



Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Halogenated flame retardants in sediments from the Upper Laurentian Great Lakes: Implications to long-range transport and evidence of long-term transformation

Jiehong Guo^a, Zhuona Li^a, Prabha Ranasinghe^a, Karl J. Rockne^b, Neil C. Sturchio^{c,1}, John P. Giesy^d, An Li^{a,*}

^a School of Public Health, University of Illinois at Chicago, Chicago, IL, USA

^b Department of Civil and Materials Engineering, University of Illinois at Chicago, Chicago, IL, USA

^c Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, IL, USA

^d Department of Veterinary Biomedical Sciences and Toxicology Centre, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

ARTICLE INFO

Editor: R Teresa

Keywords:

Great Lakes

Sediment

Halogenated flame retardants

Long range transport

Long-term transformation

ABSTRACT

Most hydrophobic halogenated flame retardants (HFRs) are highly accumulative and persistent in aquatic sediments. The objective of this study was to reveal spatial distributions, temporal trends, and transformation of selected legacy and emerging HFRs in sediments of Lakes Superior, Michigan, and Huron. We collected Ponar grab samples at 112 locations and sediment cores at 28 sites in the three lakes, and measured concentrations of 19 brominated FRs and 12 chlorinated FRs. Based on grab samples, concentrations were higher at southeastern and sites near Sleeping Bear Dunes of Lake Michigan, and Saginaw Bay and the North Channel of Lake Huron. The annual loadings of polybrominated diphenyl ether (PBDEs) and Dechlorane Plus (DPs) to sediment have leveled off or been declining since 2000, while loadings of DBDPE and Dec604 have increased since the 1960s in most cores. The concentration ratio of BB101 to BB153 increased with sediment depth, suggesting the occurrence of *in situ* debromination of BB153. The ratio of dechlorinated *anti*-Cl₁₁DP over *anti*-DP increases with the increasing latitude of sampling locations, suggesting the occurrence of dechlorination of *anti*-DP to *anti*-Cl₁₁DP during transport. This ratio also increases with increasing sediment age in most cores, implying *in situ* dechlorination over time.

1. Introduction

Flame retardants have been widely used in furniture, vehicles, electronic devices, plastics, fabrics, and other materials to prevent or slow down the spreading of fire (Alaee et al., 2003; de Wit et al., 2011). Halogenated flame retardants (HFRs) contain bromine and chlorine atoms which are released during combustion. The halogens act to capture free radicals and thereby terminate the chain reactions of combustion (Alaee et al., 2003). HFRs comprise brominated FRs (BFRs) such as polybrominated diphenyl ethers (PBDEs) and biphenyls (PBBs), and chlorinated FRs (CFRs) such as dechlorane (mirex) and dechlorane plus (DP), halogenated organophosphate esters, and others. Widespread use of HFRs has caused various health concerns. Animal studies showed that PBDEs have hepatotoxicity, embryo toxicity, and can affect the thyroid (Darnerud et al., 2001). PBBs cause chronic toxicity and cancer

in animals, and studies suggest they might be transformed to toxic polybrominated dibenzofurans during combustion (WHO, 1994). Mirex is considered a potential carcinogen for humans (WHO, 1984). Oral exposure to DP can induce hepatic oxidative damage and perturbations of metabolism and signal transduction in male mice (Wu et al., 2012). DP also exhibits neurotoxicity in zebrafish when they are co-exposed with 3-methylphenanthrene (Chen et al., 2019). Dechlorane 602 (Dec602) might have immune and neuronal toxicity to mice (Tao et al., 2019). Although production of PBDEs, PBBs, and mirex has ceased in the United States, their replacement HFRs are synthesized and commercially produced. Bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH) and 2-ethylhexyl, 2,3,4,5-tetrabromobenzoate (EHTBB) mixture, 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE), and decabromodiphenylethane (DBDPE) are the major replacements of commercial penta-BDE, octa-BDE and deca-BDE, respectively (Van den Eede

* Corresponding author at: Environmental and Occupational Health Sciences, School of Public Health, University of Illinois at Chicago, 1603 West Taylor St., Chicago, IL, 60612, USA.

E-mail address: anli@uic.edu (A. Li).

¹ Current address: Department of Geological Sciences, University of Delaware, Newark, Delaware, USA.

<https://doi.org/10.1016/j.jhazmat.2019.121346>

Received 4 August 2019; Received in revised form 22 September 2019; Accepted 27 September 2019

0304-3894/ © 2019 Elsevier B.V. All rights reserved.

et al., 2012).

The Great Lakes of North America is the largest freshwater system on Earth. The “upper” lakes include Lakes Superior, Michigan, and Huron, which together cover a total water surface area of 200,000 km² and a total drainage area of 400,000 km² (USEPA, 2019a). Major coastal cities in the upper Great Lake region include Chicago, Detroit, Duluth, Milwaukee, and others. Many chemical industries have production facilities in the region, including those of organohalogenes. Legacy and emerging HFRs have been found ubiquitously in the environment of the Great Lakes, including air (Hoh et al., 2005, 2006; Salamova and Hites, 2011; Strandberg et al., 2001), water (Venier et al., 2014), sediment (Shen et al., 2010; Song et al., 2004, 2005a; Song et al., 2005b; Sverko et al., 2008; Yang et al., 2012, 2011; Zhu and Hites, 2005), fish (Luross et al., 2002; Su et al., 2017; Tomy et al., 2007; Zhu and Hites, 2004), and herring gulls (Gauthier et al., 2007, 2008; Gauthier and Letcher, 2009; Gauthier et al., 2009; Norstrom et al., 2002). In the environment, HFRs may be dehalogenated through chemical, biological, or photochemical processes (Brazeau et al., 2018). For example, DPs have been found dehalogenated in sludge of waste water treatment plants (Zeng et al., 2014).

This work is part of the Great Lakes Sediment Surveillance Program. The objective of the program was to survey the spatial distributions and temporal trends of persistent, bioaccumulative, and toxic chemicals in sediments of the Laurentian Great Lakes. Results have been published from this study for per- and poly-fluorinated alkyl substances (PFASs) (Christensen et al., 2019; Codling et al., 2018a, b; Codling et al., 2014), organophosphate esters (OPes) (Cao et al., 2017), atrazine and other herbicides (Guo et al., 2016), polyhalogenated carbazoles (PHCZs) (Guo et al., 2014a, 2017a), and legacy chlorinated persistent organic pollutants (Li et al., 2018) including polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), naphthalenes (PCNs), and diphenyl ethers (PCDEs). In this paper, we report new data for 31 HFRs in 112 Ponar grab and 28 core sediment samples from upper Great Lakes. The target HFRs included 9 PBDEs, 2 PBBs, 8 other BFRs, 11 dechlorane related HFRs, and one other CFR. With this data set, we provide estimates of the current loads, past and recent input rates, and characterize the spatial distribution patterns and temporal trends of HFR contamination in the sediment of the upper Great Lakes. The findings are discussed in the context of their long-range transport, long-term transformation, and potential sources in the upper Great Lakes region.

2. Material and methods

2.1. Sampling and sediment characterization

Ponar surface grab and core sediment samples were collected from Lakes Michigan, Superior, and Huron onboard the U.S. EPA Research Vessel (*R/V Lake Guardian*) during 2010–2012. A total of 112 surface grab samples were collected including 29 from Lake Michigan, 24 from Lake Superior, and 59 from Lake Huron, using a Ponar grab sampler. Sediment cores were collected using a box corer or an Ekman dredge corer for sites in Lake Michigan (N = 10), or an MC400 multi-corer (Ocean Instruments, San Diego, California) for sites in Lakes Superior (N = 9) and Huron (N = 9). Each sediment core was sectioned into about 25 segments at intervals ranging from 0.5 to 2 cm. Sampling sites can be found in Figure S1 in Supplementary Material (SM). Detailed information for sample handling can be found elsewhere (Guo et al., 2016; Li et al., 2018).

All the samples were measured for bulk density, water and solid content, total organic carbon (TOC), and organic matter content (OM). Activities of radionuclides ²¹⁰Pb and ¹³⁷Cs in core segments were measured by gamma spectrometry using HPGe well detectors (Ortec) interfaced with DSPEC-Plus digital signal processors, from gamma emissions at 46.5 keV and 661.6 keV, respectively. The mass sedimentation rates (MSR) and focusing factors (FF) were obtained from

cumulative excess ²¹⁰Pb inventories. MSR ranged from < 0.01 to 0.16 g/cm²-y, and FF ranged from < 0.1 to 3. Additional description of the laboratory procedures and detailed results are given elsewhere (Bonina et al., 2018; Corcoran et al., 2018).

2.2. Chemical analysis

Nine congeners of PBDEs (IUPAC No. 28, 47, 99, 100, 153, 154, 183, and 209) were among targeted BFRs. Ten other BFRs were analyzed, including hexabromobenzene (HBBz), pentabromobenzene (PBBz), pentabromotoluene (PBT), pentabromoethylbenzene (PBEbZ), 2,2',4,5,5'-pentabromobiphenyl (BB101), 2,2',4,4',5,5'-hexabromodiphenyl (BB153), decabromodiphenylethane (DBDPE), 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethylhexyl-1,2,3,4,5-tetrabromobenzoate (EHTBB), bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH). Target CFRs included *syn*-dechlorane plus (*syn*-DP), *anti*-dechlorane plus (*anti*-DP), Dechlorane (mirex), Dechlorane plus monoadduct (DPMA), Chlordane plus (CP) and dechlorinated *anti*-DPs (aCl₁₁DP and aCl₁₀DP), Dechlorane 601 (Dec601), Dechlorane 602 (Dec602), Dechlorane 603 (Dec603), Dechlorane 604 components A and B (Dec604 and Dec604 CB). Purchasing information for all these targeted compounds, as well as solvents, sorbents, and other chemicals and reagents can be found in the SM.

A detailed description of treatment of samples and chemical analysis procedures was published elsewhere (Guo et al., 2014b). In brief, about 5 g of freeze-dried sediment of each sample was extracted with an accelerated solvent extraction system (Dionex ASE350, Thermo Fisher Scientific, Inc.). After concentration, the extract was cleaned up in a silica gel and alumina combined column. Most target analytes were eluted in the 4:1 hexane:dichloromethane (DCM) mixture. After concentration and solvent exchange to hexane, injection standard ¹³C labeled 2,3,3',4,4',5,5',6-octachlorobiphenyl (PCB205 L) was added before instrumental analysis. Additional description of the procedures can be found in the SM.

