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Brominated Flame Retardants in Sediment Cores from Lakes Michigan and Erie

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The history of polybrominated diphenyl ethers (PBDEs) and the major polybrominated biphenyl congener (BB-153) was studied in dated sediment cores taken from Lakes Michigan and Erie. The surficial concentration of total PBDE (320 ng/g dry weight) in Lake Michigan was about 10 times higher than that in Lake Erie (40 ng/g) and in Lake Superior (∼12 ng/g). The concentrations of total PBDEs in these sediments have increased rapidly, with doubling times of 5−10 years, reflecting the increasing market demand for these flame retardants over the last 30 years. BDE-209 was found to be the predominant congener in both sediment cores, making up 95−99% of the total PBDE load. The inventories of total PBDEs in Lakes Michigan and Erie were 190 and 40 ng/cm^2, respectively. The total burdens of these compounds in the sediment of Lakes Michigan and Erie were 110 and 10 metric tons, respectively. We estimate that the total burden of these compounds in all of the Great Lakes is on the order of 200 tons. In both lakes, BB-153 was found to increase rapidly during the 1970s and to peak around 1980.

Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants that are widely used in a variety of consumer and commercial products, such as furniture, textiles, polyurethane foam, and thermoplastics (*1*−*3*). PBDEs can escape from these products during their production, use, and disposal (*4*), and as a result, these compounds are now ubiquitous in the environment and in people. Recently, Hites (*5*) summarized PBDE concentrations in different environmental media and reported that total PBDE concentrations in human blood, milk, and tissue have increased exponentially by a factor of ∼100 during the last 30 years. Some PBDE congeners bioaccumulate and biomagnify in both aquatic and terrestrial ecosystems (*6*), and some PBDE congeners may affect liver enzyme activity, induce immunotoxicity, and affect neurological development at a sensitive period of brain growth in mice and rats (*7*−*10*). Because of their increasing levels in the environment and their potential human health effects, lower molecular weight PBDEs have been banned in Europe and in certain U.S. states (*11*). In fact, the major manufacturer of these compounds has voluntarily stopped their production (*12*), and soon decabromodiphenyl ether will be the only PBDE in production and use.

Many semivolatile organic compounds can be transported through the atmosphere, enter the water column, and deposit in the sediment (*13*); in fact, atmospheric deposition is the major source of PBDEs to many aquatic sediments and terrestrial soils (*14*). Given that PBDEs are lipophilic and have low vapor pressures and high octanol−water partition coefficients (*10*), it is not surprising that PBDEs bind well to particles and have a tendency to accumulate in lake sediments (*9*, *15*). PBDEs have been found in sediments from Japan (*16*), the Baltic Sea (*17*), Europe (*18*, *19*), and the United States (*20*). Assuming that the sediment accumulates regularly over time, a sediment core can serve as an historical archive of the deposition of persistent organic pollutants into a lake's ecosystem. This approach has been widely used for polychlorinated pesticides, biphenyls, dibenzo-*p*-dioxins, and dibenzofurans and for polycyclic aromatic hydrocarbons (*21*−*24*).

There have been few such studies of the deposition of PBDEs to sediments. These studies have focused on time trends of PBDEs in sediment cores from the Baltic Sea; from Oslo, Norway; from Osaka Bay, Japan; and from Lake Superior (*17*, *25*, *26*). In this paper, we present results on PBDE concentrations, fluxes, and burdens as a function of time in sediment cores from two of the Great Lakes: Lakes Michigan and Erie. We also include information on the historical deposition of a polybrominated biphenyl (PBB) into the Great Lakes. These flame retardants were banned in 1976 in the United States after a disastrous accident that caused many human and animal health problems (*27*), but as we will show, PBBs are still present in the Great Lakes.

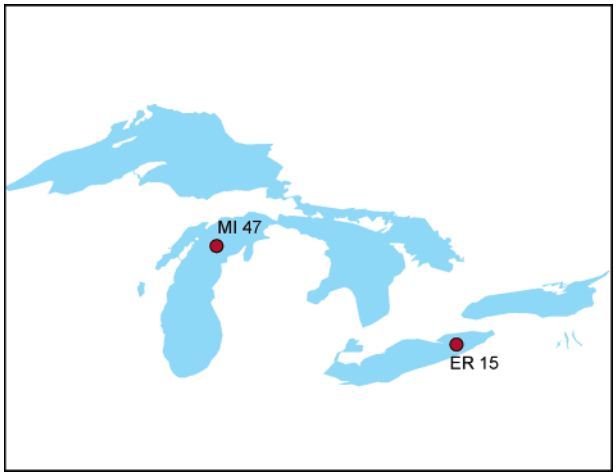

FIGURE 1. Map of the Great Lakes showing the sediment core sampling locations in Lakes Michigan and Erie.

