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Polybrominated Diphenyl Ethers in the Sediments of the Great Lakes. 4. Influencing Factors, Trends, and Implications

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A total of 199 sediment samples were collected from 16 locations in the five Laurentian Great Lakes, and each was analyzed for 10 congeners of polybrominated diphenyl ethers (PBDEs) as well as selected polychlorinated biphenyls (PCBs). This paper presents a comprehensive analysis on previously published results for individual lakes. The total accumulation of nine tri- to hepta-PBDE congeners ($\sum_9$BDEs) in the sediments of all the Great Lakes was estimated to be approximately 5.2 ± 1.1 tonnes, and that of decabromodiphenyl ether (BDE209) was 92 ± 13 tonnes, around year 2002. The inventories of $\sum_9$BDEs and major individual PBDE congeners show strong dependence on the latitude of sampling sites, and such dependence is believed to reflect both the influence of urbanization, which shows south-to-north gradient in the region, and the general direction of long-range transport of airborne pollutants in the northern hemisphere. From the 1970s to 2002, the increases in PBDE input flux to the sediments are exponential at all locations, with doubling times (t_2) ranging from 9 to 43 years for $\sum_9$BDEs, and from 7 to >70 year for BDE209. The longer t_2 values found in sediments compared with those in human and fish in the region suggest the slower response of sediment to emissions. The correlations between the concentrations of $\sum_9$BDEs or BDE209 in surface sediments and latitude are strengthened by normalization of the concentrations with sediment contents of the organic matter or organic carbon, but not soot carbon. Multivariate linear regression equations were developed using data obtained with sediment segments deposited after 1950. All the regressions are statistically significant; and the three independent variables—year of deposition, latitude, and organic matter content of the sediments—account for 73% and 62% of the variations in the concentrations or the fluxes of $\sum_9$BDEs and BDE209, respectively, in the Great Lakes sediments.

Introduction

The Laurentian Great Lakes, Superior, Michigan, Huron, Erie, and Ontario, comprise the largest fresh surface water system with a total volume of approximately 23 000 km^3. The drainage area of this system covers a total area of 750 000 km^2; of which 244 000 km^2 is the water surface of the lakes. The hydraulic residence time of each lake ranges from 3 y in Lake Erie to 197 y in Lake Superior. The location of the Great Lakes is in close proximity to some of the most densely populated and highly industrialized areas of North America. All these features contribute to the vulnerability of the Great Lakes to the input of various pollutants from air and other sources (*1*).

The Great Lakes do not mineralize all the pollutants they receive. While a small fraction of the total amount may exit the system via water outflows, the vast majority of the pollutants accumulate within the lakes. For hydrophobic and persistent organic pollutants such as polychlorinated biphenyls (PCBs), sediments have become the largest depository, and retrieved sedimentary records have been used to reconstruct history of their input from air deposition as well as other sources (*2*). Similar approaches are expected to be valid for polybrominated diphenyl ethers (PBDEs), a group of flame retardants widely used since the 1970s. This expectation stemmed from the considerations that fluvial input of PBDEs is minimal to most open lake basin locations, that the equilibrium between air and water is rapid as is the case for PCBs (*3*), that the affinity of PBDEs for particulate matter in the water column is likely to be strong, and that PBDE degradation after burial is likely to be slow.

A research project was carried out to investigate the chronology of air deposition of PBDEs into the Great Lakes as recorded in the sediments. The hypotheses of this research were that (i) atmospheric deposition is the major source of PBDEs in the sediments of the Great Lakes, (ii) the temporal trend of PBDE fluxes reflects their production history and is different from those of PCBs, (iii) the spatial distribution of PBDEs provides evidence that PBDEs are predominantly from anthropogenic sources, and (iv) the relative BDE congener distribution in sediments is different than those seen in air and fish, in that more heavily brominated congeners like decabromodiphenyl ether (BDE209) will predominate. In this project, 16 sediment cores from all of the Great Lakes were collected and horizontally sectioned. The samples were characterized for physical and chemical parameters, dated using Pb-210 alpha spectroscopy, and analyzed for PBDE as well as PCB concentrations. Lake-specific results of this work have been published previously in this series (*4*−*6*). In addition, soot deposition to the Great Lakes as well as the degradation and diagenesis of organic matter in the lake sediments have also been examined in this project and the results are reported elsewhere (*7*, *8*). A complete dataset of results and additional information can be found in our comprehensive Final Report to U.S. Environmental Protection Agency (USEPA) (*9*). This paper provides a descriptive and quantitative summary of the results with the objectives of providing a new and better system-wide understanding, and drawing conclusions where possible, from the data with respect to the hypotheses stated above.

