Polybrominated Diphenyl Ethers in the Sediments of the Great Lakes. 3. Lakes Ontario and Erie

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Sediment cores were taken in 2002 in Lakes Ontario and Erie at four locations. A total of 48 sediment samples were characterized, dated using ^{210}Pb, and analyzed for 10 congeners of polybrominated diphenyl ethers (PBDEs) including BDE209 as well as 39 congeners of polychlorinated biphenyls (PCBs). The surficial concentrations of nine tri- through hepta-BDE congeners (Σ_9PBDE) are 4.85 and 6.33 ng g^{-1}, at sampling sites ON40 and ON30 in Lake Ontario, and 1.83 and 1.95 ng g^{-1} at ER37 and ER09 in Lake Erie, respectively, based on dry sediment weight. The surficial BDE209 concentrations are 242 and 211 ng g^{-1} at ON40 and ON30 and 50 and 55 ng g^{-1} at ER37 and ER09. The Σ_9-PBDEs fluxes to the sediment around 2002 are 147 and 195 pg cm^{-2} year^{-1} at ON40 and ON30 and 136 and 314 pg cm^{-2} year^{-1} at ER37 and ER09, respectively. The fluxes of BDE209 are 6.5 and 7.3 ng cm^{-2} year^{-1} at ON30 and ON40 and 3.7 and 8.9 ng cm^{-2} year^{-1} at ER37 and ER09, respectively. Dramatic increases in PBDE concentrations and fluxes upward toward the sediment surface and the present time are evident at both locations in Lake Ontario, while PCBs concentrations peak in the middle of sediment cores around the dated time of 1970s and 1960s. For both locations of Lake Erie, the increasing trends of both PBDEs and PCBs from the bottom to the surficial segments were distorted by sediment mixing. BDE209 is the most abundant congener among PBDEs in the sediments, constituting about 96 and 91% of the total PBDEs on mass basis in Lakes Ontario and Erie, respectively.

Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of additive flame retardants that have been found in measurable amounts in various samples around the world (*1*). The United States is the world's largest consumer of PBDEs, particularly penta-BDE products. In the past decades, North and South Americas, led by the U.S. and Canada, have accounted for half of the total PBDE and 95% of the penta-BDE consumptions of the world (*2*). A research project has been conducted

to assess the extent of PBDE pollution to the Laurentian Great Lakes and provide evidence of their long-range atmospheric transport. This paper presents the results on the spatial distribution and input chronology of PBDEs in the sediments of Lakes Ontario and Erie, following our previous reports on Lakes Superior, Michigan, and Huron (*3, 4*).

Lakes Ontario and Erie are the smallest in water area and volume, respectively, among the five Great Lakes. The water in these two lakes has much shorter retention times than in the other three lakes. Both lakes are located in the southeast of the Great Lakes region and stretch from west to east. Water from the upper lakes flows into Lake Erie via the St. Clair and Detroit Rivers. Through the Niagara River, the water in Lake Erie flows into Lake Ontario, which is at the lowest elevation among the five lakes. Water in Lake Ontario is drained into Atlantic Ocean through the St. Lawrence River. Compared with the other Great Lakes, both Lakes Erie and Ontario are exposed to much greater effects from urbanization and agriculture. Seventeen metropolitan areas, each with populations over 50 000, are located within the Lake Erie basin. The lake also receives runoff from the agricultural area of southwestern Ontario and parts of Ohio, Indiana, and Michigan. It is the shallowest and the most eutrophic among the Great Lakes. Lake Ontario is much deeper than its neighbor Lake Erie; major urban industrial centers such as Toronto and Hamilton are located on its shore.