Experiment Section

Sampling Sites. A sediment core was taken from northern Lake Michigan at the end of April, 2004, at site MI47, where the water depth was 197 m. A sediment core was also taken from the eastern basin of Lake Erie at site ER15 in August, 2003, where the water depth was 62 m. This Lake Erie site has a particularly high rate of sediment deposition. Details on both sites are given in Figure 1 and Table 1. In both cases, a 30 cm × 30 cm × 52 cm box corer was deployed from the U.S. EPA's research vessel, the *Lake Guardian*. Once the box core was back on the deck, three subcores were taken by carefully inserting subcore tubes (10 cm i.d. × 60 cm) into the sediment box in such a way as to avoid distortion of the sediment. These cores were 51 cm in length. For Lake Michigan, the cores were cut into 0.5-cm intervals down to 10 cm and in 1-cm intervals afterward. For Lake Erie, the

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TABLE 1. Sampling Locations, Sedimentation Rates, and Focusing Factors at Two Sites in the Great Lakes

site	sampling location lat. (N)	sampling location long. (W)	A_0 (dpm/g)	A_f (dpm/g)	sediment rate ($g \cdot cm^{-2}$ $year^{-1}$)	FF
Michigan	45° 10.704′	86° 22.521′	69.62	3.39	0.051	3.3
Erie	42° 31.030′	79° 53.642′	11.60	2.98	0.73	7.9

cores were cut into 1-cm intervals down to 30 cm and in 2-cm intervals afterward. The samples were immediately frozen, stored at −30 °C, and returned to our laboratory.

Sediment Dating. One of the subcores from each location was used for dating by measuring the specific activities of ^{210}Pb. These samples were air-dried for 2 weeks, ground in a mortar, and sieved through a 2-mm mesh screen. Each sample was loaded into a Petri dish (50 mm o.d. × 9 mm), and the ^{210}Pb activities were measured by γ-spectrometry at 46.54 keV, using a high-purity germanium detector (Canberra GL 2820R, Canberra Industries, Meriden, CT).

Materials. The 18 PBDE congeners investigated in this study were 2,2′,4-TrBDE (BDE-17); 2,4,4′-TrBDE (BDE-28); 2,2′,4,4′-TeBDE (BDE-47); 2,2′,4,5′-TeBDE (BDE-49); 2,3′,4,4′-TeBDE (BDE-66); 2,3′,4′,6-TeBDE (BDE-71); 2,2′,3,4,4′-PeBDE (BDE-85); 2,2′,4,4′,5-PeBDE (BDE-99); 2,2′,4,4′,6-PeBDE (BDE-100); 2,2′,3,4,4′,5′-HxBDE (BDE-138); 2,2′,4,4′,5,5′-HxBDE (BDE-153); 2,2′,4,4′,5,6′-HxBDE (BDE-154); 2,2′,3,4,4′,5′,6-HpBDE (BDE-183); 2,3,3′,4,4′,5,6-HpBDE (BDE-190); 2,2′,3,3′,4,4′,5,5′,6-NonaBDE (BDE-206) (Wellington Laboratories, Ontario, Canada); 2,2′,3,3′,4,4′,5,6,6′-NonaBDE (BDE-207) (Wellington Laboratories); 2,2′,3,3′,4,5,5′,6,6′-NonaBDE (BDE-208) (AccuStandard, New Haven, CT); and decabromodiphenyl ether (BDE-209). All of these compounds, except for the nonabrominated BDEs, were purchased in nonane solution from Cambridge Isotope Laboratories (Cambridge, MA). In addition, we investigated an abundant polybrominated biphenyl (PBB) congener, 2,2′,4,4′,5,5′-hexabromobiphenyl (BB-153), a standard of which was purchased from Ultra Scientific (North Kingstown, RI). The standard compound, 2,3′,4,4′,5-PeBDE (BDE-118), was donated to us by Cambridge Isotope Laboratories. This compound is not present in the ambient environment. All the solvents used for the extraction and cleanup procedures were residue-analysis grade.

Sample Preparation. Approximately 15 g of wet sediment was well-mixed with 100 g of precleaned, anhydrous Na_2SO_4 (to remove water) and with 20 g of precleaned granular copper (20−30 mesh, J. T. Baker), which was used to remove elemental sulfur (*28*). After spiking with a known amount of the standards $^{13}C_{12}$-2,3,3′,4,4′,5-hexachlorodiphenyl ether (CDE-156) and $^{13}C_{12}$-2,2′,3,3′,4,4′,5, 5′-octachlorodiphenyl ether (CDE-194) (Cambridge Isotope Laboratories), the samples were Soxhlet extracted for 24 h with a 1:1 acetone−hexane mixture. Throughout the extraction and analysis procedure, the analytes were protected from light by wrapping the containers with aluminum foil or by using amber glassware.