Results Summary

Sampling locations are shown in Figure S1 with geographic coordinates given in Table S1 of the Supporting Information. In the discussion below, $\sum_9$BDEs refers to the sum of BDEs 28, 47, 66, 85, 99, 100, 153, 154, and 183. Discussions on PCBs are mainly based on the sum of 11 PCB congeners ($\sum_{11}$PCBs), including PCBs 8, 18, 28, 52, 44, 66, 153, 187, 180, 195, and 206, which are the PCB congeners analyzed for all the sampling locations.

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TABLE 1. Total Load[a] and Surface Annual Load[b] of PBDEs and PCBs in the Great Lakes around Year 2002 (Mean ± SD)

			Σ_9BDEs[c]		BDE209		Σ_{11}PCBs[d]	
	water surface area (km^2)	N	total load (tonnes)	annual load (tonnes yr^{-1})	total load (tonnes)	annual load (tonnes yr^{-1})	total load (tonnes)	annual load (tonnes yr^{-1})
Superior	82100	4	0.51 ± 0.39	0.012 ± 0.008	3.89 ± 1.22	0.10 ± 0.02	3.86 ± 1.90	0.034 ± 0.017
Michigan	57800	3	1.48 ± 0.83	0.036 ± 0.023	38.8 ± 10.3	0.75 ± 0.41	11.83 ± 3.38	0.151 ± 0.101
Huron	59600	3	0.85 ± 0.42	0.031 ± 0.013	9.04 ± 4.30	0.58 ± 0.23	4.70 ± 3.98	0.117 ± 0.046
Erie	25700	2	1.80 ± 0.28	0.058 ± 0.032	18.5 ± +1.50	1.62 ± 0.95	23.29 ± 8.56	0.282 ± 0.062
Ontario	18960	2	0.63 ± 0.25	0.032 ± 0.006	21.6 ± 7.26	1.31 ± 0.11	25.39 ± 0.37	0.165 ± 0.008

[a] Total load = inventory × water surface area of the lake. [b] Annual load = input flux at sediment surface × water surface area of the lake. [c] The sum of BDEs 28, 47, 66, 85, 99, 100, 153, 154, and 183. [d] The sum of PCBs 8, 18, 28, 52, 44, 66, 153, 187, 180, 195, and 206.

The concentration of PBDEs in surface sediments ranged from 0.5 to 6.7 ng g^{-1} dry weight (dw) and from <4 to >240 ng g^{-1} dw for Σ_9BDEs and BDE209, respectively. Zhu and Hites (*10*) reported surface concentrations of 63 ng g^{-1} dw for BDE209 and 65 ng g^{-1} dw for the sum of 18 congeners including BDE209 at LM-18. These agree well with our results of 50 ng g^{-1} dw for BDE209 and 53 ng g^{-1} dw for total PBDEs, and the difference may indicate an increase of about 12 ng g^{-1} dw in PBDE concentration in surface sediments at LM-18 from 2002 to 2004. In Lake Ontario, Breivik et al. (*11*) measured PBDEs in a sediment core collected west of ON-40 in 1998, and reported surface concentrations of BDEs 47 and 209 are about two-thirds of those observed in our work at ON-40 in 2002. For Lake Erie, previously reported surface concentrations of BDE209 (39 ng g^{-1} dw) and sum of tri- to hepta-BDEs (1.1 ng g^{-1} dw) (*10*) are also in agreement with our results.

Comparisons among sampling locations are shown in Figure S2 in the Supporting Information. Among the five lakes, Lake Ontario has the highest concentrations of both Σ_9BDEs and PCBs on dry weight basis. However, the organic carbon normalized Σ_9BDEs concentrations in Lakes Ontario and Erie are comparable; and both are higher than those in the other lakes. In Lake Ontario, both sampling locations had surface BDE209 concentrations exceeding 200 ng g^{-1} dw, more than double that at LM-18 and quadruple those in Lake Erie. The inventory, or accumulation over time, of BDE209 is the highest (141 ng cm^{-2}) at location ON-40 among all sampling sites. The inventory of Σ_9BDEs was found to be high in Lake Erie, with 7.8 and 6.2 ng cm^{-2} for the east (ER-09) and west (ER-37) basins, respectively. The current (2002) chemical flux, or input rate, at ER-09 stands out among all locations having the highest values of 0.31, 8.9, and 1.6 ng cm^{-2} y^{-1} for Σ_9BDEs, BDE209, and Σ_{11}PCBs, respectively.