An Agilent 7890 gas chromatography (GC) coupled with Agilent 7001B triple quadrupole mass spectrometry (QQQMS) with electron impact (EI) ion source was used to analyze PBDEs (except BDE209), and other brominated flame retardants except EHTBB and DBDPE. Agilent 6890/5973 GC-MS (Agilent Technologies, Santa Clara, CA) equipped with electron capture negative ionization (ECNI) source was used to analyze BDE209, EHTBB, DBDPE, and all the chlorinated flame retardants. Detailed information about columns, instrument conditions and monitored ions used in both instruments are provided in the SM.

2.3. Quality control

Blanks (Na₂SO₄, activated at 500 °C for 8 h) were processed using the same laboratory procedures as for sediments to monitor potential contamination. These included trip blanks and field blanks from each sampling trip, and laboratory procedural blanks for each step starting from the freeze drying through extraction. Concentrations of most target compounds in the blanks were less than 0.12 ng/g dry weight (dw). Surrogates 4'-fluoro-2,3',4,6-tetrabromodiphenyl ether (F-BDE69, 4 ng), 3'-Fluoro-2,2',4,4',5,6'-hexabromodiphenyl ether (F-BDE154, 8 ng), 4'-fluoro-2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether (F-BDE208, 8 ng), and 4'-chloro-2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether (Cl-BDE208, 8 ng) were added to each sample before extraction. Their average recoveries ranged from 86% to 129%.

Duplicate samples were analyzed for each sediment core and each batch of about 12 Ponar grab samples. The median relative percentage differences (RPDs) of duplicate analyses were in the range of 9 to 40%. In addition, selected sediment samples were amended with the target analytes (8 to 24 ng each) and the average recoveries ranged from 60% to 134%. Instrument detection limits (based on three times of signal to noise ratio) ranged from 0.0005 ng/mL for BDE49 to 0.2653 ng/mL for DBDPE, which correspond to 0.0002 ng/g and 0.1061 ng/g

respectively, assuming that 5 g dw of sediment was extracted. Method detection limits, calculated using method based on U.S. EPA Standard Method SW846 and described in the SM, ranged from 0.0227 ng/g (BDE28) to 0.7854 ng/g (BDE209).

2.4. Data analysis

In data analysis, “non detect” data points were replaced with half of their respective detection limits in examining correlations between net deposition flux and other factors. Non detect data points were replaced with zero in all other calculations. Concentrations measured for sediment cores were used to estimate the following:

$$\text{Net flux}_i (\text{ng}/\text{cm}^2\text{-y}) = C_i \times \text{MSR} / \text{FF} \quad (1)$$

$$\text{Inventory} (\text{ng}/\text{cm}^2) = \sum C_i \rho_{b,i} d_i \quad (2)$$

$$\text{Annual loading rate} (\text{kg}/\text{y}) = \text{Average flux} \times \text{Lake water surface area} \times 10^{-2} \quad (3)$$

$$\text{Total load} (\text{tonnes}) = \text{Average inventory} \times \text{Lake water surface area} \times 10^{-5} \quad (4)$$

where C_i is the chemical concentration (ng/g dw), $\rho_{b,i}$ is the dry mass bulk density (g/cm³) and d_i is the thickness (cm) of segment i . The MSR is in g/cm²-y and the FF is dimensionless; their values are presented by Corcoran et al. (2018). Recent net deposition flux was estimated from the concentrations in uppermost segments of cores. The water surface areas of Lakes Michigan, Superior, and Huron are 57,800 km², 82,100 km², and 59,600 km², respectively. Other constants are for unit conversions. The “average” used in equations (3) and (4) was the lake-average net flux and inventory, respectively, using the inverse distance weighted interpolation from spatial analysis of ArcGIS 10. More detailed explanation of these parameters can be found in Li et al. (2018).

3. Results and discussion

Medians and maxima of the concentrations, inventories, recent net deposition fluxes, and the recent loading rate and total loads of analyte groups are summarized in Table 1. The same parameters for individual compounds are presented in Tables S1 through S3 of the SM.

3.1. Concentrations and total accumulations

Measured concentrations in Ponar grabs are presented graphically in Fig. 1. In general, the group sums are in the rank order of

$\Sigma_9\text{PBDEs} > \Sigma_2\text{DPs} > \Sigma_{10}\text{Other BFRs} > \Sigma_9\text{Other CFRs}$.

$\Sigma_9\text{PBDEs}$ (sum of BDEs 28, 47, 49, 99, 100, 153, 154, 183 and 209) ranged from 0.2 to 54 ng/g dw in Ponar grab samples (Fig. 1). Among these PBDE congeners, BDE209 was the most abundant, generally accounting for more than 95% of $\Sigma_9\text{PBDEs}$. The next was BDE47, which accounted for 40 to 60% of $\Sigma_9\text{PBDEs}$ (excluding BDE209). Concentrations of BDE209 were comparable to those reported previously (Song et al., 2004, 2005b; Yang et al., 2012), and lesser than those reported by Zhu and Hites for Lake Michigan (Zhu and Hites, 2005). Concentrations of $\Sigma_9\text{PBDEs}$ were generally greater in Lake Michigan (range 0.41–2.52 ng/g dw) than in Lakes Huron (range 0.002–1.63 ng/g dw) and Superior (range N.D. – 0.47 ng/g dw). These are comparable to concentrations in previous studies in the same lakes (Song et al., 2004, 2005b; Yang et al., 2012; Zhu and Hites, 2005). The total load of PBDEs in the sediment of Lake Michigan is estimated to be 45 tonnes (Table 1), which is similar to the estimate of 29 to 50 tonnes based on three cores collected in 2002 (Song et al., 2005b).

EHTBB, TBPH, BTBPE and DBDPE are considered “emerging” BFRs, as they are currently being produced as the most common replacements of commercial penta-, octa- and deca-BDEs (Van den Eede et al., 2012). Among them, BTBPE had the greatest overall frequency of detection in 88% of all Ponar grab samples collected during this study. Concentrations of BTBPE ranged from N.D. to 3.45 ng/g dw in the Ponar grab samples of the three lakes (Table S1), similar to the range previously reported (Hoh et al., 2005; Yang et al., 2012). The total load of BTBPE is about 3.23 tonnes in the three lakes, about one thirtieth of BDE209, but higher than the sum of other PBDEs. Although DBDPE was detected in < 50% of the Ponar grab samples with maximum concentration 0.71 ng/g dw, it was found more frequently in surface segments from all cores with concentrations ranging from 0.10 to 3.82 ng/g dw (Table S1). EHTBB was detected in 80% of Ponar grab sediment samples from Lakes Michigan and Huron, with concentrations < 1.40 ng/g dw. In contrast, EHTBB was not found in Lake Superior. EHTBB was used together with TBPH with the ratio of 4:1 in a currently used commercial FireMaster 550 (Stapleton et al., 2008) or 5:2 in BZ-54 (Barr et al., 2012). TBPH was not detected in any of sediment samples in this study. For comparison, EHTBB and TBPH were not detected in sediment and biota from San Francisco Bay, but found in the sediments of Daya Bay and Hong Kong Sea with sum (EHTBB + TBPH) ranging 0.044–0.80 ng/g dw (Liu et al., 2014). EHTBB and TBPH were also detected in the sediment samples collected from South Africa (La Guardia et al., 2013; Olukunle and Okonkwo, 2015). The total load of DBDPE is about one third of BTBPE, and the load of EHTBB is between those of DBDPE and BTBPE in the sediments of the upper Great Lakes (Table S3).

Table 1
Summary of measured and estimated parameters (median / maximum, or average).

Analyte group	Superior	Michigan	Huron	All Lakes	Superior	Michigan	Huron	All Lakes
	Concentration in Ponar grabs (ng/g dw)				Concentration at core surface (ng/g dw)			
$\Sigma_9\text{PBDEs}$	0.05 / 0.47	1.33 / 2.52	0.06 / 1.63	0.09 / 2.52	0.34 / 0.71	2.36 / 3.79	0.77 / 1.05	0.74 / 3.79
BDE209	0.79 / 2.60	6.51 / 37.8	2.68 / 52.4	2.67 / 52.4	11.6 / 17.4	57.4 / 88.8	34.9 / 62.2	29.8 / 88.8
$\Sigma_9\text{BFRs}$	0.08 / 0.43	0.88 / 2.68	0.53 / 11.4	0.46 / 11.4	2.42 / 6.04	4.04 / 8.00	3.26 / 6.78	3.21 / 8.00
$\Sigma_2\text{DPs}$	0.03 / 0.12	0.23 / 3.00	0.25 / 4.74	0.16 / 4.74	0.70 / 1.41	4.07 / 6.59	4.01 / 5.63	2.98 / 6.59
$\Sigma_{10}\text{CFRs}$	0.05 / 0.16	0.08 / 0.56	0.08 / 3.10	0.07 / 3.10	0.24 / 0.58	0.67 / 3.41	0.65 / 1.31	0.52 / 3.41
	Recent net flux (ng/cm ² -y)*				Inventory (ng/cm ²)			
$\Sigma_9\text{PBDEs}$	0 / 0.02	0.03 / 0.08	0.01 / 0.05	0.01 / 0.08	0.17 / 0.49	1.95 / 4.36	0.55 / 6.03	0.54 / 6.03
BDE209	0.13 / 0.16	0.74 / 1.11	0.49 / 2.13	0.44 / 2.13	4.15 / 7.75	69.4 / 153	28.1 / 420	24.2 / 420
$\Sigma_9\text{BFRs}$	0.03 / 0.05	0.05 / 0.08	0.05 / 0.26	0.05 / 0.26	0.77 / 1.42	5.16 / 11.9	5.03 / 29.0	3.85 / 29.0
$\Sigma_2\text{DPs}$	0.01 / 0.01	0.05 / 0.08	0.05 / 0.10	0.04 / 0.10	0.25 / 0.80	6.07 / 39.9	6.06 / 18.9	3.95 / 39.9
$\Sigma_{10}\text{CFRs}$	0 / 0	0.01 / 0.03	0.01 / 0.02	0.01 / 0.03	0.20 / 0.43	1.74 / 5.49	2.22 / 5.32	0.97 / 5.49
	Recent annual loading rate (kg/y)				Total load (tonnes)			
$\Sigma_9\text{PBDEs}$	3.56	17.4	7.20	28.2	0.14	1.20	0.62	1.96
BDE209	96.1	419	353	868	3.52	43.4	36.4	83.3
$\Sigma_9\text{BFRs}$	22.4	30.4	35.6	88.4	0.64	3.02	3.75	7.41
$\Sigma_2\text{DPs}$	6.63	28.8	33.6	69.0	0.28	4.83	3.73	8.84
$\Sigma_{10}\text{CFRs}$	2.44	6.43	6.28	15.2	0.17	1.33	1.18	2.68

* 0 means the value < 0.01 ng/cm²-y.