After evaporating most of the solvent, ∼4 mL of concentrated H_2SO_4 (EM Science, Gibbstown, NJ) was added to remove fat and organic polymers from the extracts. After centrifugation for 10 min, the hexane layer was recovered, 5 mL of fresh hexane was used to wash the sulfuric acid residue, and the two hexane extracts were combined. After reducing the extract volume to ∼1 mL under a clean N_2 flow, the samples were loaded onto a 3% water deactivated silica (Grace Davison, Columbia, MD) column (1.9 cm i.d. × 20 cm). One fraction of 150 mL dichloromethane was collected. The solvent was blown down with clean N_2 to 500 μL, and the samples were fractioned on an alumina (ICN Biomedicals GmbH, Eschwege, Germany) column (0.6 cm i.d. × 6 cm). The column was first eluted with 8 mL of hexane followed by 8 mL of a 2:3 dichloromethane−hexane mixture. The PBDEs eluted in the second fraction. After solvent exchange to hexane, BDE-118 and decabromobiphenyl (BB-209, purchased from Dr. Ehrenstorfer, GmbH, Augsburg, Germany) were added as standard compounds, and the samples were analyzed by GC−MS.

Instrumental Analysis. The samples were analyzed on an Agilent 6890 series gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC−MS) with helium as the carrier gas. The 2 μL injections were made in the pulse splitless mode, with a purge time of 2.0 min. The injection port was held at 285 °C. For the determination of all PBDEs and BB-153, except for the nonabrominated BDEs and BDE-209, the GC column used was a 60 m × 250 μm (i.d.) fused silica capillary tube coated with DB-5-MS (0.25 μm film thickness; J&W Scientific, Folsom, CA). A 60-m column was used to ensure separation of BDE−154 from BB-153. The GC oven temperature program was as follows: isothermal at 110 °C for 1.90 min, 15 °C/min to 180 °C, 1.85 °C/min to 300 °C, and held at 300 °C for 45 min. The GC to MS transfer line was held at 285 °C. The mass spectrometer was operated in the electron capture negative ionization mode using methane as the reagent gas, and the ion source temperature was 150 °C. Selected ion monitoring of the two bromide ions at m/z 79 and 81 was used to detect the PBDEs and BB-153. The ions at m/z 351.9 and 349.9 due to $(M - HCl + 2)^-$ and $(M - HCl)^-$ were used to detect CDE-156, and ions at m/z 457.8 and 455.8 due to $(M + 4)^-$ and $(M + 2)^-$ were used to detect CDE-194. The response factors for all compounds were determined using a solution with known amounts of all the target compounds and of all of the standard compounds. BDE-118 was used to quantitate the PBDEs (except for the nonabrominated BDEs and BDE-209) and BB-153. $^{13}C_{12}$-DE-156 was used as a retention time reference, and $^{13}C_{12}$-CDE-194 was used to monitor the experimental recovery of the above compounds.

All of the samples were quantified for the nonabrominated BDEs and BDE-209 separately on a shorter DB-5-MS column (15-m × 250-μm i.d.; 0.25-μm film thickness; J&W Scientific) with the following temperature program: 110 °C for 1 min, 15 °C/min to 300 °C, and held at 300 °C for 17 min. ECNI selected ion monitoring of the ions at m/z 486.6 and 488.6 was used to detect BDE-209; m/z 79 and 81 were used for quantitation of the nonabrominated BDEs and m/z 561.6 and 563.6 for identification. BB-209 (m/z 79 and 81) was used as the standard to quantitate the nonabrominated BDEs and BDE-209 in the sediment samples. BB-209 also served as a retention time reference. All concentrations are given on a dry weight of sediment basis.

Quality Control. Three quality control criteria were used to ensure the correct identification of the target compounds: (a) The GC retention times matched those of the standard compounds within ±0.3 min. (b) The signal-to-noise ratio was greater than 3:1. Under these conditions, the detection limits were in the range of 0.01−0.15 ng/g wet weight, depending on the individual congener. (c) The isotopic ratio between the ion pairs was within ±15% of the theoretical value. The recoveries of all the congeners except for BDE-209 were between 80 and 103%. For BDE-209, the recovery was ∼40%. All measurements were corrected for recoveries.