The total loads of PBDEs and PCBs are given in Table 1. Despite accounting for nearly one-third the total Great Lakes surface area and more than half the volume, Lake Superior accumulates, by far, the least amount of PBDEs and PCBs. Lake Erie (the second smallest by surface area) has the highest total accumulation of Σ_9BDEs (about 1.8 tonnes), followed by Lakes Michigan, Huron, and Ontario. For BDE209, the lake ranking by load is different, with Lakes Michigan > Ontario > Erie > Huron > Superior. The total amount of PBDEs accumulated in the sediments of the Great Lakes is estimated to be about 5.2 ± 1.1 and 92 ± 13 tonnes for Σ_9BDEs and BDE209, respectively, where the uncertainty of each estimate is the square root of the sum of the standard deviations for individual lakes (Table 1). These are in close agreement with the estimate of 100 tonnes of total PBDEs by Zhu and Hites (*10*). Also presented in Table 1 are the estimated annual loads to the sediments around 2002. Sediments in Lakes Erie and Ontario collected about 1.62 and 1.3 tonnes, respectively, of BDE209 in 2002, while other lakes received much less. Lake Erie has received larger amounts of Σ_9BDEs and Σ_{11}PCBs than all other lakes. This is not surprising because Lake Erie is in close proximity of a number of urban centers, and receives input from several rivers carrying discharges of treated and untreated wastewaters. Estimates of the total annual loading rate to the sediments of all Great Lakes in 2002 are 0.17 and 4.4 tonnes for Σ_9BDEs and BDE209, respectively. All the estimates are based on observations made at only 2−4 mid-basin sampling locations for each lake and thus warrant caution in interpretation.

Spatial Distribution: Dependence on Latitude and Longitude. A south-to-north decreasing gradient of PBDE levels was identified in previous studies conducted in the northern hemisphere including North America (*11*, *12*), Europe (*13*), and Asia (*14*). In this work, an obvious strong log-linear dependence of sediment PBDE levels on latitude was identified, as shown in Figure 1. The dependence on latitude is moderate for dry mass based surface concentration of Σ_9BDEs, with $R^2 = 0.49$ (Figure 1). For individual congeners, however, the correlations between surface concentration and latitude are in general much weaker, although those for BDE209 ($R^2 = 0.54$, Figure 1) as well as BDEs 99 ($R^2 = 0.61$), 100 ($R^2 = 0.37$), and 47 ($R^2 = 0.37$) are reasonably strong. The surface flux of all congeners correlates moderately with latitude, with $R^2 > 0.5$ for BDEs 47, 99, 153, 183, 209, and Σ_9BDEs. Stronger latitude dependence was observed for inventory of PBDEs (Figure 1), with an average R^2 of 0.74 and average p-value of 3.5×10^{-3}. Inventory is an accumulative quantity, thus provides a more accurate reflection of the PBDE deposition behavior over time than a “grab” sample representing surface concentration or flux. Further, inventory data were obtained by summing the concentrations in all the sediment segments of a core; thus these values are more reliable due to the possible cancellation of random errors in individual measurements. Muir et al. (*12*) examined the flux of BDE209 to lake sediments among a latitude gradient from 43° (Lake Ontario) to 80° North. The decreasing trend of concentrations with increasing latitude is obvious for the lakes outside the Arctic Circle; and the data obtained in the present work fit well into the trend line. Correlations with longitude of the sampling sites were also examined. The decreasing trend of PBDE inventory with increasing longitude is clear, as shown in Figure S3 of the Supporting Information, although none has $R^2 > 0.5$ and $p < 0.01$. Surprisingly, longitude performed equally well as latitude in correlating with the surface concentrations and fluxes of BDE209 (also in a few cases with BDE153), but not other congeners.

The dependence of PBDE inventory on latitude is believed to reflect both the influence of urbanization and the south-to-north direction of long-range transport of airborne pollutants in the northern hemisphere. To examine the urban impact, we used metropolitan population (P) and distance between the site and the city (D), and defined an urban distance factor UDF = P/D^2 (Table S2). An overall UDF for each sampling location was calculated, with >100 metropolitan and micropolitan statistical areas in both the U.S. and Canada included. A highly statistically significant correlation ($N = 14$, $R^2 = 0.80$, $F = 48$, $p = 1.6 \times 10^{-5}$) between

