution was then filtered and reduced in volume before pH adjustment and plating of ^{209}Po and ^{210}Po, the granddaughter of ^{210}Pb, on a flat copper disk. The plated disks were counted for α emissions using a Canberra Alpha Analyst system (Meriden, CT). Counting statistical errors were better than ±3%.

After corrections for detector efficiency and time elapsed between plating and counting, unsupported ^{210}Pb activities were obtained by subtracting the supported activity determined for the location from the measured value. Using both the constant initial concentration (CIC) and the constant rate of sedimentation (CRS) models (*10, 11*), the sedimentation rate was estimated from the slope of the regression of the ^{210}Pb concentration, as explained in the Supporting Information. The focusing factor at each location was determined as the ratio of the ^{210}Pb inventory to the cumulative ^{210}Pb expected from atmosphere deposition in the Great Lakes region (*12*).

Chemical Analysis. Sediment sample preparation and chemical analysis followed the same procedure used in ref *1*. Ten PBDEs were measured, including congeners 28, 47, 66, 85, 99, 100, 153, 154, 183, and 209. The number of PCB congeners analyzed was 39, including those with congener IUPAC No. 1, 2, 3, 4, 6, 8, 9, 16, 18, 19, 22, 25, 28, 52, 44, 56, 66, 67, 71, 74, 82, 87, 99, 110, 138, 146, 147, 153, 173, 174, 177, 179, 187, 180, 194, 195, 199, 203, and 206.

An aliquot of a thawed and homogenized sample was weighed and mixed with sufficient Hydromatrix (Varian, Palo Alto, CA). The dried sample was transferred to a Whatman cellulose thimble, and spiked with known amounts of PBDE surrogates ^{13}C-labeled 2,3′,4,4′,5-pentabromodiphenyl ether (BDE118) and ^{13}C-labeled BDE209, and PCB surrogate 2,3,5,6-tetrachlorobiphenyl (PCB65). The sample was then extracted in a Soxhlet extractor for 20 h with 150 mL of a 1:1 (v/v) hexane/acetone mixture. Sulfur in the sediment was removed by adding activated granular copper to the Soxhlet flask during extraction. The extract was concentrated on a Kuderna−Danish (K−D) concentrator, solvent-exchanged to hexane, and cleaned up on fully activated silica gel. The eluant was concentrated on the K−D concentrator, and the volume was further reduced to about 1 mL by a gentle stream of N_2. The final volume of the sample was 2.0 mL.

Quantitative analyses of PCBs and PBDEs were performed on an HP 6890 gas chromatograph coupled with an HP 5973 mass spectrometer. The mass spectrometer was operated in the SIM mode. For PCBs and PBDEs other than BDE209, electron impact mass spectrometry (MS) was used. PCB204 and BDE190 were used as internal standards for PBDE quantification, and PCB30 and PCB204 were used as internal standards for PCBs. BDE209 was analyzed by negative chemical ionization (NCI) MS, with a fragment ion of m/z 486 for quantitation.

Quality Control. The surrogate recoveries for tri- through hepta-BDEs were in the range of 70−170%, with a mean of 112%. The surrogate recoveries for BDE209 were in the range of 27−91%, with a mean of 57%. The mean recovery for PCBs was 116%, ranging from 60% to 160%. All the concentration data reported in this paper are after corrections using surrogate recoveries. NIST Standard Reference Material 1939a (river sediment) was analyzed, and our results were within 70−120% of the certified PCB congener concentrations. Six sediment samples, one for each core, were analyzed in duplicate. The average RSD was 12−50% for the nine PBDE congeners and 2−40% for PCBs. Method blanks were also run for each core. The levels of analytes found in method blanks were comparable to those in the matrix blanks that were pre-1900 sediment segments. The average of the chemical concentrations in the matrix blanks of each core was subtracted from the results of chemical analysis.