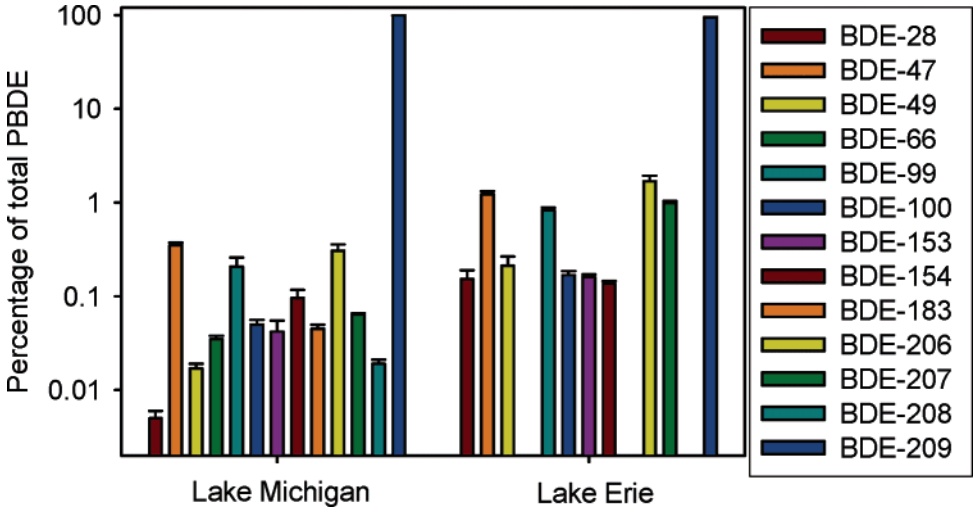

FIGURE 2. PBDE congener patterns (given as percent of total) in sediments from Lakes Michigan and Erie. Note the logarithmic scale. Congeners 17, 71, 85, 138, and 190 were not detected in any of the samples.

Each batch of eight samples included one method blank to ensure the method was responding properly. The method blank consisted of 100 g of precleaned Na_2SO_4, which was spiked with the same amounts of the standard compounds as the samples. Method blanks for all compounds were below the detection limits except for BDE-47 (0.43−2.4 ng) and BDE-99 (0.33−1.8 ng). The levels of BDE-47 and BDE-99 in the method blank were well below 5% of the levels found in the sediment samples. Because BDE-209 may easily adsorb to small dust particles in the laboratory, special precautions were taken during the whole analysis procedure. When using Soxhlet extraction, all the condensers were thoroughly rinsed with dichloromethane and hexane before and after each extraction. All glassware was covered with aluminum foil during use.

Results and Discussion

Sediment Dating. For both cores, the ^{210}Pb activities as a function of cumulative dry mass are given in the Supporting Information. Because of the high sediment deposition rate in the eastern basin of Lake Erie, sediment core ER15 was not deep enough to show background ^{210}Pb levels. Therefore, for both cores, the mass sedimentation accumulation rate was based on the ^{210}Pb profile fitted to a three parameter model

$$A_{obs} = A_f + A_0 e^{-\lambda m/r} \quad (1)$$

where the measured values are A_{obs}, which is the measured (total) specific activity of ^{210}Pb at a given depth (in counts/g), and m, which is the cumulative sediment mass above a given depth (in g/cm^2). The three fitted parameters are A_f, which is the background specific activity of ^{210}Pb due to the decay of ^{226}Ra in the Earth's crust, A_0, which is the ^{210}Pb specific activity at the surface of the sediment, and r, which is the desired mass sedimentation rate (in g·cm^{-2} year^{-1}). In this equation, λ is the radioactive decay constant for ^{210}Pb (0.0311 year^{-1}). These three parameters were fitted with the Solver feature of Microsoft Excel, and they are given in Table 1. The fitted curves are shown in the Supporting Information.

For the Lake Michigan core, our sedimentation rate was 0.051 g·cm^{-2} year^{-1}, which was somewhat higher than the value of 0.036 g·cm^{-2} year^{-1} reported by Simcik et al. for a site just south of site MI47 (at 44° 42.31′ N, 86° 41.01′ W) (*29*). For the Lake Erie core, our sedimentation rate was 0.73 g·cm^{-2} year^{-1}, which is between the values of 1.1 g·cm^{-2} year^{-1} at 42° 31.17′ N, 79° 57.70 W and 0.60 g·cm^{-2} year^{-1} at 42° 31.00′ N, 79° 53.63′ W (Brian Eadie, personal communication).