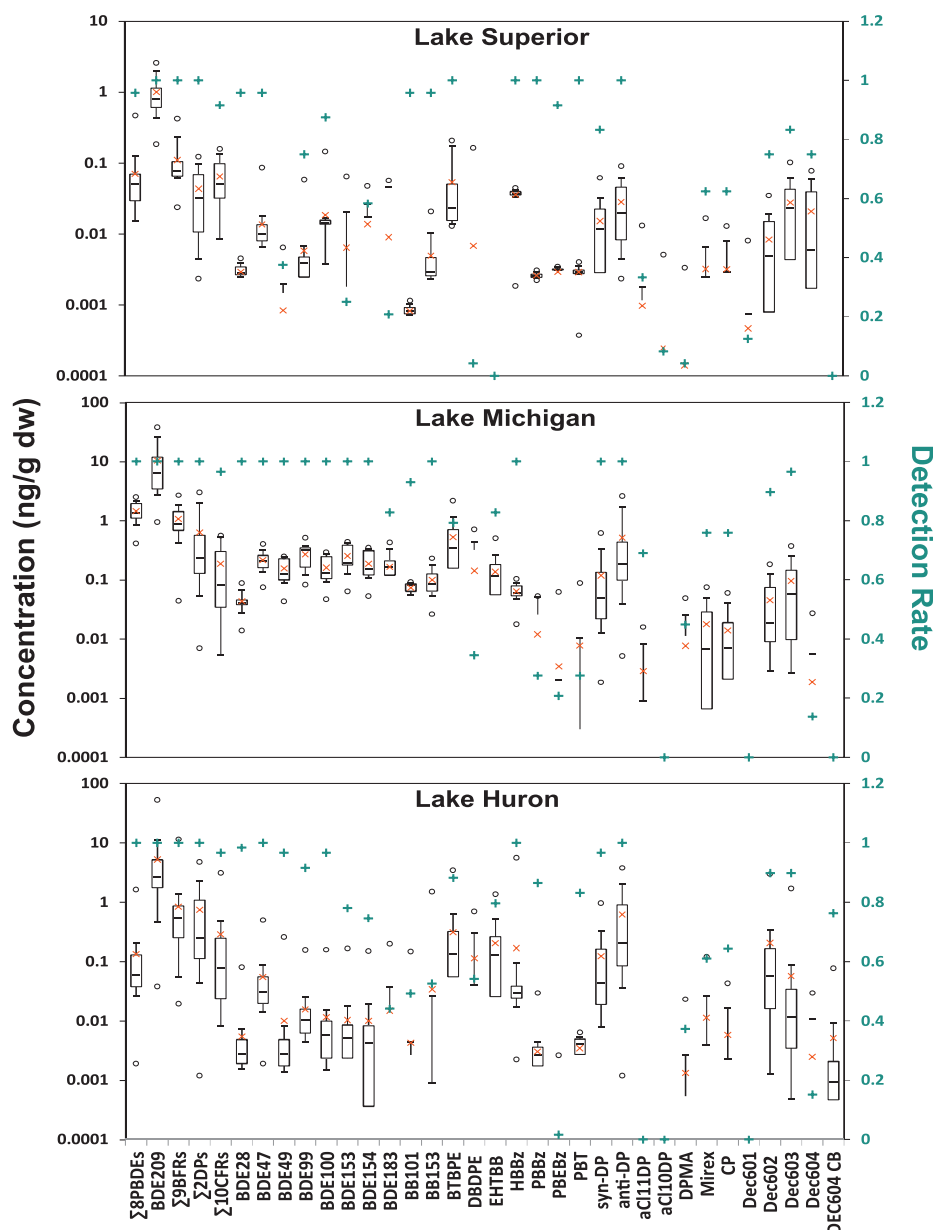


Fig. 1. Box and whisker plots of concentrations of HFRs in Ponar grab samples of sediment samples from Lakes Superior, Michigan, and Huron. Shown are average (red cross), median (lines inside the box), 25th to 75th centiles (box), 10th and 90th centiles (whiskers), minimum and maximum (circles) and detection rate (green plus) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Legacy BFRs HBBz, BB153, and BB101 were detected in both Ponar grab and surface core sediments from Lakes Michigan and Superior, with maximum concentrations 0.11 ng/g dw for HBBz, 0.23 ng/g dw for BB153, and 0.10 ng/g dw for BB101. These are comparable to a previous study in the two lakes (Yang et al., 2012; Zhu and Hites, 2005). The total loads of BB153 in Lakes Michigan, Superior, and Huron are 0.12, 0.01 and 0.13 tonne, respectively. These are much higher than the estimate of about 0.02 tonne by Zhu and Hites based on a single core in northern Lake Michigan (Zhu and Hites, 2005). The loads of BB101 are much lower (Table S3). In Lake Huron, HBBz ranged 0.002–5.56 ng/g dw for Ponar grab samples (Table S1). The loads of HBBz are comparable to those of BB153 in Lakes Michigan and Superior, but about seven times higher than BB153 in Lake Huron (Table S3). Other brominated benzenes PBBz, PBEBz, and PBT were detected in 26–74% of the Ponar grabs with relatively low concentrations (< 0.10 ng/g dw).

Among CFRs, DPs (*syn*- and *anti*-DP) were the most abundant, with Σ_2 DPs up to 4.74 ng/g dw in Ponar grabs. The total loads of DPs are

4.83 tonnes for Lake Michigan, 0.28 tonne for Lake Superior, and 3.73 tonnes for Lake Huron. These are comparable to those estimated previously from the same lake (Shen et al., 2010; Yang et al., 2011). The concentrations of Dec602 and Dec603 ranged N.D.–2.96 and N.D.–1.70 ng/g dw, respectively, which are lower than DPs but higher than other CFRs. Dec604 was detected in < 30% of the Ponar grab samples, and its concentrations were < 0.10 ng/g dw. However, Dec604 was detected in > 90% of surface segments of the cores. Total loads of Σ_3 Decs (sum of Dec602, Dec603, and Dec604) are greater in Lakes Michigan and Superior, but lesser in Lake Huron, than those reported previously (Yang et al., 2011). Mirex had a detection rate of 65%, and its concentrations (N.D.–0.12 ng/g dw) were less than those previously measured in sediments from the same lake (Shen et al., 2010; Yang et al., 2011). DPMA and aCl₁₁DP were detected in < 33%, Dec601 and aCl₁₀DP in < 3%, of the Ponar grabs. In the literature, DPMA was first found in 2010 in sediment from Lake Ontario (collected in 2007) with concentrations < 1 ng/g dw (Sverko et al., 2010). CP was

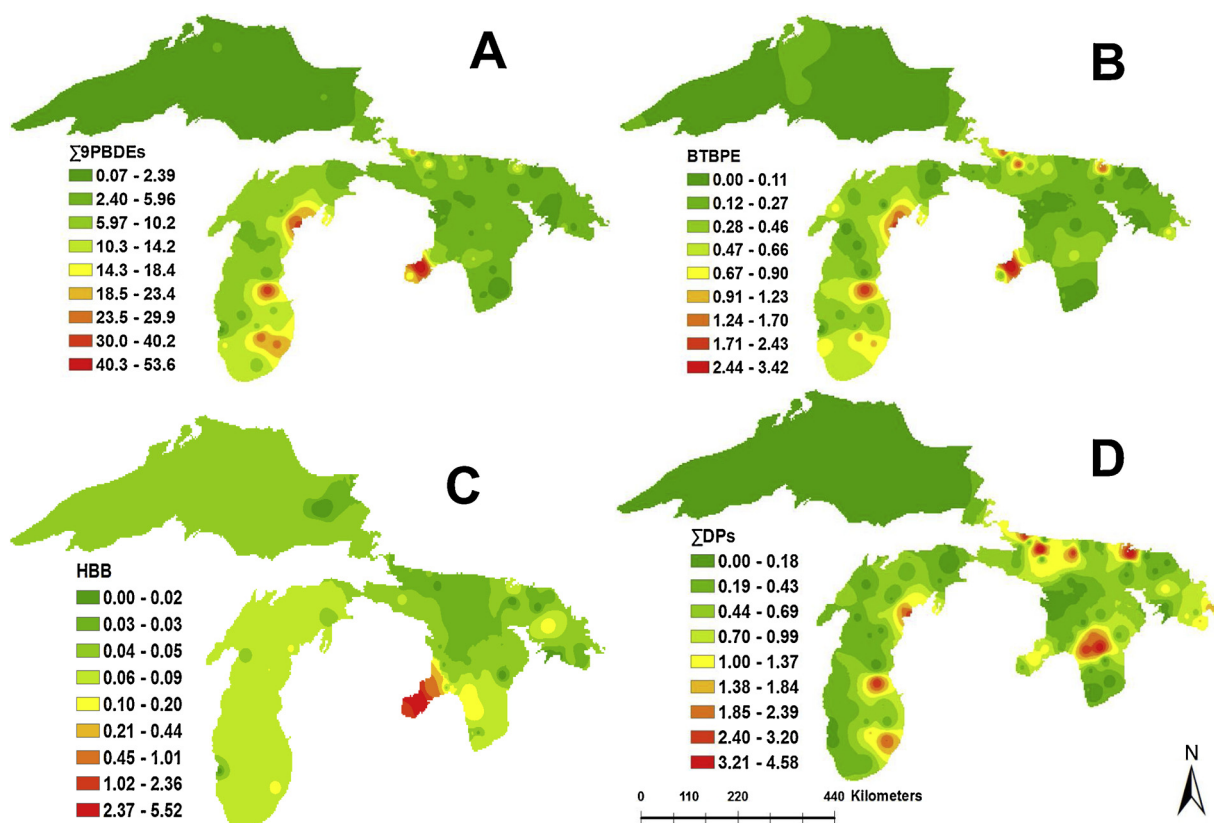


Fig. 2. Inverse distance-weighted interpolation of spatial distribution of target HFRs in surface sediment of upper Great Lakes. (Unit: ng/g dw).

first discovered in 2011 in the surface sediments collected from the Canadian tributaries around the Great Lakes during 2002–2006 with concentrations < 0.27 ng/g dw (Shen et al., 2011).

3.2. Spatial distribution indicative of known and unknown sources

Using the data obtained for Ponar grabs, the spatial patterns of selected HFRs are shown in Fig. 2. The top three sites with greatest concentrations of HFRs are summarized in Table S4. The region was further divided into eight geographic areas and compared using Fisher's exact test (Figure S1).