Studies on PBDEs in Lakes Ontario and Erie have been reported mainly of air and biota (*5−9*). PBDEs were found in all air samples collected by the International Air Deposition Network (IADN). At Sturgeon Point on the east shore of Lake Erie, the average sum of 7 PBDEs was 530 pg/m^3 in 1997−1999 (*5*). In the archived herring gull eggs and fishes, the samples from colonies in Lakes Ontario and Erie showed increasing trend of PBDEs from 1980 to 2000 (*9*). For sediment samples in Lakes Ontario, Muir et al. (*10*) have reported a rapid increase of BDE209 concentrations in three uppermost sections of a sediment core from the west basin of Lake Ontario. Compared to PBDEs, more studies on PCBs in the sediments of Lakes Ontario and Erie were reported (*11−13*). In general, the PCB concentrations in the sediment of these lakes are higher than those found in the upper Great Lakes.

In this study, a total of 48 samples from 4 sediment cores collected in Lakes Ontario and Erie were analyzed for 10 PBDE congeners as well as 39 PCBs. For each sampling location, concentration profiles were constructed against sediment depth. On the basis of the results of sediment dating using Pb-210 technique, the chronology of PBDE input flux was derived from the concentration data. Ranges of PBDE inventories in the sediments were estimated to assess the chemical accumulation.

Experimental Section

Sampling, Sample Characterization, and ^{210}Pb Dating. Sediment sampling was conducted on Lakes Ontario (ON) and Lake Erie (ER) in August 2002, onboard the EPA R/V *Lake Guardian*. Sampling and sample storage procedures as described in (*3*) 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. Sectioning was performed at 1.0 cm intervals for the first 10 cm, then in 5 cm increments for the remainder of the core. The segments in different subcores with the same depth at the same site were combined into a precleaned amber glass jar. All samples were refrigerated at 4 °C on the ship and

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FIGURE 1. Sampling locations.

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

sampling station	location latitude (N)	longitude (W)	sedimentation rate (g cm^{-2} year^{-1}) CIC	CRS	focusing factor
Erie 9	42°32′18″	79°37′00″	0.3718	0.1473	1.61
Erie 37	42°06′36″	81°34′30″	0.1058	0.0786	1.25
Ontario 30	43°32′00″	76°54′00″	0.0349	0.0385	1.19
Ontario 40	43°35′00″	78°00′00″	0.0328	0.0370	1.15

transported in coolers to the laboratory where they were frozen until analysis. Sediment characterization of each segment was carried out with the methods described in ref (*14*).

Organic carbon (OC) content was determined for desiccated samples on a Carlo Erba elemental analyzer (Flash EA1112, ThermoQuest/CE Elantech, Lakewood, NJ). Pulverized samples (10–20 mg) were placed in preweighed tin combustion boats supplied by the manufacturer, sealed, reweighed, and stored in a desiccator until analysis. Elemental analysis was conducted using automated combustion/reduction (at 900 °C) followed by molecular sieve gas chromatography (at 60 °C) and thermal conductivity detection system.

Each segment of the sediment cores was dated by ^{210}Pb method, using a ^{209}Po tracer. Detailed procedures can be found in (*3*). The constant initial concentration (CIC) and the constant rate of sedimentation (CRS) models (*15*) were adopted to estimate the sedimentation rate, 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 (*16*).

Chemical Analysis. 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 PCBs 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. Chemical analysis followed the same procedure as used in our previous work (*3, 4*). The major steps included Soxhlet extraction, Kuderna-Danish concentration, and cleanup using silica gel chromatography. Analyses of PCBs and PBDEs were performed on a HP 6890 gas chromatograph (GC) coupled with a HP 5973 mass spectrometer (MS). Selected ion monitoring (SIM) mode was used during data acquisition. For PCBs and PBDEs other than BDE209, an electron impact MS was used. PCB204 and BDE190 were used as internal standards for PBDEs quantification, and PCB30 and PCB204 were used as internal standards for PCBs. BDE209 was analyzed by negative chemical ionization (NCI) MS, with fragment ion of m/z 486 for quantitation.