The sediment at a given location in a lake has been focused to that location from the surrounding area if the sampling location is a locally deep part of the lake (as were ours) or defocused if the sampling location is on a slope (a near-shore zone, for example) (*30*). The degree of focusing is given by a focusing factor, which will be greater than 1 if the sediment is focused to that sampling site or less than 1 if the sediment is defocused away from that site. The focusing factor (FF) for our cores is the background-corrected ^{210}Pb activity integrated over the cumulative mass sedimentation rates from 0 to infinity divided by the expected total ^{210}Pb deposition, which is 34.4 counts/cm^2 in the Great Lakes (*31*, *32*):

$$FF = \frac{A_0}{34.4}\int_0^{\infty} e^{-\lambda m/r}\, dm = \frac{A_0 r}{34.4\lambda} \quad (2)$$

The resulting focusing factors are given in Table 1. For the Lake Michigan core, the focusing factor was somewhat high (3.3) because this core was taken in one of the deepest locations in the northern Lake. For the Lake Erie core, the focusing factor was very high (7.9) because of the high sedimentation rate observed at this location, which provides high temporal resolution for this sediment record.

PBDEs Concentrations. The distribution of PBDE congeners in these sediment cores is shown in Figure 2. BDE-209 makes up 95−99% of the total. The other congeners are dominated by BDE-47, -99, -206, and -207. BDE-47 and -99 are the most common congeners in people, fish, birds, and mammals (*3*). The relatively high abundance of BDE-209 and the nonabrominated BDEs in sediment is probably the result of the high production of Deca-BDE [25 000 tons were produced in the U.S. in 2000 (*1*)] and their high K_{ow} value, which force them to partition to the sinking sediment particles. Incidentally, the commercial Deca-BDE product contains a few percent nonabrominated BDEs as production byproducts (*2*). The octa- and nona-BDEs may also be formed as a result of microbial degradation of BDE-209 (*33*).

BDE-209 is the dominant congener in most sediment samples, no matter whether they were from a river (*19*), an estuary (*34*), a lake (*20*), or a sea (*35*). On the other hand, BDE-209 seems to be a minor PBDE congener in biota, perhaps because BDE-209 has not been measured as often as the less brominated congeners. BDE-209 was found at low concentrations in mussels from Osaka Bay (*36*), in eggs of wild falcons in Sweden (*37*, *38*), and in the blood of people

TABLE 2. PBDE and BB-153 Surface Concentrations, Doubling Times, Inventories, Burdens, Surface Fluxes, and Load Rates of PBDEs in Sediment from the Great Lakes

parameter		Michigan	Erie	Superior avg[b]
surface concn (ng/g)	∑PBDE′[a]	2.6	1.1	1.4 ± 0.4
	BDE-209	315	39	11 ± 2
	BB-153	0.052	0.018	–[c]
doubling time (year)	∑PBDE′	11	6.4	44 ± 6
	BDE-209	7.5	5.3	45 ± 14
	BB-153	–	–	–
inventory (ng/cm^2)	∑PBDE′	1.3	1.1	0.59 ± 0.24
	BDE-209	190	40	4.8 ± 0.7
	BB-153	0.038	0.087	–
burden (tons)	∑PBDE′	0.75	0.28	0.49 ± 0.20
	BDE-209	110	10	3.9 ± 0.6
	BB-153	0.022	0.022	–
surface flux (ng·cm^{-2} year^{-1})	∑PBDE′	0.040	0.10	0.018 ± 0.005
	BDE-209	4.9	3.6	0.14 ± 0.01
	BB-153	0.0008	0.0017	–
load rate (tons/year)	∑PBDE′	0.023	0.026	0.015 ± 0.004
	BDE-209	2.8	0.92	0.12 ± 0.01
	BB-153	0.00046	0.00043	–
lake surface area (km^2)		57750	25660	82100

[a] ∑PBDE′ refers to the sum of tri- through hepta-BDEs. [b] Data for Lake Superior are from ref *46*. [c] No data are available.

with occupational (*39*, *40*) and nonoccupational exposures (*41*). In our recent study of archived fish from the Great Lakes (*42*), we did not find BDE-209 in any sample. This observation suggests that, even though BDE-209 may be bioavailable, it may have a short half-life in biota. For example, BDE-209's half-life seems to be 2–3 days in the rat (*43*), 8–13 days in gray seals (*44*), and ~15 days in humans (*45*).

For simplicity, in the following discussion, ∑PBDE′ refers to the sum of the tri- through heptabrominated BDEs measured in this study. The surface concentrations at the Lake Michigan and Erie sites are given in Table 2 along with corresponding average values for Lake Superior measured by Song et al. (*46*). The ∑PBDE′ and BDE-209 concentrations in Lake Michigan surficial sediment are 2.6 and 315 ng/g dry weight, respectively, which are much higher than those in Lake Erie at 1.1 and 39 ng/g, respectively.