Concentrations of HFRs in sediments from Lake Superior were much less than those of the other two lakes (Table 1). Among all sites, S022 near Duluth stood out having Σ_9 PBDEs at least double those at other sites in Ponar grabs from that lake. For other analyte groups, greater concentrations were found in the northmost site S011 near Fluor Island. Despite the lesser organic matter content in sediments near the water channel of St. Mary's River, sites S001 and S002 were found to have the greatest BDE209 as well as greater-than-average levels of Σ_2 DPs in Ponar grabs from the lake. These results suggested potential sources near the twin cities of Sault Ste Marie. There are diverse industries, such as steel manufacturing and metalworking, forestry and wood processing, energy production, and aviation and aerospace in this area (InvestSaultSte.Marie, 2019).

In Lake Michigan, M009, M061, and M093 were found to have concentrations of PBDEs, BTBPE, BB153 and DPs significantly greater than those at other sites (Figs. 2 and S1). The southern basin of Lake Michigan is surrounded by densely populated urban areas and receives discharges from heavily contaminated tributaries, including the Indiana Harbor and Ship Canal in Indiana, and the St. Joseph, Kalamazoo and Grand Rivers in Michigan (Guo et al., 2017b). Albemarle, a major BFR producer, has its production facility in the coastal city of South Haven, MI near study site M009, although it is unclear whether the target HFRs

have been produced at this facility. Site M061 is located near White Lake in Muskegon County, MI, which was a previous Area of Concern (AOC) contaminated by decades of pollution from chemical industries (Hausman, 2014). For example, large amounts of chemical wastes were dumped by Hooker Chemical Company into Lake Michigan before the facility was closed in 1983 (LudingtonDailyNews, 1977). Sediment near Sleeping Bear Dunes (M093) was previously contaminated with heavy metals (Cline and Chambers, 1977), and high levels of the herbicide alachlor were detected there in previous work by our group (Guo et al., 2016). The nearby Manitou Islands are surrounded by > 50 known and many other unknown shipwrecks (MUPC, 2011), which may be the contamination source.

In Lake Huron, Saginaw Bay is heavily contaminated by BFRs. Greatest concentrations were found at site H001 for BTBPE, DBDPE, BB153, BB101, HBBz, and almost all individual PBDEs. For example, HBBz (5.56 ng/g) was 100-fold greater at H001 than the other sampling sites. The Saginaw Bay has been known to be the most contaminated part of Lake Huron because of agricultural waste from the Saginaw River basin, and chemical industries, including the DOW Chemical Company along the Tittabawassee, Pine, and Chippewa Rivers (Hites, 2006; Yun et al., 2008). Relatively greater concentrations of PBDEs were detected in sediment of the Saginaw River watershed (Yun et al., 2008). In particular, large quantities of HBBz and PBBs were discharged to the waters in this area by Velsicol Chemical Corporation (USEPA, 2019b). An elevated concentration of BB153 was found in soil collected at the Pine River (13.5 ng/g dw), next to the former Velsicol facility in St. Louis, Michigan, and in sediment from the Saginaw River (4.7 ng/g dw) (Yun et al., 2008). Velsicol is still currently an active producer of various HFRs under the tradename PyroVex, including DBDPE, TBPH, DP, and others, although the product-specific manufacturing locations are unknown.

The North Channel is about 300 km long along the north shore of Lake Huron, downstream from the port of Sault Ste. Marie USA and

Canada. This site receives water from Lake Superior through the St. Marys River. The river is an AOC and has been known to be contaminated by heavy metals and polycyclic aromatic hydrocarbons (PAHs) (Su et al., 2015). In this work, a number of sampling sites in the North Channel had higher concentrations of PBDEs, BTBPE, and DPs than the open lake (Fig. 2, A, B and D). Sites NC71 and NC76 are located near and downstream from where the St. Marys River empties into the North Channel. These sites had Σ_2 DPs concentrations two- to three-fold greater than those found at H001 in the Saginaw Bay. For comparison, herring gull eggs collected from the Five Mile Island, upper St. Mary's River, had significantly greater concentrations of PBDEs and DPs than other sites (Su et al., 2015). Connected to the North Channel is Georgian Bay, where there are three AOCs. Site GB42 is located next to the Spanish Harbour AOC, which has been contaminated by the discharge of a wastewater treatment plant and the Domtar paper mill (EC, 2014). Elevated concentrations of PCBs in sediment were also observed at GB42 (Gewurtz et al., 2008).

Principal component analysis (PCA) was used to explore correlations between and among the concentrations and sampling sites in the grab samples for the 16 selected flame retardants with detection frequency > 74%. The first three principal components (PC) explained 86% of the total variance in the data with PC1 54%, PC2 20%, and PC3 12% (Fig. 3A). PBDEs (except BDE209) were clustered together with large positive PC1 and lesser or negative PC2 and PC3. BTBPE and BDE209 were grouped closely and not far from other PBDEs. According

to score plots (Fig. 3B-D), sites in Lake Michigan had larger loadings to PC1, especially for sites near Sleeping Bear Dunes (M093a-c) and in the southeastern and eastern portions of the lake (M009, M011 and M061) due to the greater PBDE and other BFR concentrations. CFRs were separated from PBDEs with positive PC1 and PC2, and low or positive PC3. Some sites in southern Lake Huron (H002 and H027), North Channel (NC71 and NC76) and Georgian Bay (GB42) exhibited greater PC2 and PC3, contributed by CFRs.

Patterns of spatial distribution of contamination are largely affected by proximity of sampling site to potential emission sources, mobility of the contaminants with air and water prior to entering sediment, physicochemical characteristics of sediments, and geological and hydrological aspects of the water body such as water circulation pattern and sediment focusing. We have shown that proximity to point discharge sources is an important factor determining the accumulation of perfluorinated and polychlorinated persistent organic pollutant groups in sediments of the Great Lakes (Codling et al., 2018a; Li et al., 2018). The results of the present study indicate that point sources such as the production and application facilities are likely an important factor influencing the distributions of legacy and emerging halogenated flame retardant chemicals, most of which are hydrophobic thus less mobile in aquatic environment.

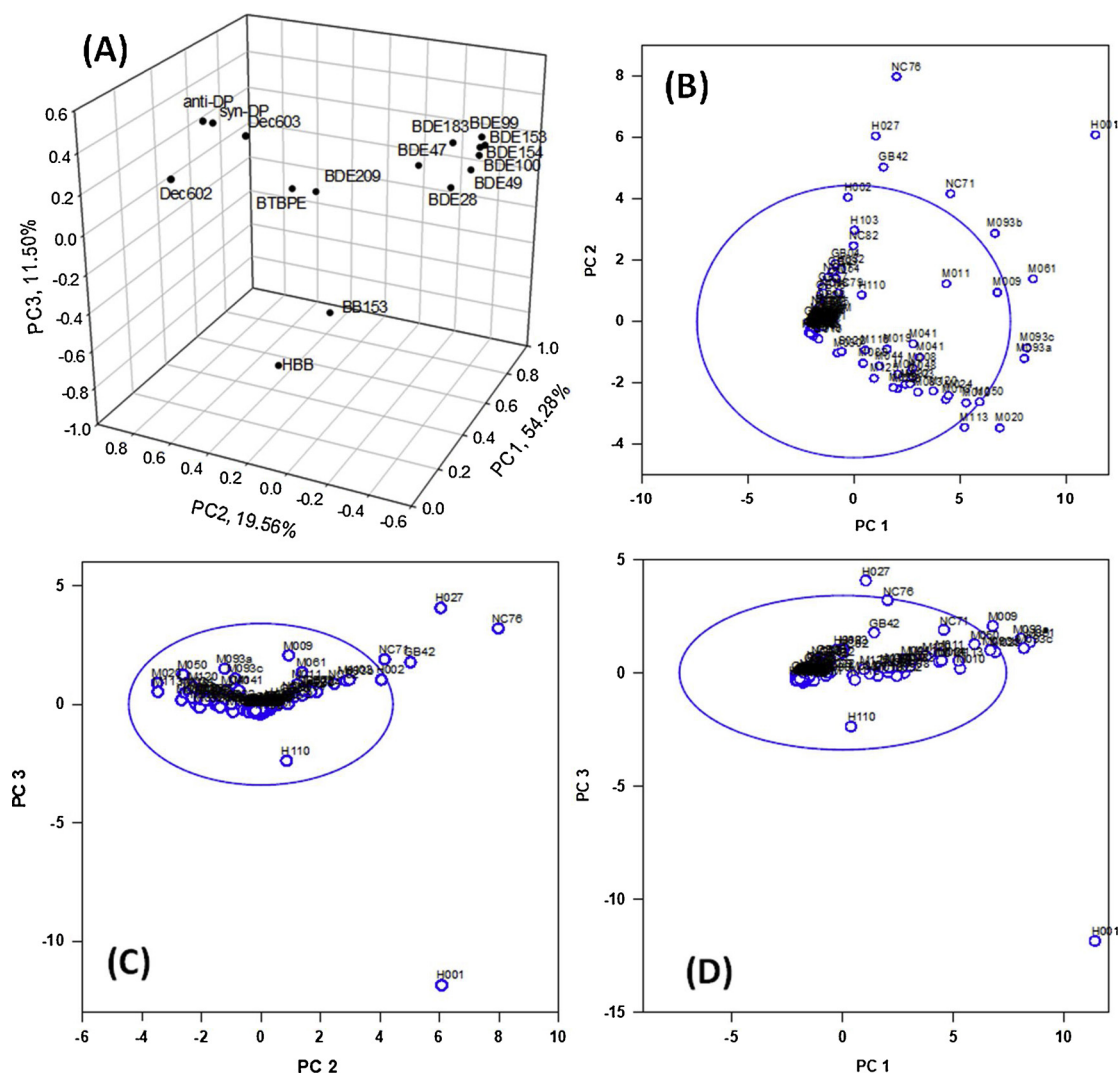


Fig. 3. Loading plot (A) and score plots (B, C, D) of 16 target HFRs in the Ponar grab sediment from upper Great Lakes.