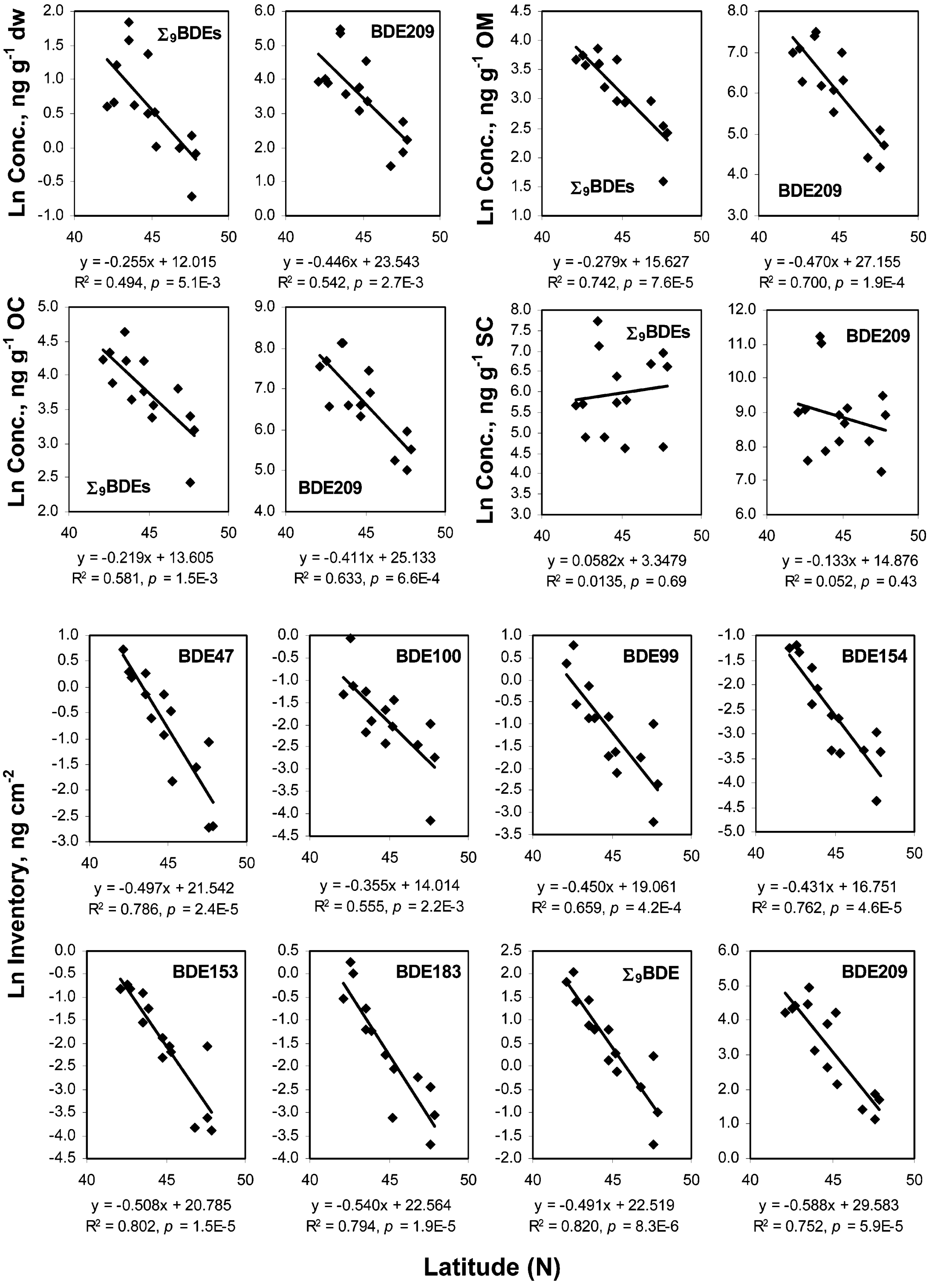

FIGURE 1. Concentration and inventory of PBDEs in sediment versus latitude.

the latitude and the UDF of the sampling sites was found. Despite the facts that UDF does not take into account the effects of prevailing wind direction and temperature gradient and that some arbitrary decisions are unavoidable in city selection, this approach provides a convenient tool to investigate the effect of a large number of metropolitan areas to all the study sites. Given the wide application of PBDEs in consumer textile and electronics products, it is likely that their emissions would be related to population density, which shows a strong south-to-north gradient in the region. However, UDF performed less satisfactorily than latitude in almost all regressions with PBDE data.