The surficial ∑PBDE′ concentration at the Lake Michigan site is somewhat higher than in another sediment core also taken from Lake Michigan in 2001, which was observed to have a concentration of 1.6 ng/g for the total of BDE-47, -66, -99, -100, -153, and -154 (*47*). Comparing these surficial PBDE concentrations to those in Lake Superior (*46*), we note that the concentration of BDE-209 in Lake Michigan was more than 25 times higher than the average in Lake Superior; the concentration of ∑PBDE′ in Lake Michigan is about the same as the average in Lake Superior. The surficial ∑PBDE′ and BDE-209 concentrations in Lake Erie were of the same order of magnitude as the Lake Superior average concentrations.

PBDEs have been studied in river, lake, and marine sediment samples all over the world. The concentration of the ∑PBDE′ and BDE-209 are highly dependent on the sampling locations. In Europe, the highest BDE-209 concentration was found in the River Mersey, UK (at 1700 ng/g) (*48*), followed by River Schelde, Belgium (at 200 ng/g). In the Swedish River Viskan, where textile industries are situated, a maximum of 390 ng/g of BDE-209 was found (*19*). At the other end of the scale, a sediment core taken from Drammenfjord near Oslo, Norway (*25*) showed surficial (1999) total PBDE concentration (including BDE-209) of 3.1 ng/g, which is much lower than the total PBDE concentrations we measured in Lake Erie (31 ng/g) and Lake Michigan (495 ng/g) in the layers representing 1999.

In a study of PBDEs in the river, estuarine, and marine sediments throughout Japan conducted by the Environmental Agency of Japan, the levels of BDE-209 were from 4 to 6000 ng/g in 1988. Globally, the highest BDE-209 level (at 6000 ng/g) was found in estuarine sediment from the Kansai region of Japan (*3*). In the United States, the highest level of BDE-209 was found in a recent study of PBDEs in sediments of Chesapeake Bay, where this concentration ranged from 9000 ng/g near a wastewater treatment plant to 2400 ng/g 6 km downstream from that plant (*49*). The concentrations of BDE-209 we observe in surficial sediment from the Great Lakes (40–300 ng/g) are somewhat lower than concentrations found around the world.

The PBDE concentrations in these cores from Lakes Michigan and Erie are shown in Figure 3 as a function of deposition year. BDE-209 was first observed at core depths corresponding to 1957 in Lake Michigan and to 1979 in Lake Erie. The latter of these dates is similar to the result reported by Zegers et al. (*25*), who found that BDE-209 first appeared in 1978 in a sediment core from Drammenfjord, Norway. This "advent date" also coincides well with the increasing production of commercial Deca-BDE beginning in the late 1970s (*50*). The cause of the earlier deposition seen in Lake Michigan is not known.

Both the ∑PBDE′ and BDE-209 concentrations in the sediment cores from Lakes Michigan and Erie increased exponentially with time. This is consistent with the increasing demand for PBDEs in the U.S. market over the last 30 years. In Lake Michigan, the BDE-209 concentration increased with a doubling time of 7.5 ± 1.2 year until ~1980, after which it seems to have leveled off. In Lake Erie, BDE-209 has a faster doubling time, 5.3 ± 0.7 year, than in Lake Michigan. ∑PBDE′ concentrations double every 11 ± 1 year in Lake Michigan and every 6.4 ± 0.5 year in Lake Erie. These various rates of change may be due to changes in the production and market demand for these compounds in North America over time, but because the production histories of these compounds are not known, we are not able to verify this supposition. Both ∑PBDE′ and BDE-209 had much slower doubling times, 44 ± 6 and 45 ± 14 year, respectively, in Lake Superior (*46*). One possible reason for this difference may be the low population and industrial activity around Lake Superior area as compared with Lakes Michigan and Erie.

PBDEs as a function of depth in dated sediment cores have been studied in Europe, and data are available for two cores. Three congeners (BDE-47, -99 and -100) were measured in a core from the Baltic Sea (*17*). The doubling time for the sum of these congeners was 11 years according to the data