Quality Control. Before extraction, the sediment samples were spiked with known amounts of surrogates, including PBDE surrogates ^{13}C-labeled 2,3′,4,4′,5-penta bromodiphenyl ether (BDE118) and ^{13}C-labeled BDE209 and PCB surrogate 2,3,5,6-tetra chlorobiphenyl (PCB65). The recovery of ^{13}C–BDE118 was in the range of 58–148%, with a mean of 102%. The recovery of ^{13}C–BDE209 was in the range of 20–88%, with a mean of 41%. For Lake Erie, the mean recovery for PCBs was 121%, ranging from 77 to 149%. For Lake Ontario, all PCB surrogate recoveries were above 90% except one, with an average of 158%. The high recovery for PCBs is similar to those in a recent report on the sediments of Lake Ontario (*17*) and most likely due to the presence of the PCB congeners, which were used as surrogates in this work, in the sediments as a result of degradation of high levels of PCBs over the past decades. No recovery-based correction was made to the PCB results for Lake Ontario. Four sediment samples, one for each core, were analyzed in duplicate. The average relative standard deviation (RSD) was in the range of 10–46% for the nine PBDE congeners and of 8–61% for PCBs. Method blanks were also run for each core. For Lake Ontario, the levels of analytes found in method blanks were comparable to those in the matrix blanks that were pre-1900 sediment segments and well below 20% of those in the upper segments. The averages of chemical concentrations in the matrix blanks of each core were subtracted from the results of chemical analysis. For Lake Erie, no segment was dated pre-1900 and no subtraction was made.

Results and Discussion

Unsupported ^{210}Pb activity is plotted against 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.

Concentrations of the sum of tri- through hepta-BDEs (Σ_9PBDEs), BDE209, and PCBs (Σ_{39}PCBs) in 48 samples of the four cores are illustrated in Figure 2 as a function of sediment depth. All the concentrations are reported based on dry sediment weight. To compare the current levels of sediment contamination at different locations, the surface concentrations at the four sites are given in Table 2. The inventory of individual PBDE and PCB congeners at each location was estimated using eq 1 as the sum of the products of the measured concentration (C_i), bulk density (ρ_b), and depth increment (d_i), of individual segments. The flux of the chemicals to the sediment was calculated using eq 2, in which R_i is sedimentation rate, and FF is focusing factor. The results are presented in Table 2. The chronology of PBDE and PCB inputs to the sediments is illustrated in Figure 3.

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

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

Sedimentation Patterns. The sedimentation rates and focusing factors at ON30 and ON40 are comparable with reported values (*18, 19*). Both the concentration and accumulation of ^{210}Pb show strong correlations ($R^2 > 0.96$) with sediment cumulative mass, and the two regression lines using the CIC and CRS models are nearly parallel (Figure S1). Lack of severe mixing is implied by these results. The average sedimentation rate obtained from using the CIC and CRS models was used in the estimation of chemical flux for the cores from Lake Ontario.