The global fractionation theory (*15*) predicts that lighter congeners have higher long-range transport potential, thus reaching remote regions in larger proportion than the heavier congeners (*16*). In European background soils, the percentages of lower congeners in the total PBDE concentrations were found to increase with latitude while the opposite tended to be true for heavier congeners (*17*). In North America, the exponential decline of input fluxes with increasing latitude in the remote region north of the Great Lakes was reported with empirical half distances (EHD) of 1168 km for BDE47 and 566 km for BDE209 (*11*). For the Great Lakes, the EHDs estimated from the slope of the regressions shown in Figure

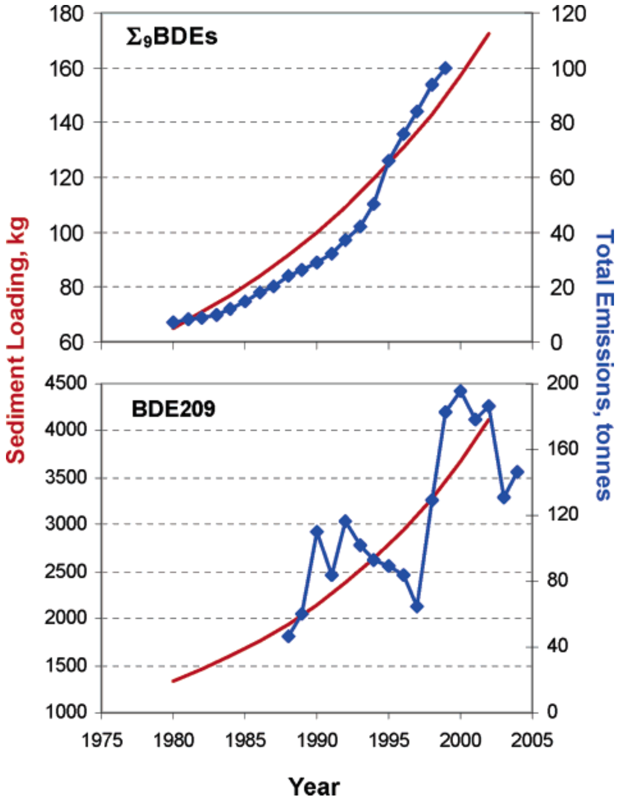

FIGURE 2. Time trends of total annual load to the sediment of all the Great Lakes compared with emission history. The annual load were estimated from the all-lake sum of lake-wide average flux, which was calculated based on exponential increase in concentration from 1980 to 2002, multiplied by the water surface area of each lake. For $\sum_9$BDEs, the emission data are for BDE47 in North America (*18*). For BDE209, the emissions are sum of total on- and off-site disposal or other releases (including off-site recycling in the Canadian database) in the U.S. States of Wisconsin, Minnesota, Illinois, Indiana, Michigan, Ohio, Pennsylvania, New York (*19*), and the Canadian Province of Ontario (*20*).

1 are approximately 300 km and 170 km for the surface concentrations of BDEs 47 and 209, respectively. The corresponding EHD values for surface flux are 150 km and 110 km. These values are much shorter than those observed in the northern remote region by Breivik et al. (*11*). This was expected from the changes in meteorological and geographical conditions and may also reflect the fact that atmospheric deposition is the dominant source of PBDEs in the remote region while urban influence via fluvial discharges can be significant to the Great Lakes, as discussed above. However, although the EHD is shorter for BDE209 than all other congeners, statistical analyses do not validate a significant decreasing trend of EHD with increasing bromination among tri- to hepta-BDEs. PBDEs partition much more strongly on particles than PCBs and PAHs (*7*). How this affects their "grasshopper" behavior and fractionation is yet to be investigated. Nonetheless, the observed latitude dependence may result at least partially from the long range atmospheric transport of PBDEs in addition to the urbanization influence.

Temporal Trends: Doubling Time and Chronology. A sharp, continuous increase in both PBDE concentration and flux since the 1970s are observed at all sampling sites. This observation agrees with the history of PBDE emissions in the region (*18*–*20*) as shown in Figure 2, and with the findings of numerous studies in recent years. This not only provides clear evidence that the sources of PBDEs are overwhelmingly anthropogenic in origin, but also indicates that sediment records can be used to reconstruct the history of emissions and uses of PBDEs within the Great Lakes basin.