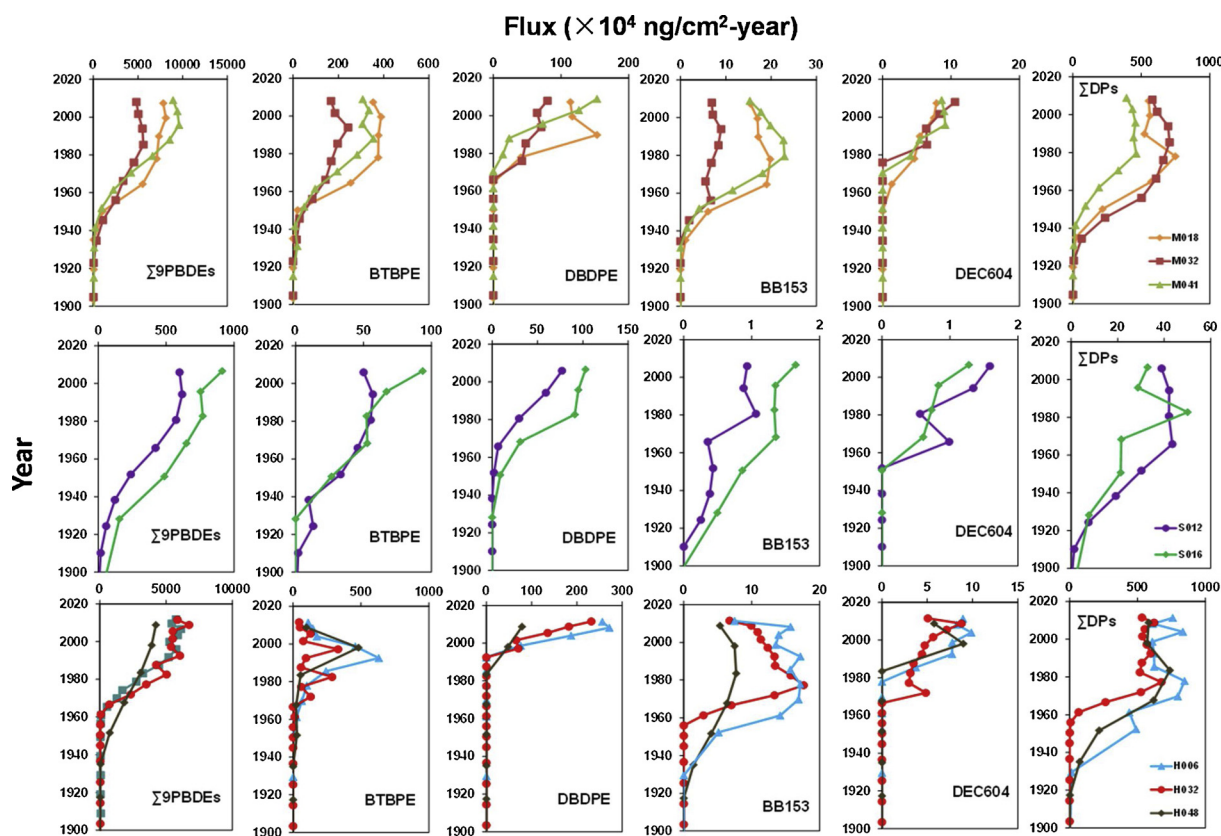


Fig. 4. Apparent deposition flux of selected HFRs to the sediment at different locations of Lakes Michigan, Superior and Huron.

3.3. Temporal profiles reflect the use history and in-situ transformation

Chronological trends are discussed here in terms of net flux, which takes into account the sediment accumulation rate and focusing. This is a more accurate reflection of the input to sediment than measured concentrations. Net flux integrates all the input and output of the chemical in each core segment. It is a scalar quantity thus its value in core segments does not indicate whether the sediment is a net sink or source of pollutants to the overlaying water (Li et al., 2018). Temporal trend profiles of selected HFRs at selected coring sites in each lake are illustrated in Fig. 4. The onset and peak years differ among the HFRs (Fig. 4). In general, legacy HFRs have been declining during the past decades or years while fluxes of emerging contaminants are increasing. Estimated half-lives ($t_{1/2}$) for decreases and doubling times (t_2) of increases were calculated by fitting first order kinetic models to the data from dated cores. When variation of flux with time is parabolic, $t_{1/2}$ and t_2 were both calculated using the data on the two sides of the peak, respectively, for a chemical at a particular sampling site. Compound-specific $t_{1/2}$ and t_2 values are summarized (Table S5).

PBDEs were observed in segments of sediment cores dated as early as the 1940s and in recent years have leveled off or started decreasing (Fig. 4). The time trend of PBDE flux in most cores fits the first order kinetic model for the period up to the 2010s. The t_2 values are similar to those measured in previous studies (Yang et al., 2012; Zhu and Hites, 2005). Based on data presented here, the net fluxes of PBDEs at 17 out of 24 coring sites are decreasing since late 1990s or 2000. At these locations the fluxes deviated from the first-order regression lines fluxes in top segments as they decreased or flattened. The estimated lake-wide annual loading rate of PBDEs in Lake Michigan was 430 kg/y, which is significantly less than the annual loading rate of 750 kg/y reported in 2002 (Song et al., 2005b). These observations indicate that the phase-out of PBDEs in the 2000s may have resulted in less PBDEs entering Lake Michigan.

In sediment cores, BTBPE started increasing from the 1940s to 1950s and has leveled off since the 1980s (Fig. 4). Such trends are similar to those reported previously (Hoh et al., 2005; Yang et al., 2012). An exponential increase of BTBPE concentration was found in lake trout collected from Lake Ontario from 1979 to 1993 and the estimated doubling time was 6 years (Ismail et al., 2009). In air sampled between 2005 and 2013, concentrations of BTBPE did not change at most locations near Lake Michigan, but decreased at Eagle Harbor of Lake Superior (Liu et al., 2016). Fluxes of EHTBB increased with time in most cores from Lakes Michigan and Huron with apparent t_2 values ranging from 8 to 67 years (Table S5), which are longer than the t_2 values of 2 to 5 years in air (Liu et al., 2016). EHTBB is a relatively polar compound and its detection in the deep sediment may be due to post-depositional downward diffusion with sediment porewater.

Concentrations of DBDPE in surface sediments of cores taken from Lakes Michigan and Superior were slightly greater than those measured in 2007 for the same lake (Yang et al., 2012), which may indicate a continuously increasing trend. Concentrations of DBDPE have been increasing at most sampling sites, but in recent years the rate of the increases appears to be slowing. Doubling times of DBDPE ranged from 4 to 18 years (Table S5), which is longer than the estimated 3 to 7 years previously reported for the Great Lakes (Yang et al., 2012) and 2 to 3 years at sampling sites near manufacturing facilities in southern Arkansas (Wei et al., 2012). In recent years decreases have been observed in cores from southern portions of Lakes Michigan and Huron. DBDPE concentration in air sampled from Sleeping Bear Dune near Lake Michigan was also decreasing with $t_{1/2}$ of 3.6 ± 1.1 years (Liu et al., 2016).

PBT and PBEBz can form when a methyl bond in DBDPE molecules is cleaved (Arp et al., 2011; de Wit et al., 2011). In most sediment cores that DBDPE and PBT (or PBEBz) are detected, the ratio of PBT or PBEBz to DBDPE increases with increasing depth in sediments (Figure S3). However, it is difficult to determine whether the PBT and PBEBz

observed in sediment cores are the degradation products of DBDPE. DBDPE was manufactured since the early 1990s by Chemtura in the U.S. and was commercially available in Europe in the mid 1980s. Its US production volume in 2006 was in the range of 4500–22,500 tonnes and has been increasing since then (Yang et al., 2012). PBT and PBEBz have been on the market since the 1970s (Arp et al., 2011), but little production information is publicly available. Annual volume of PBT production is categorized as moderate (1000–5000 tonnes per year) (de Wit et al., 2011). Inputs of PBT and PBEBz were increased between the 1950s and the 2000s, but have been decreasing in the past decade. Concentrations of PBEBz in lake trout of Lake Ontario was relatively constant between 1979–2004 (Ismail et al., 2009).

BB153 and BB101 were components in the commercial FireMaster BP-6 and FF-1, in which BB153 were accounting > 60% and BB101 < 3%. These two congeners were found to be the most abundant polybrominated biphenyl in Great Lakes fish (Luross et al., 2002). In this work, log-transformed concentrations of BB101 and BB153 were found significantly correlated ($R^2 = 0.81$, $p < 0.0001$). Both chemicals also have similar time profiles in sediment cores. The flux time profile showed that BB153 and BB101 peaked in the 1970s to 1980s (Fig. 4). Although they have been banned for more than 30 years, decreases in concentrations in sediments seem slow at most locations. After reaching a maximum, BB153 has been slightly decreasing but concentrations of BB101 have been relatively constant. The time trend was similar to that reported by Zhu and Hites (2005). Concentrations of BB153 in fishes collected from Lake Huron have significantly decreased from 1980 to 2000, while no significant changes were observed for the four other lakes (Zhu and Hites, 2004). In this work, we found that the ratio of BB101 to BB153 increases significantly with depth in sediment cores from H001, where BB101 and BB153 were detected at greater concentrations than at other sites (Fig. 5). This observation may suggest the occurrence of *in situ* debromination of BB153 by losing a Br in the para position, which results in formation of BB101 in deeper sediments. Debromination of BB153 in para and meta positions in three different types of sediments was previously reported (Morris et al., 1992). The percentage of PCBs with para chlorines have been decreasing with sediment depth in cores from Lake Ontario (Li et al., 2009). Our observation may also suggest that BB101 is more persistent than BB153 in the sediment.

Fluxes of HBBz to sediment in Lakes Michigan and Superior have been relatively small. Air concentration of HBBz have been decreasing with $t_{1/2}$ of 4–13 years at most sites of the Great Lakes (Liu et al., 2016). However, at site H001 in southern Lake Huron, the flux observed during the present study was as great as 0.05–0.15 ng/cm²-year (Table S2). In cores H001, H006, H012, and H032, net fluxes of HBBz started to increase in the 1960s. Fluxes peaked around the 1970s and have

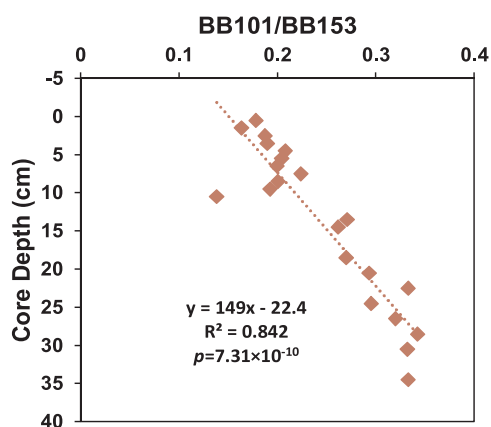


Fig. 5. The ratio of BB101 over BB153 dependence on core depth at sampling site H001 (Note: four points with BB101 < 0.04 ng/g dw and BB153 < 0.1 ng/g dw were excluded).

remained relatively constant since then. PBBz can be produced by reductive debromination of HBBz in rats (Yamaguchi et al., 1988). In this study, the flux of PBBz was positively correlated with that of HBBz, but the ratio of PBBz to HBBz had no obvious trend with depth in sediment cores.

The loading profiles of Dec602, 603, *syn*-DP, *anti*-DP, Cl₁₁DP and CP were very similar on a temporal basis. Fluxes started to increase in the 1920s and have leveled-off or slowly decreased since the 1980s (Fig. 4). Similar trends have been observed during other studies of sediment from the Great Lakes (Shen et al., 2010; Yang et al., 2012). In contrast, fluxes of Dec604 were rapidly increasing from the 1960s until recently at most coring sites of Lakes Michigan and Huron (Fig. 4). Calculated t_2 for Dec604 was 9–20 years. This result might indicate continued releases of Dec604 to the environment.