Results and Discussion

Unsupported ^{210}Pb activity is plotted against the cumulative dry mass of sediment in Figures S1 and S2 of the Supporting Information. Sedimentation rates and focusing factors calculated from these data are summarized in Table 1. The average sedimentation rate obtained from using the CIC and CRS models was used in the estimation of chemical flux. Concentrations of the sum of 9 PBDE congeners with 3−7 bromines ($\sum_9$PBDEs), BDE209, and PCBs ($\sum_{39}$PBDEs) in 75 samples from 6 cores were quantitatively measured, and are illustrated in Figure 2 as a function of sediment depth. To compare the current levels of sediment contamination at different locations, the surface concentrations at each of the six sampling sites are given in Table 2. All concentrations are reported on the basis of the dry sediment weight. The inventory and flux of the chemicals to the sediment were estimated using eqs 1 and 2

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

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

respectively (*1*), where C_i is the concentration in sediment segment i (ng g^{-1} of dry weight), ρ_b is the dry mass bulk density ($g\ cm^{-3}$), d_i is the thickness of segment i, FF is the focusing factor of the location, and R_i is the sedimentation rate ($g\ cm^{-2}\ yr^{-1}$). The results of the calculations are presented in Table 2. The chronology of PBDE and PCB inputs to the sediments is illustrated in Figure 3.