TABLE 2. Doubling Time of PBDE Concentrations at Each Location[a]

	t_2 (year)			t_2 (year)	
ID	Σ9BDEs	BDE209	ID	Σ9BDEs	BDE209
SU-08	11 ±1 (4)	74 ± 73 (3)	HU-12	11 ± 1 (12)	9 ± 3 (8)
SU-12	19 ± 3 (4)	62 ± 33 (4)	HU-38	32 ± 6 (6)	20 ± 6 (5)
SU-16	43 ± 63 (3)	28 ± 1 (3)	HU-48	13 ± 1 (5)	9 ± 1 (4)
SU-22	15 ± 2 (7)	27 ± 16 (4)	ER-09	20 ± 3 (12)	9 ± 5 (6)
MI-18	11 ± 2 (6)	19 ± 5 (6)	ER-37	16 ± 3 (11)	
MI-41	14 ± 2 (10)	21 ± 12 (7)	ON-30	15 ± 3 (10)	7 ± 1 (7)
MI-47	9 ± 1 (7)	12 ± 2 (6)	ON-40	11 ± 2 (9)	16 ± 4 (6)

[a] t_2 ± standard error (number of data points). The t_2 for individual sampling sites was estimated from the slope of regression of ln concentration vs number of years before 2002. All the regressions are graphically presented in ref *9*. The standard error was estimated proportionally from the standard error of the slope.

The increase in PBDE concentration over time is more exponential than linear at most locations in the Great Lakes, based on regression coefficients. Using all the data obtained for samples dated 1950 and later, the doubling time (t_2) of PBDEs in the sediment was calculated from the linear regression of natural logarithm concentration versus the difference between the year of sampling (2002) and the year of deposition determined from sediment dating. The regressions are fairly strong, with the average R^2 being 0.84 and 0.71 for $\sum_9$BDEs and BDE209, respectively. Table 2 summarizes the estimated t_2 values. For $\sum_9$BDEs, the mean and median t_2 values are 17 and 14 years, respectively, and 12 out of 14 t_2 values are within the range of 9–19. For BDE209, the estimated doubling times range from 7 to 28 years, except at sites SU-08 and SU12, where t_2 of >60 years was obtained. In general, the t_2 values for BDE209 are less statistically certain, especially for Lake Superior, than those of $\sum_9$BDEs, because of limited numbers of data points. The t_2 for BDE209 at ER-37 is not provided because of the lack of correlation ($R^2 < 0.05$) due to the zigzag pattern of BDE209 concentration versus depth (*6*). It is important to realize that t_2 may be affected by sediment focusing, i.e., shorter t_2 values may result from greater sediment focusing. This may explain the relatively long t_2 values at SU-12, SU-22, and HU-38; all of which have focusing factors less than 0.8 (Table S1). The t_2 value for PBDEs in the sediments of the Great Lakes reported by Zhu and Hites is 5–10 years (*10*), estimated based primarily on two sites where extremely high focusing occurs (The reported focusing factors are 3.3 and 7.9 for the sites in Lakes Michigan and Erie, respectively) (*10*).

Comparison among locations indicates that the t_2 of BDE209 tends to be shorter than that of $\sum_9$BDEs in Lakes Huron, Erie, and Ontario, while the opposite is true in Lake Superior (Table 2). As discussed above, long-range transport of BDE209 may be slower than other congeners, which may result in longer t_2 at more remote locations. In fact, a statistically significant dependence of ln t_2 on latitude of the sampling sites was identified for BDE209 ($N = 13$, $R^2 = 0.60$, $F = 16.5$, $p = 0.002$). Such dependence was not found for $\sum_9$BDEs.

Compared with reported PBDE t_2 values in food web biota (*21*, *22*) and humans (*23*) in the region, the t_2 in Great Lakes sediments are generally longer. This is not unexpected because in aquatic systems, sediment is the slowest compartment in responding to a change in pollutant atmospheric deposition. Photolysis and other degradation processes in the atmosphere and water column before PBDEs deposit to and become buried in the sediments, as well as sediment re-suspension and distribution by water flow, may contribute to the relatively slower accumulation compared with other media. By the same argument, we expect that if PBDE emissions cease, half-life values ($t_{1/2}$) of PBDEs in the sediments could be longer than in other media.

The time trend of PBDE flux was compared with that of PCBs to test the hypothesis that PBDE deposition history in the Great Lakes is different from PCBs. There have been reports of strong correlations between PBDEs and PCBs concentrations in both air (*24*) and fish (*25*) in the Great Lakes. In our study, we also found that surface concentrations of PBDEs and PCBs are correlated, as shown in Figure S4. Such correlations point to common or similar mechanisms of transport and/or source zones for these two groups of pollutants. However, chronological analysis of these compounds indicates differences in temporal trends. When plotting the input fluxes of PBDEs and PCBs versus sediment deposition year, PCB input commenced and peaked ahead of PBDEs at all locations, as can be seen from the four examples presented in Figure S5. The concentration of PCBs in the Great Lakes has declined during the last decades, in agreement with published air and fish data from previous studies (*26*, *27*). This is not the case for PBDEs at present, which show an increased loading during this time.