Among the two isomers of DP, the f_{syn} (fraction of *syn*-DP in Σ_2 DPs) varied in technical standards around 0.25 to 0.36 (Qiu et al., 2007; Shen et al., 2010; Sverko et al., 2008). In this study, f_{syn} ranged from 0.1 to 0.5 in sediment cores, similar to the site average ratio range 0.15 to 0.40 in another study (Yang et al., 2011). The ratio was greater in Lake Superior than in Lakes Michigan and Huron. Values of f_{syn} in surface layers of cores were positively correlated with latitudes of the core sampling sites (Figure S4-A), implying the degradation of *anti*-DP during long range transport from the source in Niagara Falls to the north and west in the region (Yang et al., 2011). It has been reported that the f_{syn} increase from 0.37 to 0.67 with decreasing latitude is likely caused by photolysis by UV light degradation of *anti*-DP during transport away from the source in Western Europe (Möller et al., 2010). In addition, at site M047 in a deposition zone in northern Lake Michigan, f_{syn} decreased significantly with increasing sediment depth ($r = 0.87$, $p = 0.0048$, Figure S4-B), which indicated persistence of *anti*-DP and the degradation of *syn*-DP in deeper sediments, which agrees with previous reports (Qiu et al., 2007; Yang et al., 2011). However, this trend of decreasing f_{syn} with sediment depth was not found in other cores of this study.

When *anti*-DP loses one chlorine atom, aCl₁₁DP is produced. Concentrations of aCl₁₁DP measured in this work were ten to a hundred-fold less than those of *anti*-DP. In the surface layer of cores, the ratio of aCl₁₁DP over *anti*-DP (aCl₁₁DP/*anti*-DP) increased with the latitudes of cores (Fig. 6-A, $r = 0.75$, $p < 0.001$), which implied dechlorination of *anti*-DP to aCl₁₁DP while being transported from south to north. In most sediment cores, the ratio (aCl₁₁DP/*anti*-DP) is greater in sediment deposited before the 1970s (Fig. 6-B). The ratio was < 0.02 and relatively constant in core segments dated between the 1970s and the 2010s, then it increased to as large as 0.06 in sediment before the 1970s. We attribute this to the *in situ* transformation of *anti*-DP to aCl₁₁DP in early deposited sediments. Under anaerobic conditions, DPs have been found metabolized to monohydrodechlorinated products in waste water treatment plants by microbes (Sverko et al., 2015). Dechlorinated DP might also form during the DP synthesis process (Brazeau et al., 2018).

4. Conclusions

Halogenated flame retardants have been used for decades and most of them are highly accumulative and persistent in sediment. The spatial distribution of both legacy and emerging flame retardants are affected by multiple factors including the locations of chemical industries in the region. The time trends showed that the inputs of legacy PBDEs and PBBs are having a decreasing trend while those of their replacements such as DBDPE and Dec604 are increasing, and most other flame retardants targeted in this study have been leveled off or slightly decreasing. Dehalogenation of some halogenated flame retardants may have occurred during the long range transport or during settling into the deep sediment. Further research are suggested to understand the mechanisms and pathways of degradation and the potential environmental risks of the parent HFRs and their degradation products.

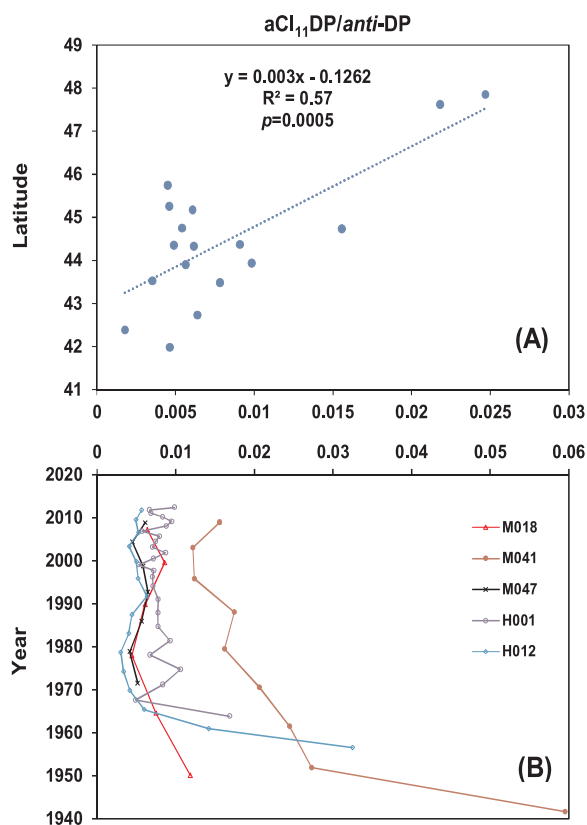


Fig. 6. Variation in concentration ratios of aCl₁₁DP over anti-DP with (A) the latitude of surface layer of sediment cores; (B) deposition year in selected sediment cores.

Acknowledgements

This research was part of the Great Lakes Sediment Surveillance Program (GLSSP) funded by a Cooperative Agreement from the US EPA Great Lakes Restoration Initiative with Assistance No. GL-00E00538. Partial support for J. Guo was provided by the Institute for Environmental Science and Policy at the University of Illinois at Chicago through its Predoctoral Fellowship. Professor John P. Giesy was supported by the Canada Research Chairs Program of the Natural Sciences and Engineering Research Council of Canada. We thank the crew of *R/V Lake Guardian* for their assistance during sampling. We acknowledge the participation in sediment samplings by Margaret B. Corcoran, Solidea M. C. Bonina, Soheil Hosseini, Colin Smalley, Andy L. Sandy, Gregory Bourgon, Garry Codling, Kelly Granberg, Rajashankar Kaliappan, Felipe Tendick-Matesanz, and Yawei Wang.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2019.121346>.

References

Alaee, M., Arias, P., Sjodin, A., Bergman, A., 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ. Int.* 29, 683–689.

Arp, H.P.H., Moskeland, T., Andersson, P.L., Nyholm, J.R., 2011. Presence and partitioning properties of the flame retardants pentabromotoluene, pentabromoethylbenzene and hexabromobenzene near suspected source zones in Norway. *J. Environ. Monit.* 13, 505–513.

Bearr, J.S., Mitchelmore, C.L., Roberts, S.C., Stapleton, H.M., 2012. Species specific differences in the in vitro metabolism of the flame retardant mixture, firemaster® BZ-54. *Aquat. Toxicol. (Amsterdam, Netherlands)* 124–125, 41–47.

Bonina, S.M.C., Codling, G., Corcoran, M.B., Guo, J., Giesy, J.P., Li, A., Sturchio, N.C.,

Rockne, K.J., 2018. Temporal and spatial differences in deposition of organic matter and black carbon in Lake Michigan sediments over the period 1850–2010. *J. Great Lakes Res.* 44, 705–715.

Brazeau, A.L., Pena-Abaurrea, M., Shen, L., Riddell, N., Reiner, E.J., Lough, A.J., McCrindle, R., Chittim, B., 2018. Dechlorinated analogues of dechlorane plus. *Environ. Sci. Technol.* 52, 5619–5624.

Cao, D., Guo, J., Wang, Y., Li, Z., Liang, K., Corcoran, M.B., Hosseini, S., Bonina, S.M.C., Rockne, K.J., Sturchio, N.C., Giesy, J.P., Liu, J., Li, A., Jiang, G., 2017. Organophosphate esters in sediment of the Great Lakes. *Environ. Sci. Technol.* 51, 1441–1449.

Chen, X., Chen, Y., Huang, C., Dong, Q., Roper, C., Tanguay, R.L., Zhu, Y., Zhang, Y., 2019. Neurodevelopmental toxicity assessments of alkyl phenanthrene and dechlorane plus co-exposure in zebrafish. *Ecotoxicol. Environ. Saf.* 180, 762–769.

Christensen, E.R., Zhang, R., Codling, G., Giesy, J.P., Li, A., 2019. Poly- and per-fluoro-alkyl compounds in sediments of the Great Lakes: Loadings, temporal trends, and sources determined by positive matrix factorization. *Environ. Pollut.* 255, 113166.

Cline, J.T., Chambers, R.L., 1977. Spatial and temporal distribution of heavy metals in lake sediments near Sleeping Bear Point, Michigan. *J. Sediment. Res.* 47, 716–727.

Codling, G., Hosseini, S., Corcoran, M.B., Bonina, S., Lin, T., Li, A., Sturchio, N.C., Rockne, K.J., Ji, K., Peng, H., Giesy, J.P., 2018a. Current and historical concentrations of poly and perfluorinated compounds in sediments of the Northern Great Lakes – Superior, Huron, and Michigan. *Environ. Pollut.* 236, 373–381.

Codling, G., Sturchio, N.C., Rockne, K.J., Li, A., Peng, H., Tse, T.J., Jones, P.D., Giesy, J.P., 2018b. Spatial and temporal trends in poly- and per-fluorinated compounds in the Laurentian Great Lakes Erie, Ontario and St. Clair. *Environ. Pollut.* 237, 396–405.

Codling, G., Vogt, A., Jones, P.D., Wang, T., Wang, P., Lu, Y.L., Corcoran, M., Bonina, S., Li, A., Sturchio, N.C., Rockne, K.J., Ji, K., Khim, J.-S., Naile, J.E., Giesy, J.P., 2014. Historical trends of inorganic and organic fluorine in sediments of Lake Michigan. *Chemosphere* 114, 203–209.

Corcoran, M., Sherif, M.I., Smalley, C., Li, A., Rockne, K.J., Giesy, J.P., Sturchio, N.C., 2018. Accumulation rates, focusing factors, and chronologies from depth profiles of ²¹⁰Pb and ¹³⁷Cs in sediments of the Laurentian Great Lakes. *J. Great Lakes Res.* 44, 693–704.

Darnerud, P.O., Eriksen, G.S., Jóhannesson, T., Larsen, P.B., Viluksela, M., 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. *Environ. Health Perspect.* 109, 49.

de Wit, C., Kierkegaard, A., Ricklund, N., Sellström, U., 2011. Emerging brominated flame retardants in the environment. In: Eljarrat, E., Barceló, D. (Eds.), *Brominated Flame Retardants*. Springer, Berlin Heidelberg, pp. 241–286.

EC, 2014. Spanish Harbour Area of Concern. (Accessed 09/02/2016). <https://www.ec.gc.ca/raps-pas/default.asp?lang=En&n=5D7CE315-1>.