For both cores from Lake Erie, the results from the CIC and CRS models do not agree well (Figure S2). The correlations are poor between unsupported ^{210}Pb activity in individual sediment segments and the cumulative dry mass of sediment (CIC model), especially for ER09. This indicates severe sediment disturbance, which have brought about
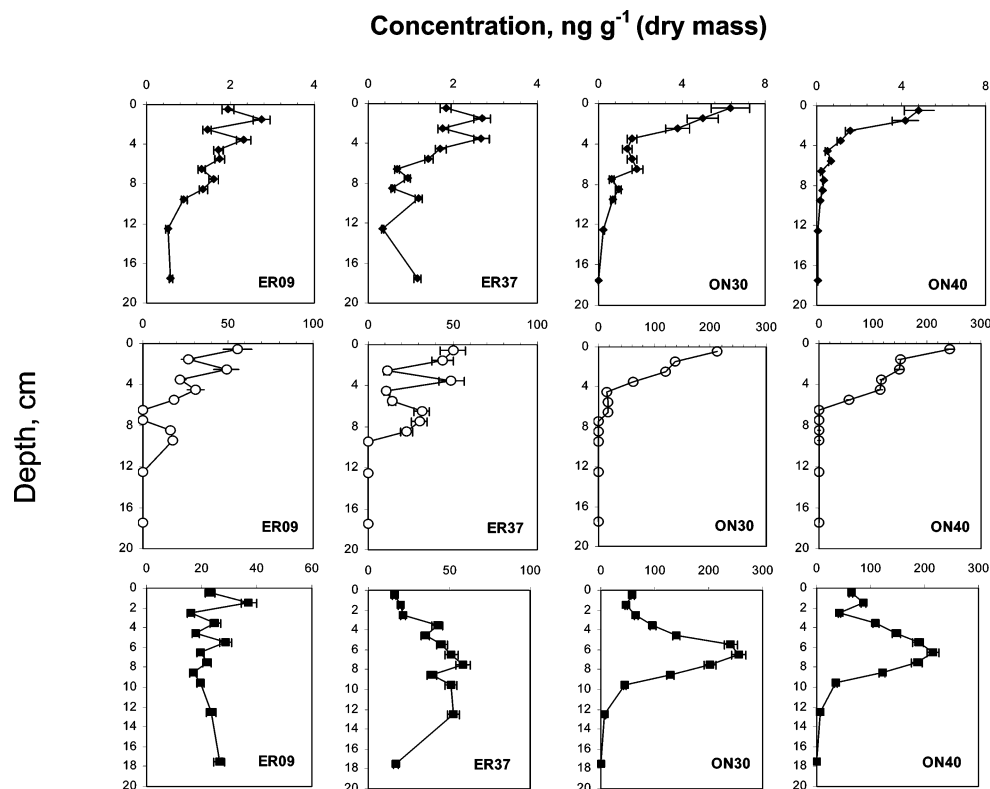
Concentration, ng g⁻¹ (dry mass)

FIGURE 2. Concentrations vs depth in Lakes Erie and Ontario. Filled diamond, Σ_9PBDEs; empty circle, BDE209; gray square, Σ_{39}PCBs.

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

sampling station	Σ_9PBDEs			BDE209			Σ_{39}PCBs		
	surface concn (ng g⁻¹)	inventory (ng cm⁻²)	surface flux (ng cm⁻² year⁻¹)	surface concn (ng g⁻¹)	inventory (ng cm⁻²)	surface flux (ng cm⁻² year⁻¹)	surface concn (ng g⁻¹)	inventory (ng cm⁻²)	surface flux (ng cm⁻² year⁻¹)
Erie 9	1.95	7.75	0.314	55.4	76.2	8.93	23.0	169.2	3.71
Erie 37	1.83	6.24	0.136	50.2	68.0	3.71	28.3	196.5	2.09
Ontario 30	6.33	4.25	0.195	211.2	86.7	6.50	58.3	262.9	1.79
Ontario 40	4.85	2.40	0.147	242.0	140.8	7.33	63.6	255.2	1.92

impairment to the integrity of the sediments. As Lake Erie is much shallower than the other Great Lakes, the sediments may be more susceptible to the impacts of wind and water movement, and benthic organisms may be more active. Both hydrological and biological disturbances can cause sediment resuspension and mixing. The CIC model is much more sensitive to sediment disturbance and mixing than the CRS model, because the former uses the unsupported ^{210}Pb activity in individual sediment segments, while the latter is based on accumulative unsupported ^{210}Pb activity in the entire core. Because of the weak correlation coefficients (Figure S2), the sedimentation rates estimated by the CIC model was not considered reliable. As a result, only the CRS derived sedimentation rates were used in the estimation of chemical flux in Lake Erie. The sedimentation rates in Lake Erie are much higher than those in Lake Ontario and the other Great Lakes. Marvin et al. also reported that sediment down flux rate measured is far greater in Lake Erie than in Lake Ontario and characterized as predominantly resuspended bottom sediments (20).