Role Played by Sediment Organic Content. It is well-established that hydrophobic organic pollutants like PAHs and PCBs preferentially sorb to organic rich components in sediment. In this work, we examined whether normalization of the PBDE data by organic matter (OM), organic carbon (OC), or soot carbon (SC) would strengthen the latitudinal correlation. As shown in Figure 1, significant impact was observed by normalizing to OC and OM. On the other hand, the correlations are weakened to near randomness by SC normalization; in contrast to our results showing highly significant correlations between SC deposition and PAH concentration in the sediments of Lake Michigan (*7*). Both SC and PAHs originate from incomplete combustion emissions, which have declined significantly over the past decades. It is also widely recognized that the stronger sorption to soot of PAHs relative to PCBs and chlorinated benzenes stems from their planar molecular structures. Both PCBs and PBDEs do not share common emission sources with soot. In addition, PBDE molecules, in which the two phenyl rings are connected by an oxygen, do not possess a stable planar conformation. These may explain the lack of significant correlations between PBDEs and SC in sediment. However, the affinity of PBDEs to OM and solid surfaces from both air and water may be stronger than PAHs and PCBs, due to their lower vapor pressure and higher octanol−air and octanol−water partition coefficients, as we demonstrated previously (*7*).

Variation in Congener Patterns. The mass-based concentration ratios of major congeners are illustrated in Figure 3. All these ratios are log-normally distributed, with the arithmetic mean close to the 75% percentile. The latitudinal dependence of various congener ratios for both concentration and inventory was examined, but none turned out to be statistically significant. Correlations among individual PBDE congeners are all significant, as shown in Table S3, despite the fact that they are from three different technical mixtures.

BDE209 is clearly the dominant congener in the sediments of all the Great Lakes. Its mass fraction of the total PBDEs averaged 94% on a mass basis and 89% on a molar basis. Based on 10 and 90% percentiles, BDE209 is about 20−200 times higher than BDE47, and about 6 −60 times higher than Σ_9BDEs by mass. The dominance of BDE209 in sediments is in clear contrast with the lack of BDE209 in fish and humans (*23*), and its relatively low fraction in air (*28*). Among the other nine BDE congeners, BDE47 outweighs BDE99 in 90% of the samples to be the most abundant. In general, heavier congeners are present in higher proportions in sediments than in air, water and fish, as we have shown and discussed for individual lakes (*4*−*6*). Together, these results provide clear validation of our hypothesis that the congener pattern in Great Lakes sediments is different from those in other environmental media.

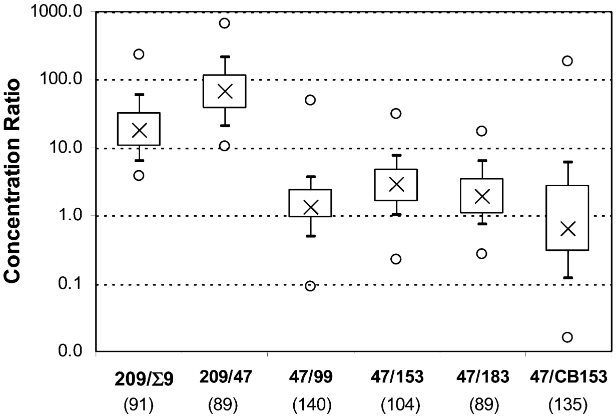

FIGURE 3. Box and whisker plot of concentration ratios of major congeners in Great Lakes sediments. $\Sigma 9 = \Sigma_9$BDEs, and CB = PCB. Shown are median percentiles 25−75% percentiles (box), 10% and 90% percentiles (whiskers), and the minimum and maximum (circles). The number of data points is given in the parentheses.