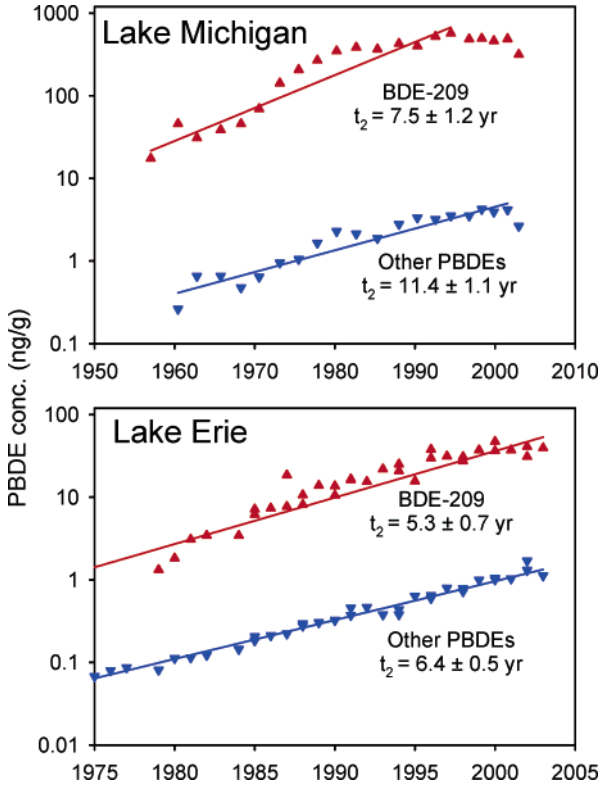

FIGURE 3. Concentrations of BDE-209 and other PBDEs (∑PBDE′) as a function of deposition year in Lakes Michigan and Erie. Note the logarithmic scale for the concentrations.

extracted by Hites from the original paper (*5*). In another study, a sediment core taken from Drammenfjord near Oslo, Norway (*25*) showed a doubling time of 8.4 years starting in the mid-1980s for BDE-209. These values are close to our ∑PBDE′ results for Lakes Michigan and Erie but much faster than the results of Song et al. for Lake Superior.

BDE-209 is a minor congener in biota and was not found in fish samples from the Great Lakes (*42*); thus, to make comparisons of PBDEs in fish and sediment from the same lake, only ∑PBDE′ concentrations are compared. In our previous study, the temporal trends of PBDEs in lake trout from the Great Lakes also demonstrated an exponential increase with time. This result confirms that PBDE concentrations in North American aquatic systems have increased rapidly during the last 30 years. The doubling time of ∑PBDEs in fish, 3 years for both lakes, was shorter than that in sediments, 5−10 years, suggesting that the shorter doubling time of PBDEs in fish may be due to relatively high bioaccumulation factors of tetra- and penta-PBDEs in biota, on one hand, and sediment resuspension, on the other.

PBDE Inventories and Fluxes. The PBDE inventories (I in ng/cm^2) represent the total integrated mass of these compounds per unit area from the onset to present

$$I = (\sum C_i \rho_i d_i)/\mathrm{FF} \quad (3)$$

where C_i is the concentration in each sediment segment (in ng/g), ρ_i is the dry density of each wet segment (in g/cm^3), and d_i is the thickness of each increment (in cm). Inventories were divided by the focusing factor to account for the lateral movement of sediment. These results are given in Table 2.

The focus-corrected ∑PBDE′ and BDE-209 inventories were 1.3 and 190 ng/cm^2, respectively, in Lake Michigan and 1.1 and 40 ng/cm^2, respectively, in Lake Erie. Compared with the results from Song et al. (see Table 2) (*46*), the inventory of BDE-209 in Lake Michigan is ∼40 times higher than in Lake Superior. Interestingly, the total PBDE inventory (∑PBDE′ plus BDE-209) in Lake Michigan was close to the inventory of PCBs in this lake, which was in the range of 33−205 ng/cm^2 from 1991 to 1998 (*51*). For Lake Erie, the inventories of ∑PBDE′ and BDE-209 are higher than the average inventories for Lake Superior. We estimate that the total burden of ∑PBDE′ to Lake Michigan is 0.75 metric ton or 110 metric tons if BDE-209 is included. For Lake Erie, we estimate that the total burden of ∑PBDE′ is 0.28 metric ton or 10 metric tons if BDE-209 is included.

The focus-corrected surficial sediment fluxes (in ng·cm^{-2} year^{-1}) were calculated from the surficial concentrations, the sedimentation rates, and the focusing factors

$$\mathrm{flux} = C_{\mathrm{surf}} r/\mathrm{FF} \quad (4)$$

These fluxes for ∑PBDE′ and BDE-209 at the two locations are given in Table 2. The surficial fluxes for ∑PBDE′ and BDE-209 to Lake Michigan are 0.040 and 4.9 ng·cm^{-2} year^{-1}, respectively, which are much higher than those average fluxes to Lake Superior. Using these fluxes to the surface layer, representing 2003−2004, the current load rate of ∑PBDE′ to Lake Michigan is estimated to be 0.023 t/year, or 2.8 t/year if BDE-209 is included. The surficial fluxes for ∑PBDE′ and BDE-209 to Lake Erie are 0.10 and 3.6 ng·cm^{-2}year^{-1}, respectively, which are similar to the fluxes to Lake Michigan but much higher than the average fluxes to Lake Superior. Over the time period 2003−2004, the current loading rate of ∑PBDE′ to Lake Erie is estimated to be 0.026 t/year, or 0.95 t/year if BDE-209 is included. It is not clear why the concentration, inventory, and flux of BDE-209 are relatively high at this northern Lake Michigan site.