PBDEs in Lakes Ontario and Erie. As can be seen in Figure 2, PBDE concentrations in the sediment of Lake Ontario follow general increasing trends from bottom to the surface, with the maximum concentrations at the surficial segments of sediment cores. In the uppermost three or four segments, PBDEs concentrations increase more rapidly than

in the deeper segments. The Σ_9PBDE concentrations in surficial sediments at ON30 and ON40 are 6.3 and 4.8 ng g⁻¹ dry sediment weight, respectively (Table 1). On the basis of OC, they are 102 and 67 ng g⁻¹ OC for ON30 and ON40, respectively. The surficial BDE209 concentrations are 211 and 242 ng g⁻¹ dry weight and 3406 and 3350 ng g⁻¹ OC at ON30 and ON40, respectively. Muir et al. (10) reported BDE209 surficial sediment concentration of 112 ng g⁻¹ at the west basin of Lake Ontario, which was sampled in 1998. The concentrations of the second uppermost sections of cores ON30 and ON40, with estimated dates of sediment deposition around 1996, are 136 and 150 ng g⁻¹, respectively, which compare well with the value reported in ref 10.

For the sediment cores from Lake Erie, as the depth of the sediment core increases, a sketchy decreasing trend could be vaguely observed with zigzag patterns at ER09 and ER37. Greater fluctuations can be seen for BDE209 than Σ_9PBDEs. Compared with other congeners, BDE209 is more hydrophobic and particle bound, thus may be more susceptible to particle mixing than other congeners (10). These complicated sediment records of PBDEs for Lake Erie result most likely from the significant sediment resuspension and mixing, as revealed by the ^{210}Pb dating results. Although fluctuating, the increasing trends in PBDE concentration toward sediment surfaces are still evident, in agreement with the assumed continuously increasing input since the 1970s. The concen-
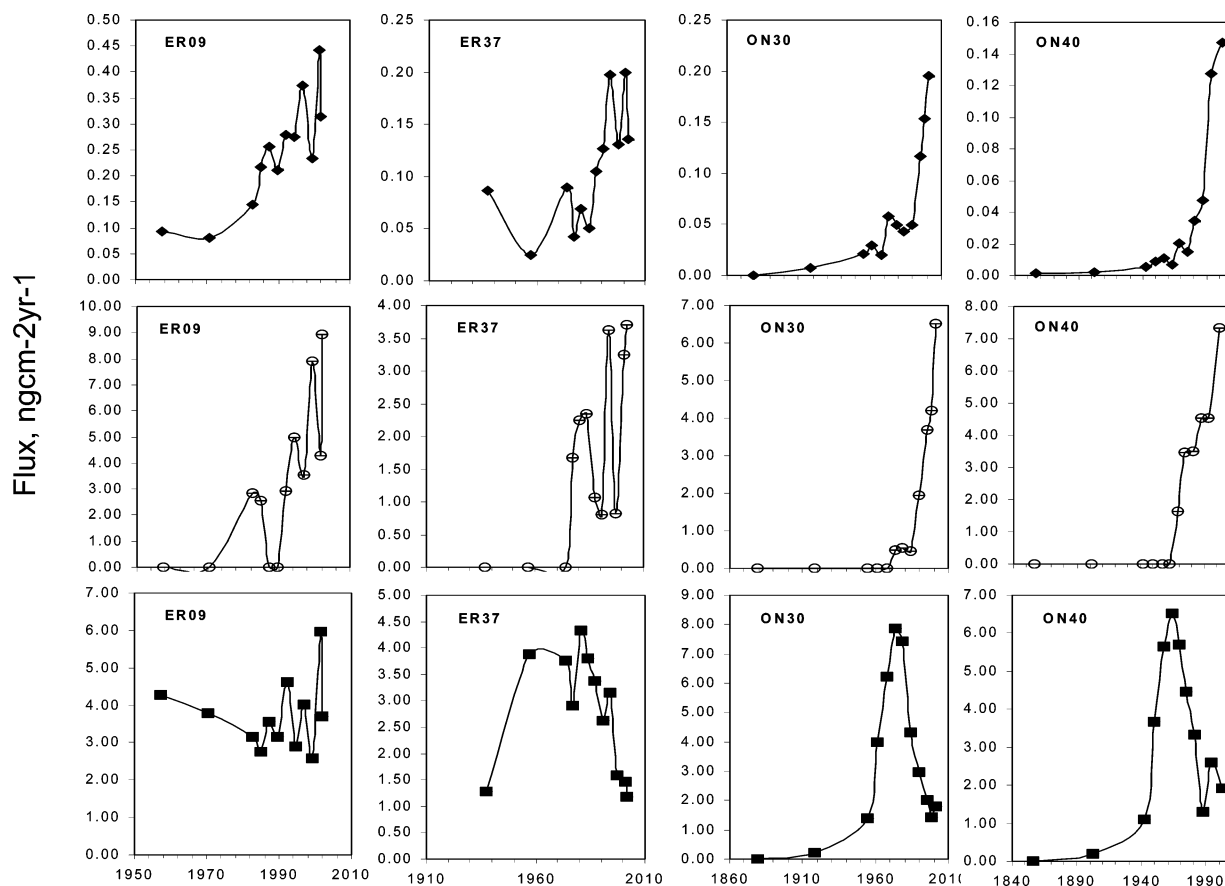
FIGURE 3. Fluxes to the sediments of Lakes Erie and Ontario. Filled diamond, Σ_9PBDEs; empty circle, BDE209; gray square, Σ_{39}PCBs.