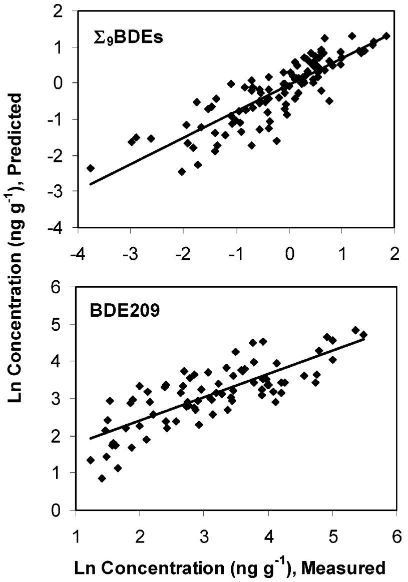

FIGURE 4. Predicted versus measured concentration (ng g^{-1} dw) of sediment PBDEs. The prediction equations are Ln Σ_9BDEs = −82.6 (±6.97) + 0.0453 (±0.0034) × deposition year − 0.235 (±0.0318) × latitude (N) + 0.721 (±0.160) × Ln OM (mg g^{-1}) with $N = 106$, $R^2 = 0.73$, $F = 92.5$, $p = 6 \times 10^{-29}$; and Ln BDE209 = −37.4 (±12.4) + 0.0241 (±0.006) × deposition year − 0.332 (±0.042) × latitude (N) + 1.75 (±0.220) × Ln OM (mg g^{-1}) with $N = 81$, $R^2 = 0.63$, $F = 43.1$, $p = 2 \times 10^{-16}$. Similarly strong regression statistics were obtained for the input fluxes of Σ_9BDEs and BDE209 (see Table S4 in the Supporting Information).

Implications to Air Deposition. Based on the discussions above, we hypothesize that time (year), location (latitude), and sediment organic contents (OM content) will be the major factors influencing the PBDE levels in the Great Lakes. Forward stepwise multivariate regression analyses were carried out using all the data obtained from sediment segments deposited starting at 1950. The regression results are presented in Table S4 for Σ_9BDEs and BDE209. Predicted concentrations using two three-variable models are compared with the measured values in Figure 4. In these models, deposition year, latitude, and organic matter content of the sediment account for 73 and 62% of the variation in the concentrations or fluxes of Σ_9BDEs and BDE209, respectively. The applicability of these models may be limited to the time period in which the exponential increase in the PBDE input to the Great Lakes sediment continues. These models provide a predictive tool for reconstructing PBDE deposition history in the Great Lakes, and are expected to be useful for regulatory purposes aimed at managing the pollution of PBDEs in the region and beyond.

Data of PBDE concentrations in the water and its subcompartments such as suspended and settling solids in the Great Lakes are not available at present. This makes it difficult to estimate the total input and accumulation of PBDEs in the lakes. Palm et al. (*29*) has estimated the equilibrium distribution of BDEs 47, 99, and 209 in a generic environment, using the equilibrium criteria (EQC) model (*30*). Their results show that only 2% of the total amount of PBDEs in the water body would be in the water column containing suspended solids and fish; while the remaining 98% is in the sediment, no matter whether the emission medium (or input source within the context of this paper) is air or water. Although the dimensions, including the relative volumes of different compartments, of the Great Lakes differ from that of the generic environment defined by the EQC model, we expect that sediment is the largest depository of PBDEs in the Great Lakes. Therefore, the inventory of PBDEs presented in this paper may reflect their accumulation in the Great Lakes with fair accuracy.

Air deposition is recognized as a major source of many pollutants, including PCBs and mercury, to the Great Lakes (*1*). The importance of air deposition relative to other input pathways varies among both pollutants and lakes, and may also change with time. For example, about 72−96% of benzo[a]pyrene in all the Great Lakes were estimated to be from air (*31*). In comparison, the total atmospheric input of PCBs, including wetfall, dryfall, and gas exchange, contributed 91, 78, 58, 13, and 7% of the total PCBs in Lakes Superior, Michigan, Huron, Erie, and Ontario, respectively, in the late 1980s (*31*). These percentages for PCBs may have changed during the last two decades due to the reduction in emissions from point sources, many of which are at lower latitude locations in the Great Lakes region.

A quantitative assessment of the contribution from air deposition to the PBDEs in the Great Lakes sediments requires more monitoring data than we can provide here and is beyond the scope of this study. Although air deposition may outweigh other inputs in some locations such as mid-lake basins, fluvial input from tributaries may contribute a significant fraction of the total PBDE load in the Great Lakes. The role played by the connecting channels, the St. Clair/Detroit River between Lakes Huron and Erie, and the Niagara River between Lake Erie and Ontario, may also be important and contribute substantially to the greater PBDE loading in the lower Great Lakes. This possibility is supported by the recent report that significant amounts of PBDEs derived from wastewater treatment plants enter Lake Ontario via the Niagara River (*32*). Finally, although no consideration is given here to degradation (nor is it in fact possible from the data), the role degradation plays in PBDE attenuation in the sediments should be investigated.

Acknowledgments

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Supporting Information Available

Additional tables and figures of our analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

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