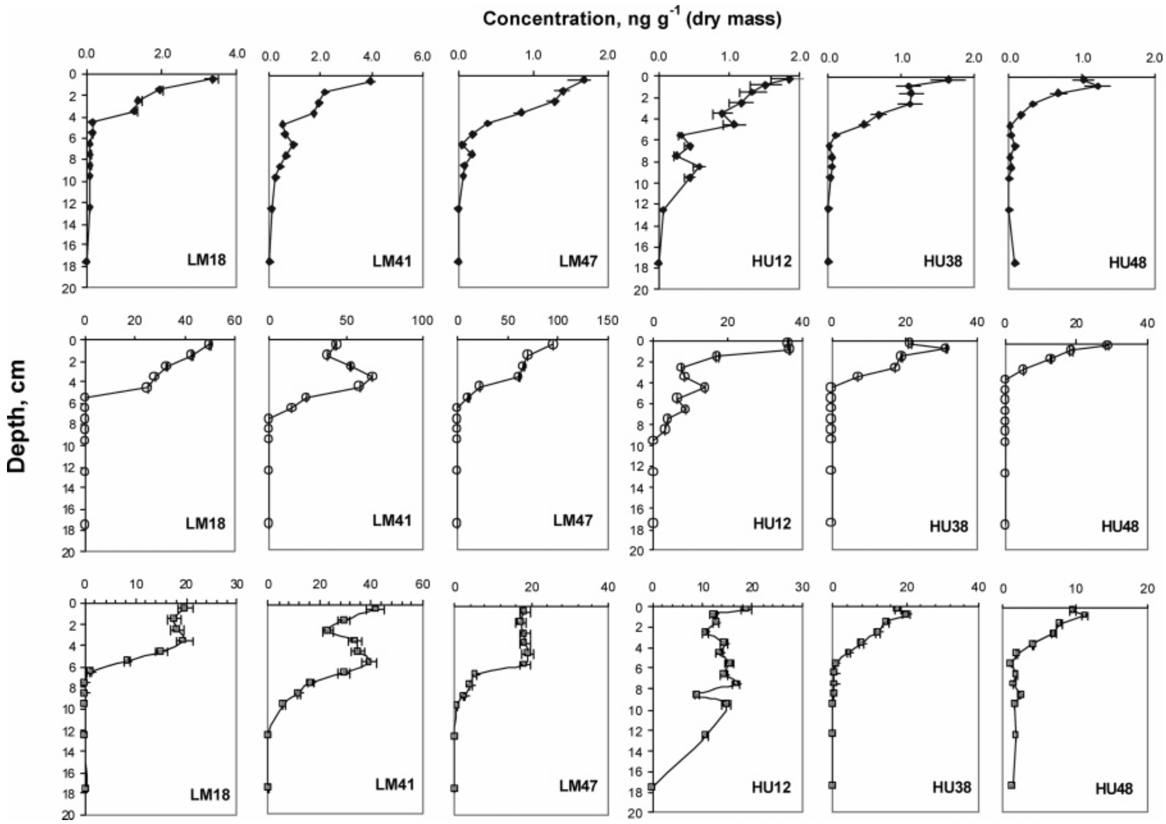

FIGURE 2. Concentrations versus depth in Lakes Michigan and Huron: filled tilted square, $\sum_9$PBDEs; empty circle, BDE209; gray square, $\sum_{39}$PCBs.

TABLE 2. Surface Concentration, Surface Flux, and Inventory of PBDEs and PCBs in the Sediments of Lakes Michigan and Huron

	$\sum_9$PBDEs			BDE209			$\sum_{39}$PCBs		
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})
LM18	3.34	4.12	0.043	49.9	82.0	0.64	19.8	45.7	0.25
LM41	3.97	2.22	0.109	43.9	48.6	1.20	41.7	48.1	1.14
LM47	1.67	1.32	0.036	95.6	68.5	2.04	18.3	27.3	0.39
HU12	1.87	2.23	0.073	36.0	25.1	1.41	18.7	56.3	0.73
HU38	1.65	1.14	0.051	21.5	14.0	0.67	17.6	12.5	0.54
HU48	1.02	0.90	0.030	28.8	8.64	0.86	7.8	6.21	0.23

PBDEs in Lake Michigan. The concentrations of $\sum_9$PBDEs in the surficial sediments at sampling locations LM18, LM41, and LM47 are 3.3, 4.0, and 1.7 ng g^{-1} of dry weight, respectively. On the basis of organic carbon (OC), the corresponding values at the three locations are 48, 67, and 29 ng g^{-1} of OC, with an average of 48 ng g^{-1} of OC, nearly double the average of 28 ng g^{-1} of OC in Lake Superior (*1*). Compared to Hadley Lake in Indiana, which is 1.3 km away from the research and development facility of a PBDE-producing manufacturer, the average $\sum_9$PBDE concentration in surficial sediments of Lake Michigan is about half that in Hadley Lake, 103 ng g^{-1} of OC (*13*). As the depth of the sediment cores increases, the $\sum_9$PBDE concentration decreases in a generally monotonic pattern. These concentration profiles reflect well the increasing production and usage of the commercial PBDE products in recent decades. The fact that the maximum concentrations appear in the top layers of sediments implies the possibility that the increasing trend of PBDE inputs to the lake continues after 2002. Using the data measured in segments deposited in the early 1970s, the time for the concentration to double, t_2, in the sediments ranges from 10 yr at LM41 to 13 yr at LM47. These t_2 values are apparently longer than the 3 yr reported for Great Lakes fish (*5*) and the 5 yr reported for human blood and tissues (*14*). This may reflect the recycling of chemicals due to sediment resuspension (*15*, *16*), which dilutes the concentrations and impedes the increasing trend of chemicals in the sediments. Biological transformation in the sediment is also a potential sink for PBDEs.

The concentration of BDE209 in the surficial sediments is 63 ng g^{-1} of dry weight or 1050 ng g^{-1} of OC, averaged over the three sampling sites in Lake Michigan. The concentration is lower than 112 ng g^{-1} of dry weight, the reported BDE209 concentration in a surficial sediment of Lake Ontario (*17*). The concentrations increase toward the sediment surface in two of the three cores. At LM41, BDE209 peaked at a sediment depth of 3−4 cm. The reason for this is not clear. However, examinations of the profiles of ^{210}Pb concentration versus cumulative dry mass of the sediment (Figure S1) and PCB concentration versus depth (Figure 1) indicate the possibility of severe sediment mixing around 1980 at this site. Compared with other congeners, BDE209 is more hydrophobic and particle bound, and thus may be more susceptible to particle mixing than other congeners (*17*).