Gauthier, L.T., Hebert, C.E., Weseloh, D.V.C., Letcher, R.J., 2007. Current-use flame retardants in the eggs of herring gulls (*Larus argentatus*) from the Laurentian Great Lakes. *Environ. Sci. Technol.* 41, 4561–4567.

Gauthier, L.T., Hebert, C.E., Weseloh, D.V.C., Letcher, R.J., 2008. Dramatic changes in the temporal trends of polybrominated diphenyl ethers (PBDEs) in herring gull eggs from the Laurentian Great Lakes: 1982–2006. *Environ. Sci. Technol.* 42, 1524–1530.

Gauthier, L.T., Letcher, R.J., 2009. Isomers of dechlorane plus flame retardant in the eggs of herring gulls (*Larus argentatus*) from the Laurentian Great Lakes of North America: temporal changes and spatial distribution. *Chemosphere* 75, 115–120.

Gauthier, L.T., Potter, D., Hebert, C.E., Letcher, R.J., 2009. Temporal trends and spatial distribution of non-polybrominated diphenyl ether flame retardants in the eggs of colonial populations of Great Lakes Herring Gulls. *Environ. Sci. Technol.* 43, 312–317.

Gewurtz, S.B., Shen, L., Helm, P.A., Waltho, J., Reiner, E.J., Painter, S., Brindle, I.D., Marvin, C.H., 2008. Spatial distributions of legacy contaminants in sediments of lakes huron and superior. *J. Great Lakes Res.* 34, 153–168.

Guo, J., Chen, D., Potter, D., Rockne, K.J., Sturchio, N.C., Giesy, J.P., Li, A., 2014a. Polyhalogenated carbazoles in sediments of Lake Michigan: a new discovery. *Environ. Sci. Technol.* 48, 12807–12815.

Guo, J., Li, Z., Sandy, A.L., Li, A., 2014b. Method development for simultaneous analyses of multiple legacy and emerging organic chemicals in sediments. *J. Chromatogr. A* 1370, 1–8.

Guo, J., Li, Z., Ranasinghe, P., Bonina, S., Hosseini, S., Corcoran, M.B., Smalley, C., Kaliappan, R., Wu, Y., Chen, D., Sandy, A.L., Wang, Y., Rockne, K.J., Sturchio, N.C., Giesy, J.P., Li, A., 2016. Occurrence of atrazine and related compounds in sediments of Upper Great Lakes. *Environ. Sci. Technol.* 50, 7335–7343.

Guo, J., Li, Z., Ranasinghe, P., Bonina, S., Hosseini, S., Corcoran, M.B., Smalley, C., Rockne, K.J., Sturchio, N.C., Giesy, J.P., Li, A., 2017a. Spatial and temporal trends of polyhalogenated carbazoles in sediments of Upper Great Lakes: insights into their origin. *Environ. Sci. Technol.* 51, 89–97.

Guo, J., Romanak, K., Westenbroek, S., Hites, R.A., Venier, M., 2017b. Current-use flame retardants in the water of Lake Michigan tributaries. *Environ. Sci. Technol.* 51, 9960–9969.

Hausman, J.S., 2014. Muskegon County's White Lake Officially Delisted As 'Toxic Hot Spot'; One of Michigan's First Removed. (Accessed 09/02/2016). http://www.mlive.com/news/muskegon/index.ssf/2014/10/muskegon_countys_white_lake_of.html.

Hites, R.A., 2006. Persistent Organic Pollutants in the Great Lakes: An Overview, Persistent Organic Pollutants in the Great Lakes. Springer, pp. 1–12.

Hoh, E., Zhu, L., Hites, R.A., 2005. Novel flame retardants, 1,2-Bis(2,4,6-Tribromophenoxy)ethane and 2,3,4,5,6-pentabromoethylbenzene, in United States' environmental samples. *Environ. Sci. Technol.* 39, 2472–2477.

Hoh, E., Zhu, L., Hites, R.A., 2006. Dechlorane plus, a chlorinated flame retardant, in the great lakes. *Environ. Sci. Technol.* 40, 1184–1189.

InvestSaultSte.Marie, 2019. Key Sectors. Sault Ste. Marie Economic Development Corporation. Sault Ste. Marie, on, Canada. (Accessed 7/30/2019). <https://>

- investsaaltsternarie.com/key-sectors/.
- Ismail, N., Gewurtz, S.B., Pleskach, K., Whittle, D.M., Helm, P.A., Marvin, C.H., Tomy, G.T., 2009. Brominated and chlorinated flame retardants in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*) between 1979 and 2004 and possible influences of food-web changes. *Environ. Toxicol. Chem.* 28, 910–920.
- La Guardia, M.J., Hale, R.C., Newman, B., 2013. Brominated flame-retardants in Sub-Saharan Africa: burdens in inland and coastal sediments in the Ethekekwini Metropolitan Municipality, South Africa. *Environ. Sci. Technol.* 47, 9643–9650.
- Li, A., Guo, J., Li, Z., Lin, T., Zhou, S., He, H., Ranansinghe, P., Sturchio, N.C., Rockne, K.J., Giesy, J.P., 2018. Legacy polychlorinated organic pollutants in the sediment of the great lakes. *J. Great Lakes Res.* 44, 682–692.
- Li, A., Rockne, K.J., Sturchio, N., Song, W., Ford, J.C., Wei, H., 2009. Pcb's in sediments of the Great Lakes—distribution and trends, homolog and chlorine patterns, and in situ degradation. *Environ. Pollut.* 157, 141–147.
- Liu, H.-H., Hu, Y.-J., Luo, P., Bao, L.-J., Qiu, J.-W., Leung, K.M.Y., Zeng, E.Y., 2014. Occurrence of halogenated flame retardants in sediment off an urbanized coastal zone: association with urbanization and industrialization. *Environ. Sci. Technol.* 48, 8465–8473.
- Liu, L.-Y., Salamova, A., Venier, M., Hites, R.A., 2016. Trends in the levels of halogenated flame retardants in the Great Lakes atmosphere over the period 2005–2013. *Environ. Int.* 92–93, 442–449.
- LudingtonDailyNews, 1977. Claims Montague Plant Dumped 500,000 Gallons of Toxic Waste Into Lake Michigan in 1970-76. (Accessed 8/1/2019). <https://news.google.com/newspapers?nid=110&dat=19770820&id=ao4vAAAIBAJ&sjid=ldwFAAAAIBAJ&pg=2865,4475073&hl=en>.
- Luross, J.M., Alae, M., Sergeant, D.B., Cannon, C.M., Michael Whittle, D., Solomon, K.R., Muir, D.C.G., 2002. Spatial distribution of polybrominated diphenyl ethers and polybrominated biphenyls in Lake Trout from the Laurentian Great Lakes. *Chemosphere* 46, 665–672.
- Möller, A., Xie, Z., Sturm, R., Ebinghaus, R., 2010. Large-scale distribution of dechlorane plus in air and seawater from the Arctic to Antarctica. *Environ. Sci. Technol.* 44, 8977–8982.
- Morris, P.J., Quensen, J.F., Tiedje, J.M., Boyd, S.A., 1992. Reductive debromination of the commercial polybrominated biphenyl mixture firemaster BP6 by anaerobic micro-organisms from sediments. *Appl. Environ. Microbiol.* 58, 3249–3256.
- MUPC, 2011. Manitou Passage Underwater Preserve. (Accessed 8/1/2019). <http://www.michiganpreserves.org/manitou.htm>.
- Norstrom, R.J., Simon, M., Moisey, J., Wakeford, B., Weseloh, D.V.C., 2002. Geographical distribution (2000) and temporal trends (1981–2000) of brominated diphenyl ethers in Great Lakes Herring Gull Eggs. *Environ. Sci. Technol.* 36, 4783–4789.
- Olukunle, O.I., Okonkwo, O.J., 2015. Concentration of novel brominated flame retardants and HBCD in Leachates and sediments from selected municipal solid waste landfill sites in Gauteng Province, South Africa. *Waste Manag.* 43, 300–306.
- Qiu, X., Marvin, C.H., Hites, R.A., 2007. Dechlorane plus and other flame retardants in a sediment core from Lake Ontario. *Environ. Sci. Technol.* 41, 6014–6019.
- Salamova, A., Hites, R.A., 2011. Dechlorane plus in the atmosphere and precipitation near the Great Lakes. *Environ. Sci. Technol.* 45, 9924–9930.
- Shen, L., Reiner, E.J., MacPherson, K.A., Kolic, T.M., Helm, P.A., Richman, L.A., Marvin, C.H., Burniston, D.A., Hill, B., Brindle, I.D., McCrindle, R., Chittim, B.G., 2011. Dechloranes 602, 603, 604, dechlorane plus, and chlordene plus, a newly detected analogue, in tributary sediments of the Laurentian Great Lakes. *Environ. Sci. Technol.* 45, 693–699.
- Shen, L., Reiner, E.J., MacPherson, K.A., Kolic, T.M., Sverko, E., Helm, P.A., Bhavsar, S.P., Brindle, I.D., Marvin, C.H., 2010. Identification and screening analysis of halogenated norbornene flame retardants in the Laurentian Great Lakes: dechloranes 602, 603, and 604. *Environ. Sci. Technol.* 44, 760–766.
- Song, W., Ford, J.C., Li, A., Mills, W.J., Buckley, D.R., Rockne, K.J., 2004. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 1. Lake Superior. *Environ. Sci. Technol.* 38, 3286–3293.
- Song, W., Ford, J.C., Li, A., Sturchio, N.C., Rockne, K.J., Buckley, D.R., Mills, W.J., 2005a. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 3. Lakes Ontario and Erie. *Environ. Sci. Technol.* 39, 5600–5605.
- Song, W., Li, A., Ford, J.C., Sturchio, N.C., Rockne, K.J., Buckley, D.R., Mills, W.J., 2005b. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 2. Lakes Michigan and Huron. *Environ. Sci. Technol.* 39, 3474–3479.
- Stapleton, H.M., Allen, J.G., Kelly, S.M., Konstantinov, A., Klosterhaus, S., Watkins, D., McClean, M.D., Webster, T.F., 2008. Alternate and new brominated flame retardants detected in U.S. house dust. *Environ. Sci. Technol.* 42, 6910–6916.
- Strandberg, B., Dodder, N.G., Basu, I., Hites, R.A., 2001. Concentrations and spatial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes Air. *Environ. Sci. Technol.* 35, 1078–1083.
- Su, G., Letcher, R.J., McGoldrick, D.J., Backus, S.M., 2017. Halogenated flame retardants in predator and prey fish from the Laurentian Great Lakes: age-dependent accumulation and trophic transfer. *Environ. Sci. Technol.* 51, 8432–8441.
- Su, G., Letcher, R.J., Moore, J.N., Williams, L.L., Martin, P.A., de Solla, S.R., Bowerman, W.W., 2015. Spatial and temporal comparisons of legacy and emerging flame retardants in herring gull eggs from colonies spanning the Laurentian Great Lakes of Canada and United States. *Environ. Res.* 142, 720–730.
- Sverko, E., McCarry, B., McCrindle, R., Brazeau, A., Pena-Abaurrea, M., Reiner, E., Anne Smyth, S., Gill, B., Tomy, G.T., 2015. Evidence for anaerobic dechlorination of dechlorane plus in sewage sludge. *Environ. Sci. Technol.* 49, 13862–13867.
- Sverko, E., Reiner, E.J., Tomy, G.T., McCrindle, R., Shen, L., Arsenaault, G., Zaruk, D., MacPherson, K.A., Marvin, C.H., Helm, P.A., McCarry, B.E., 2010. Compounds structurally related to dechlorane plus in sediment and Biota from Lake Ontario (Canada). *Environ. Sci. Technol.* 44, 574–579.
- Sverko, E., Tomy, G.T., Marvin, C.H., Zaruk, D., Reiner, E., Helm, P.A., Hill, B., McCarry, B.E., 2008. Dechlorane plus levels in sediment of the Lower Great Lakes. *Environ. Sci. Technol.* 42, 361–366.
- Tao, W., Tian, J., Xu, T., Xu, L., Xie, H.Q., Zhou, Z., Guo, Z., Fu, H., Yin, X., Chen, Y., Xu, H., Zhang, S., Zhang, W., Ma, C., Ji, F., Yang, J., Zhao, B., 2019. Metabolic profiling study on potential toxicity in male mice treated with dechlorane 602 using UHPLC-ESI-IT-TOF-MS. *Environ. Pollut.* 246, 141–147.
- Tomy, G.T., Pleskach, K., Ismail, N., Whittle, D.M., Helm, P.A., Sverko, E., Zaruk, D., Marvin, C.H., 2007. Isomers of dechlorane plus in Lake Winnipeg and Lake Ontario food webs. *Environ. Sci. Technol.* 41, 2249–2254.
- USEPA, 2019a. Physical Features of the Great Lakes. (Accessed 08/30/2019). <https://www.epa.gov/greatlakes/physical-features-great-lakes>.
- USEPA, 2019b. Velsicol Chemical Corp. (Michigan) St. Louis, Mi. Site Documents & Data. (Accessed 6/12/2019). <https://cumulis.epa.gov/supercpad/SiteProfiles/index.cfm?fuseaction=second.docdata&id=0502194#SC>.
- Van den Eede, N., Dirtu, A.C., Ali, N., Neels, H., Covaci, A., 2012. Multi-residue method for the determination of brominated and organophosphate flame retardants in indoor dust. *Talanta* 89, 292–300.
- Venier, M., Dove, A., Romanak, K., Backus, S., Hites, R., 2014. Flame retardants and legacy chemicals in Great Lakes' water. *Environ. Sci. Technol.* 48, 9563–9572.
- Wei, H., Aziz-Schwanbeck, A.C., Zou, Y., Corcoran, M.B., Poghosyan, A., Li, A., Rockne, K.J., Christensen, E.R., Sturchio, N.C., 2012. Polybromodiphenyl ethers and decabromodiphenyl ethane in aquatic sediments from Southern and Eastern Arkansas, United States. *Environ. Sci. Technol.* 46, 8017–8024.
- WHO, 1984. International Programme on Chemical Safety: Environmental Health Criteria 44, Mirex. (Accessed 06/04/2015). <http://www.inchem.org/documents/ehc/ehc/ehc44.htm>.
- WHO, 1994. EHC-152: Polybrominated Biphenyls; International Program on Chemical Safety. (Accessed 06/04/2015). <http://www.inchem.org/documents/ehc/ehc/ehc152.htm>.
- Wu, B., Liu, S., Guo, X., Zhang, Y., Zhang, X., Li, M., Cheng, S., 2012. Responses of mouse liver to dechlorane plus exposure by integrative transcriptomic and metabolomic studies. *Environ. Sci. Technol.* 46, 10758–10764.
- Yamaguchi, Y., Kawano, M., Tatsukawa, R., 1988. Tissue distribution and excretion of hexabromobenzene and its debrominated metabolites in the rat. *Arch. Environ. Contam. Toxicol.* 17, 807–812.
- Yang, R., Wei, H., Guo, J., Li, A., 2012. Emerging brominated flame retardants in the sediment of the Great Lakes. *Environ. Sci. Technol.* 46, 3119–3126.
- Yang, R., Wei, H., Guo, J., McLeod, C., Li, A., Sturchio, N.C., 2011. Historically and currently used dechloranes in the sediments of the Great Lakes. *Environ. Sci. Technol.* 45, 5156–5163.
- Yun, S.H., Addink, R., McCabe, J.M., Ostaszewski, A., Mackenzie-Taylor, D., Taylor, A.B., Kannan, K., 2008. Polybrominated diphenyl ethers and polybrominated biphenyls in sediment and floodplain soils of the Saginaw River Watershed, Michigan, USA. *Arch. Environ. Contam. Toxicol.* 55, 1–10.
- Zeng, L., Yang, R., Zhang, Q., Zhang, H., Xiao, K., Zhang, H., Wang, Y., Lam, P.K.S., Jiang, G., 2014. Current levels and composition profiles of emerging halogenated flame retardants and dehalogenated products in sewage sludge from municipal wastewater treatment plants in China. *Environ. Sci. Technol.* 48, 12586–12594.
- Zhu, L.Y., Hites, R.A., 2004. Temporal trends and spatial distributions of brominated flame retardants in archived fishes from the Great Lakes. *Environ. Sci. Technol.* 38, 2779–2784.
- Zhu, L.Y., Hites, R.A., 2005. Brominated flame retardants in sediment cores from Lakes Michigan and Erie. *Environ. Sci. Technol.* 39, 3488–3494.