trations of Σ_9PBDEs in the surficial sediments at ER09 and ER37 are 2.0 and 1.8 ng g^{-1} dry weight or 76.7 and 68.0 ng g^{-1} OC, respectively. The concentration of BDE209 in the surficial sediments is 52.8 ng g^{-1} dry weight or 2022 ng g^{-1} OC, averaged over the two sampling sites in Lake Erie. These results are comparable with the concentrations of ΣPBDEs (tri- through hepta-BDE congeners, 1.1 ng g^{-1} dry weight) and BDE209 (39 ng g^{-1} dry weight) in the surficial sediment at ER15 (21).

Interestingly, although the average PBDE concentration in surficial sediments of Lake Ontario is much higher than that of Lake Erie based on dry sediment weight, the OC-normalized concentrations are close in both Lakes, due to the relatively high OC contents in Lake Ontario. This situation is similar to one observed for Lakes Michigan and Huron, where OC-normalized surficial concentrations are much closer than those based on dry weight of sediments. Compared to Lakes Michigan (LM), Huron (HU), and Superior (SU) (3, 4), which have average surficial Σ_9PBDEs concentrations of 2.99, 1.51, and 1.43 ng g^{-1} dry weight and BDE209 concentrations of 63, 16, and 6 ng g^{-1} dry weight, respectively, the average surficial sediment concentrations of Σ_9PBDEs are in the order ON > LM > ER > HU $\approx$ SU, while those of BDE209 are in the order of ON > ER $\approx$ LM > HU > SU. In another core recently taken from northern Lake Michigan (21), a similar surficial ΣPBDEs (tri- to hepta-BDEs) concentration of 2.6 ng g^{-1} dry weight and a higher BDE209 concentration of 315 ng g^{-1} dry weight were observed. Reported PBDE concentrations in fish of the Great Lakes often vary significantly. Zhu and Hites (6) reported concentrations of total PBDEs in fish taken in the Great Lakes in 2000, with an order of LM > SU > ER > ON > HU. Luross et al. (7) reported PBDEs in lake trouts taken in 1997 followed the order of ON > SU > HU > ER. The complicated factors influencing the intake of PBDEs in fish, as well as the

differences in the nature of sediment and lake water among lakes, make it difficult to compare the geographic ranks reported for fish with the results in sediments. It is also noticed that the average Σ_9PBDE concentrations in surficial sediments of Lakes Ontario and Erie are still lower than the 103 ng g^{-1} OC observed in 2000 at Hadley Lake, Indiana, which is 1.3 km away from the research and development facility of a PBDE producing manufacturer (8).