Inventory of the contaminants in sediments represents the total integrated mass of the compounds of interest per

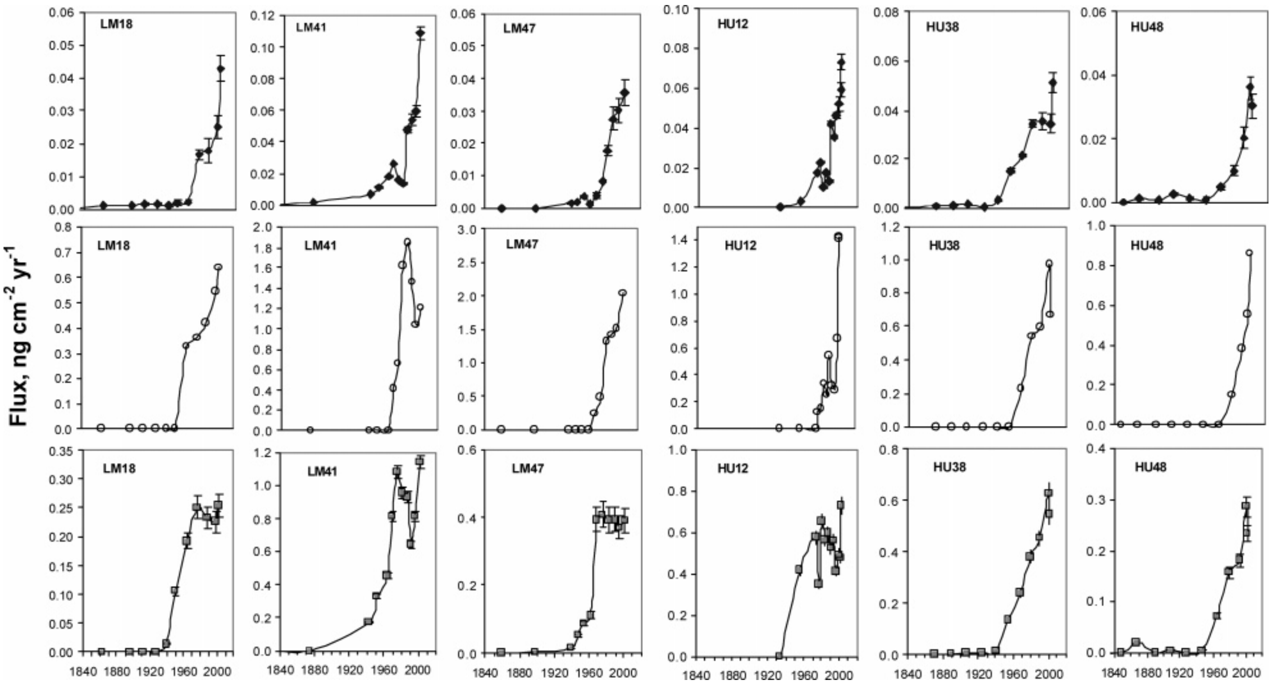

FIGURE 3. Fluxes to the sediments of Lakes Michigan and Huron: filled tilted square, $\sum_9$PBDEs; empty circle, BDE209; gray square, $\sum_{39}$PCBs.

unit area. In Lake Michigan, the inventories for $\sum_9$PBDEs range from 1.3 to 4.1 ng cm^{-2}, and those of BDE209 from 49 to 82 ng cm^{-2} (Table 2). The inventories at three sampling locations are in the order LM18 > LM41 > LM47, the same order of proximity to the large urban areas in the region. Using the inventory values at these locations, we estimate that the total load of $\sum_9$PBDEs in the sediments of Lake Michigan, which has a water surface area of 57800 km^2, would be in the range of 760−2400 kg. If BDE209 is included, the total load of PBDEs is estimated to range from 29000 to 50000 kg.