If the sites that have already been sampled in the Great Lakes are typical of the Lakes as a whole, we estimate that the sediment of the Lakes has a burden on the order of 200 metric tons of PBDEs; of this, most is BDE-209 and most seems to be in Lake Michigan. Although 200 tons may seem like a lot, it is a small fraction of the annual production of these compounds, which recently was on the order of 33 000 tons (*1*).

BB-153 Time Trends. The commercial production of polybrominated biphenyls in the U.S. started in 1970 (*27*). These compounds proved to be a popular flame retardant until 1973, when PBBs were inadvertently substituted for magnesium oxide as a supplement in cattle feed (*52*). This contaminated feed was used throughout Michigan for several weeks until the problem was discovered. As a result of this accident, Michigan's entire ecosystem (including people) was contaminated, and the production of PBBs was banned. Here we have investigated the time trend of the most predominant PBB congener, BB-153, in these sediment cores; the concentrations (ng/g) are shown in Figure 4 as a function of year of deposition. In Lake Erie, BB-153 was found in the deepest layer, representing 1972; the concentrations reached a maximum in ∼1980 and have decreased ever since. The profile was similar in Lake Michigan, where BB-153 was first detected in 1970, peaked in 1980, and decreased gradually afterward. Despite the ban on the production and use of PBBs in the U.S. in 1976, these sediment cores suggest that the peak concentration occurred about 5 years after the ban. This phenomenon was also observed in PCB concentrations in a sediment core from Japan (*24*).

This observation suggests that the time-dependent signal in sediment may lag behind the market's production and usage. The products that were manufactured before the ban were still in use, and PBB continued to be released from these products even after the ban. The history of PBB deposition revealed in these sediment cores suggests that the ban on these compounds was effective, given that the concentrations have decreased from their peak 20−25 years

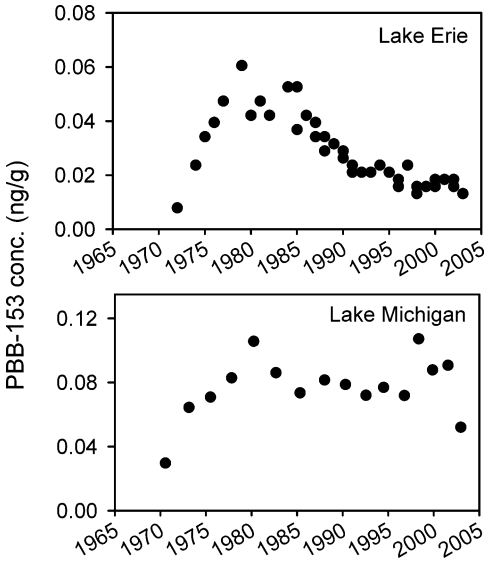

FIGURE 4. Concentrations of BB-153 as a function of deposition year in Lakes Michigan and Erie depth.

ago. However, the BB-153 concentrations in the surface layers of these cores are higher than at the core bottom, which implies that PBBs are circulating in the environment even today. Incidentally, BB-153 was also identified in archived fish samples collected from the Great Lakes in 2000 (*42*).

The inventories and fluxes were calculated for BB-153, and they are given in Table 2. On the basis of an inventory of 0.038 ng/cm^2 and a surface flux of 0.0008 ng·cm^{-2} year^{-1}, the loading rate of BB-153 to Lake Michigan is estimated as 0.00046 t/year and the total burden is ~0.02 tons. On the basis of an inventory of 0.087 ng/cm^2 and a surface flux of 0.0017 ng·cm^{-2}year^{-1}, the loading rate of BB-153 to Lake Erie is estimated as 0.00043 t/year and the total burden ~0.02 tons. The similarity of these two burdens suggests that atmospheric deposition is the source of BB-153 to these two Lakes.

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Supporting Information Available

^{210}Pb activities and fitted three-parameter model (see eq 1) for cores from Lakes Michigan and Erie; note that here $K = -\lambda/r$. This material is available free of charge via the Internet at http://pubs.acs.org.

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