Inventory of the contaminants in sediments represents the total integrated mass of the compounds of interest per unit area. In Lake Ontario, the average inventories over two locations for Σ_9PBDEs and BDE209 are 3.3 and 114 ng cm^{-2}, respectively. In Lake Erie, the average inventories over the two locations for Σ_9PBDEs and BDE209 are 7 and 72 ng cm^{-2}, respectively (Table 2). By use of the average inventories estimated for the two sampling sites, we estimate that the total load of Σ_9PBDEs in the sediments of Lake Ontario, which has a water surface area of 18960 km^2, would be around 630 kg. If BDE209 is included, the total load of PBDEs in Lake Ontario is estimated to be around 22 tons. Lake Erie has a water surface area of 25700 km^2. The total load of Σ_9PBDEs in the sediments would be around 1800 kg and that of BDE209 is about 18 tons.

Fluxes of the chemicals into sediments are plotted against the sediment deposition year in Figure 3. As expected, rapid and continuous increases in PBDE fluxes since the 1970s are obvious in both Lakes Erie and Ontario, despite the fluctuations in Lake Erie caused by sediment disturbance and mixing. By use of the data in Table 2, we estimate that the current loading rates to Lake Ontario sediments are around 32 kg year^{-1} for Σ_9PBDEs and 1311 kg year^{-1} for BDE209. The Σ_9-PBDE fluxes around 2002 are 314 pg cm^{-2} year^{-1} at ER09 and 136 pg cm^{-2} year^{-1} at ER37, nearly four times of those in Lake Michigan (4). On the basis of the average of the surface fluxes, we estimate that the loading rate of Σ_9PBDE to Lake
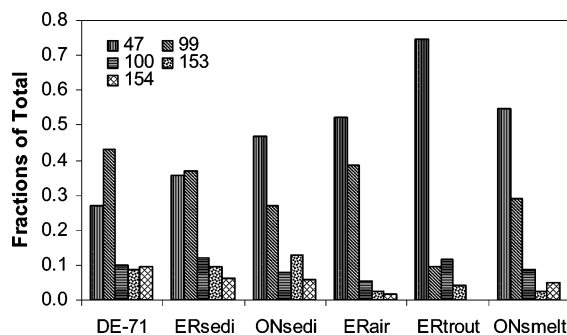
FIGURE 4. Comparison among PBDE congener patters in sediments and fish of Lake Erie and Lake Ontario (*11, 12*), air samples close to Lake Erie (*9*), and commercial penta mixture (*12*). For Lake Erie trout, data on BDE154 is not available, and the fractions are based on the sum of the other four congeners.

Erie is around 58 kg year^{-1}. The total loading of PBDEs, including BDE209, would be at a rate of around 3400 kg year^{-1} in year 2002. The high PBDE fluxes suggest that direct input from polluted water inflow may be an important source besides atmospheric deposition in Lakes Erie and Ontario. The Detroit River has been proved to be an important source of persistent organic pollutants such as PCBs to Lake Erie and so has the Niagara River to Lake Ontario (*22−25*).

In both Lakes Ontario and Erie, BDE209 dominates the total PBDEs in sediments. The average inventories of BDE209 are 91% in Lake Erie and 96% in Lake Ontario, of the total PBDEs by mass, similar to those found in Lakes Huron and Michigan (*4*) and in agreement with the findings of Zhu and Hites (*21*). BDE209 counts for about 75% of the total PBDE demands in Americas (*1*). Its higher percentage in the sediment reflects not only the higher consumption but also its higher affinity to the sediment organic matter compared with other congeners. By consideration of the close proximity of Lakes Ontario and Erie to the centers of human activities, direct input of PBDEs originated from sources such as municipal and industrial discharges may contribute more significantly to the total burdens in these two than in the other Great Lakes. Similar to the results for the other Great Lakes, BDE47 and BDE99 are more abundant than other tri- to hepta-BDEs in the sediments of Lakes Ontario and Erie. These two congeners constitute 51, 53, 45, and 57% of Σ_9-PBDE inventories at ON30, ON40, ER09, and ER37, respectively. In Figure 4, the sediment pattern of the five frequently found PBDE congeners is compared with those in the U.S. commercial product DE-71 (*8*) and the air and fish samples collected in Lakes Erie and Ontario (*5, 7, 8*). In general, the sediment pattern resembles the commercial Penta mixture, but higher fraction of BDE47 and lower fraction of BDE99 were observed in the sediments relative to those in the commercial mixture. BDE183 is also relatively abundant, ranging from 12 to 14% (wt) of total Σ_9PBDE. As the marker of octa-BDE products, the presence of BDE183 indicates the input of octa-BDE commercial mixtures to the sediments.