Flux of the chemicals into a sediment segment was calculated by dividing the product of the concentration and the sedimentation rate by the focusing factor (eq 2 in ref *1*). The fluxes are plotted against the sediment deposition year in Figure 3. The current $\sum_9$PBDE fluxes, as observed at the sediment surface for the three locations in Lake Michigan, are in the range of 36−109 pg cm^{-2} yr^{-1}, with an average of 60 pg cm^{-2} yr^{-1}, nearly 3 times higher than that of Lake Superior (*1*). On the basis of the range of the flux, we estimate that the loading of $\sum_9$PBDE to Lake Michigan is from 20 to 63 kg yr^{-1}. The total loading of PBDEs, including BDE209, would be at a rate of 390−1200 kg yr^{-1} in the year 2002.

As expected, the PBDE fluxes at all locations were generally in continuous and obvious increase since the 1970s when PBDE commercial production began, and the temporal trends coincide well with the increasing PBDE production and usage. However, in contrast to the patterns of surficial concentration and inventory, the surficial flux of $\sum_9$PBDEs at site LM41 is about twice that at LM18 and LM47 (see Table 2). For BDE209, the current fluxes are in the order LM47 > LM 41 > LM18. Higher input rates of polycyclic aromatic hydrocarbons (PAHs) in the northern basin relative to the southern basin of the lake have been reported (*12*), and these correspond to the rate of soot deposition (*9*). In addition to air deposition and sediment focusing within the basin, the inputs of PBDEs at LM41 and LM47, both in the northern basin, may include the transport of contaminated sediments, especially the resuspended fine particles, from the southern basin to the northern basin in the water column. The sediment resuspension in the southern basin is discussed by Lou et al. (*18*). Although the majority of the fine sediment particles in the southern basin are focused to deep quiescent zones, a portion of the suspended and resuspended particles in the south basin are constantly transported by the water current across the sill that separates the north and south basins (*12*). Because PBDEs are in general more particle bound than PAHs and PCBs, we speculate that the fractions of PBDE transported across the basins in this way are more significant than those reported for PAHs and PCBs (*12*), adding to the input from the atmosphere and other sources to the north basin of the lake.

PBDEs in Lake Huron. The sampling locations HU38 and HU48 are in the Manitoulin Basin of Lake Huron. HU12 is southeast, thus downstream, of the Saginaw Bay, into which the Saginaw River flows, carrying pollutants such as PCBs (*3*, *19*). The $\sum_9$PBDE concentrations in surficial sediments at the three sites range from 1.0 to 1.9 ng g^{-1} of dry weight, with an average of 1.5 ng g^{-1} of dry weight. Similar to Lake Michigan, the concentrations in the cores of Lake Huron decrease with increasing core depth in most cases. An exception is the concentration of $\sum_9$PBDEs at HU48, where the maximum concentration appeared in the second uppermost segment. Interestingly, although the average $\sum_9$PBDE concentration in surficial sediments of Lake Huron is only about half that in Lake Michigan on the basis of dry sediment weight, the OC-normalized concentration, averaging 44 ng g^{-1} of OC, is close to that in Lake Michigan, due to relatively low OC contents in Lake Huron. The concentration doubling time (t_2) for $\sum_9$PBDEs is similar to that in Lake Michigan, ranging from 10 to 12 yr with the exception of HU38, where t_2 is found to be ∼20 yr. The concentrations show a south to north gradient, and the relatively high concentration in HU12 may relate to the potential input of PBDEs from the Saginaw River and Bay area. For northern Lake Huron, given the fact that the area is sparsely populated and lacks a large river input, the PBDEs found at HU38 and HU48 may represent the background air deposition to the area.

The inventories of both $\sum_9$PBDEs and BDE209 are in the order HU12 > HU38 > HU48 (Table 2), again showing the dependence on the proximity to urban areas. Though direct inputs of PBDEs from local industries, waste treatment effluents, and other urban sources cannot be ruled out, a

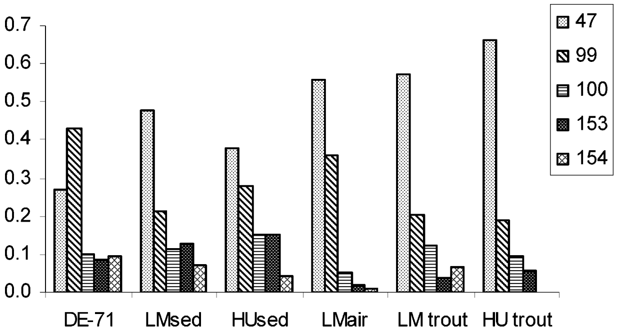

FIGURE 4. Comparison among PBDE congener patterns in sediments and trout fish of Lake Michigan and Lake Huron (*6, 14*), air samples close to Lake Michigan (*21*), and the commercial penta mixture (*13*). For Lake Huron trout, data on BDE154 are not available, and the fractions are based on the sum of the other four congeners.

decreasing trend of PBDE inventory with increasing latitude is observed for both Lake Michigan and Lake Huron. Additional data over a much longer distance in North America are needed to examine the dependence of the PBDE inventory on latitude. Using the inventory values given in Table 2, the total load of $\sum_9$PBDEs in the sediment of Lake Huron (water surface area 59600 km^2) is estimated to be in the range of 540−1330 kg. When BDE209 is included, the total loads of PBDEs are estimated to range from 6000 to 15000 kg.

The $\sum_9$PBDE fluxes to Lake Huron around 2002 are in the range of 30−73 pg cm^{-2} yr^{-1}, with an average of 50 pg cm^{-2} yr^{-1}. The surficial $\sum_9$PBDEs fluxes are in the order HU12 > HU38 > HU48, while BDE209 fluxes follow the order HU12 > HU48 > HU38. For BDE209, the average flux is 0.98 ng cm^{-2} yr^{-1}, ranging from 0.67 to 1.41 ng cm^{-2} yr^{-1}. Using these data, we estimate that the current loading rates to Lake Huron sediments are 18−43 kg yr^{-1} for $\sum_9$PBDEs and 400−840 kg yr^{-1} for BDE209.

PBDE Congener Patterns. In both Lakes Michigan and Huron, the predominance of BDE209 among the total PBDEs in sediments is unquestionable. The inventories of BDE209 in Lakes Michigan and Huron are in the range of 95−98% (average 96%) and 87−93% (average 91%), respectively, of total PBDEs by mass. Compared to Lake Superior, where the inventories ranged from 83% to 94% (average 89%), the fraction of total PBDEs represented by BDE209 in Lake Michigan is noticeably higher than those of Lakes Huron and Superior. BDE209 counts for 82% of the total PBDE production in 1999 (*4*). Its higher percentage in the sediment reflects its higher affinity for the sediment organic matter compared with those of other congeners. In addition, it has a relatively short characteristic travel distance (CTD) in the atmosphere (*20*). Its long-range transport, however, is evidenced by its measurable concentrations in the sediments of not only the remote Great Lakes but also the Arctic lakes (*17*).