PCBs in Lakes Ontario and Erie. The trends of PCB concentration vs sediment depth are shown in Figure 2. In Lake Erie, the PCB concentrations fluctuate over the whole sediment core at ER09, while a gross broad elevation of PCB concentration appears in the middle of the sediment core at ER37. The complication of PCB concentration patterns at ER09 and ER37 indicates sediment disturbance and mixing at both sites, as discussed above. The surficial PCB concentrations are given in Table 2. Organic carbon normalized surficial PCB concentrations are 940, 880, 905, and 1051 ng g^{-1} OC at ON30, ON40, ER09, and ER37, respectively. Similar to PBDEs concentrations in Lakes Ontario and Erie, OC normalization brings the surficial PCBs concentrations in the two lakes fairly close, as observed for Lakes Michigan

and Huron. The maximum PCBs concentrations are 255, 215, 37, and 70 ng g^{-1} dry weight at ON30, ON40, ER09, and ER37, respectively. Spatial and chronological distributions of PCBs in the sediments of Lakes Ontario and Erie were reported (*12, 17*). For Lake Ontario, the lakewide average concentration of total PCBs (103 congeners) in 1998 was 100 ng g^{-1}, while in 1981 the total concentrations ranged from 510 to 630 ng g^{-1}. For Lake Erie, lakewide average sums of 24 dominant congeners in surficial sediment concentrations in 1971 and 1997 were reported to be 136 and 43 ng g^{-1}. Taking into account of the different number of PCB congeners analyzed in this work, our results are comparable with the literature values, except for ER09 where the sediment core was severely disturbed. A comparison among all five Great Lakes was made based on 11 PCB congeners with IUPAC No. 8, 18, 28, 44, 52, 66, 153, 180, 187, 195, and 206. The result shows that, on dry weight basis, average surficial PCBs concentrations in Lakes Erie and Ontario are about three and nine times that in Lake Superior, respectively. The surficial PCBs concentrations are in the order of ON > ER ≈ LM > HU > SU, in agreement with spatial distribution of PCBs in Lake trout reported by Luross et al. (*11*).

As indicated in Table 2, the concentrations and inventories of PCBs are lower at ER09 (eastern basin) than at ER37 (central basin), in agreement with the decreasing trend of PCB levels from west to central and to east basins reported by Marvin et al. (*13*). The PCBs contamination levels at ON30 and ON40 are close and are higher than those in Lake Erie. The inventories in Lakes Ontario and Erie are about four and six times those in Lake Michigan (*4*). Many areas of concern in the region, as well as the Detroit River and the Niagara River, have been proved to be important sources for PCBs contaminations historically and currently in Lakes Erie and Ontario, respectively (*20, 22−27*).

As illustrated in Figure 3, the peak fluxes of Σ_{39}PCBs at ON30 and ON40 are 7.9 and 6.5 ng cm^{-2} year^{-1}, respectively, both during the period from the 1960s to the 1970s. Lake Ontario responded more quickly to the ban of PCBs than the other Great Lakes (*3, 4*), although a slight but noticeable rise-up appears in recent years at ON40 (Figure 3). The ban on PCB production and usage led to a rapid decrease of large-scale direct release of PCBs, which could be sensitively recorded in sediments contaminated mainly by direct local input. However, when direct discharge comes down to a certain level, residuals of historic discharges and nonpoint sources such as air deposition may make it difficult for the PCB concentration in the sediment to decrease further (*28*). Fluvial input of PCBs from tributaries continues to date. For example, water samples from Niagara River collected in 2001 still contained about 100 ng g^{-1} of PCBs in the particulate phase (*25*).

Supporting Information Available

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

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