Among the nine non-deca congeners, BDE47 and BDE99 are more abundant than the others. These two congeners constitute 44−65% of the $\sum_9$PBDE inventories over the three locations in Lake Michigan, and 42−52% in Lake Huron. In Figure 4, the lakewise sediment pattern of the five most frequently found non-deca-PBDE congeners is compared with those in the U.S. commercial product DE-71 (*13*), and the air and fish samples collected in Lake Michigan and Huron (*6, 14, 21*). As can be predicted from the relative hydrophobicity and affinity for solids, higher fractions of more heavily brominated congeners are found in sediment than in air and fish. The sediment pattern resembles the commercial penta mixture, except the abundance shift between BDE47 and BDE99. BDE47, 2,2′,4,4′-tetrabromodiphenyl ether, is more volatile than BDE99, 2,2′,4,4′,5-pentabromodiphenyl ether, thus present in air in a higher amount and with a concomitantly farther transport distance (*21*). Recent studies also reveal that BDE47 is relatively stable when exposed to sunlight due to the lower number and the substitution position of the bromine atoms compared to those of many other BDE congeners (*22*). The formation of BDE47 in the environment, resulting from the photolysis of BDE209, is also possible (*23, 24*). The sediment congener pattern observed in this work, as well as that found in fish (*4−7, 14*), seems to support these findings.

PCBs in Lakes Michigan and Huron. A noticeable difference between the concentration profiles of PBDEs and PCBs is that PCB concentrations level off at most locations while PBDEs increase monotonically to the sediment surface, as shown in Figure 2. The surficial PCB concentration ranges from 8 ng g^{-1} at HU48 to 42 ng g^{-1} at LM41 (Table 2), comparable to those reported in the past (*3, 25−27*). Similar to $\sum_9$PBDE results, the average $\sum_{39}$PCB concentration in surficial sediments of Lake Michigan is nearly twice that in Lake Huron on the basis of the dry sediment weight, while the OC-normalized concentration levels are similar for both lakes. A comparison with Lake Superior was made on the basis of 11 PCB congeners with IUPAC Nos. 8, 18, 28, 44, 52, 66, 153, 180, 187, 195, and 206. The result shows that, on a dry weight basis, PCB concentrations in Lakes Michigan and Huron are about 4 and 2 times that in Lake Superior, respectively.

The inventories of PCBs at LM18 and LM41 are similar, and greater than that at LM47. The average inventory at these three locations is 40 ng cm^{-2}. The surface fluxes of $\sum_{39}$PCB in Lake Michigan are in the range of 0.25−1.14 ng cm^{-2} yr^{-1} (Table 2), which is in rank order agreement with the results reported previously (*25, 26*), and about 5 times higher than that of Lake Superior on the basis of a comparison of the 11 congeners mentioned above. As illustrated in Figure 3, peaks or plateaus of PCB fluxes were observed in the 1970s, followed by a decrease in later years. However, a noticeable increase appears in recent years at site LM41. The complexity of PCB flux trends reflects the status of PCB pollution in the region. Since the ban on PCB production and usage in the 1970s, large-scale direct release of PCBs has been halted. However, due to historic discharges, many nonpoint sources still exist, and several areas of concern with heavy PCB pollution still require cleanup. For example, the Kalamazoo and Sheboygan Rivers in the southern region and the Fox and Manistique Rivers in the northern region have brought significant amounts of PCBs to Lake Michigan (*2*). In addition, the emissions from PCB waste storage facilities, and evaporation from contaminated soil and solid surfaces in urban areas, may constitute sources of continued input of PCBs in recent decades (*19*).

The PCB inventories in Lake Huron show a latitudinal gradient of HU12 > HU38 > HU48, with an average of 25 ng cm^{-2}. This gradient may be due only partially to the atmospheric deposition during their long-range transport from the source region to the polar region, because HU12 has likely received PCBs from direct discharge sources in the Saginaw River and Bay area (*3, 19*), and the relative contributions from different sources are not clear. The recent fluxes of $\sum_{39}$PCB in Lake Huron are in the range of 0.23−0.73 ng cm^{-2} yr^{-1}, which are comparable with those observed for Lake Michigan (see above). At HU38 and HU48, the decrease in PCB flux seems not to have occurred until after the mid-1990s, evidenced by the increases toward the sediment surface until the second uppermost segments.

Acknowledgments

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Supporting Information Available

Two figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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