Supplementary Material

**Halogenated Flame Retardants in the Sediments of Upper Great Lakes:
implications to long-range transport and evidence of long-term transformation**

Jiehong Guo, Zhuona Li, Prabha Ranasinghe,
Karl J. Rockne, Neil C. Sturchio, John P. Giesy, An Li*

* Corresponding author email: anli@uic.edu

Table of Content

(5 Tables, 4 Figures, 14 pages)

Text. Material and Methods

Table S1. Median and maximum concentrations of individual analytes

Table S2. Median and maximum inventories and recent fluxes of individual analytes

Table S3. Recent annual loading rate and total load of individual analytes

Table S4. Top three most contaminated sites in individual lakes

Table S5. Half-life ($t_{1/2}$) and doubling time (t_2) of target compounds in the sediment cores
deposited after 1900s

Figure S1. Sampling Sites.

Figure S2. Comparison in geometric mean concentrations of selected HFRs among geographic
areas.

Figure S3. The variation in concentration ratios of PBT over DBDPE and PBEB over DBDPE
with depth in selected sediment cores.

Figure S4. The correlations of f_{syn} in surface sediment with latitude and in core sediment with
depth at site M047.

Material and Methods

Sampling and sediment characterization. Ponar surface grab and core sediment samples were collected from Lakes Michigan, Superior and Huron onboard the US EPA Research Vessel (*R/V Lake Guardian*) during 2010 and 2012. Surface grab sediments were collected using a Ponar grab sampler with N=29 for Lake Michigan, N=24 for Lake Superior and N=59 for Lake Huron. Sediment cores were collected using a box corer or an Ekman dredge corer for those from Lake Michigan (N = 10), or an MC400 multi-corer (Ocean Instruments, San Diego, California) for those from the Lakes Superior (N = 9) and Huron (N = 9). Detailed description of the sampling sites with a map, and procedures for sample handling can be found elsewhere (Corcoran et al., 2018; Guo et al., 2016).

All the samples were measured for bulk density, water and solid contents, total organic carbon (TOC), and organic matter content (OM) using the procedures previously described (Guo et al., 2016). Activities of radionuclides ^{210}Pb and ^{137}Cs in core segments were measured by gamma spectrometry using HPGe well detectors (Ortec) interfaced with DSPEC-Plus digital signal processors, from gamma emissions at 46.5 keV and 661.6 keV, respectively. The mass sedimentation rates (MSR) and focusing factors (FF) were obtained from cumulative excess ^{210}Pb inventories. MSR ranged from <0.01 to 0.16 g/cm²-y, and FF ranged from <0.1 to 3. Additional description of the laboratory procedures and detailed results are given elsewhere (Corcoran et al., 2018; Guo et al., 2016).

Chemicals and Reagents. Target analytes *syn*-dechlorane plus (*syn*-DP), *anti*-dechlorane plus (*anti*-DP), mirex and internal standard ^{13}C labeled 2,3,3',4,4',5,5',6-octachlorobiphenyl (PCB205L) were purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA). Target analytes 2-ethylhexyl, 2,3,4,5-tetrabromobenzoate (EHTBB), bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH), Pentabromoethylbenzene (PBEBz), Dechlorane plus monoadduct (DPMA), Chlordane plus (CP), Dechlorane 604 component B (Dec604 CB) and dechlorinated DP (aCl₁₁DP) were purchased from Wellington Laboratories (Ontario, Canada). Target analyte 1,2,3,4,5-pentabromobenzene (PBBz) was purchased from Sigma-Aldrich (St. Louis, Missouri). The target PBDE congeners (BDEs 28, 47, 99, 100, 153, 154, 183 and 209), as well as hexabromobenzene (HBBz), 2,2',4,5,5'-pentabromobiphenyl (BB101), 2,2',3,4,4',5,5'-heptabromodiphenyl (BB153), decabromodiphenylethane (DBDPE), pentabromotoluene (PBT) and 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE) were purchased from AccuStandard (New Haven, CT). Dechlorane 602 (Dec602), Dechlorane 603 (Dec603), Dechlorane 604 component A (Dec604) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). Surrogate 4'-chloro-2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether (Cl-BDE208) was purchased from Wellington Laboratories. Internal standard decabromobiphenyl (BB209), surrogates 4'-fluoro-2,3',4,6-tetrabromodiphenyl ether (F-BDE69), 3'-Fluoro-2,2',4,4',5,6'-hexabromodiphenyl ether (F-BDE154) and 4'-fluoro-2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether (F-BDE208) were purchased from AccuStandard.

All solvents were HPLC or Optima grade and purchased from Fisher Scientific (Pittsburgh, PA). Silica gel (100-200 mesh, 75–150 μm , Grade 644), alumina (neutral, Brockmann I, 50-200 μm by Acros Organics), granular anhydrous sodium sulfate (Na₂SO₄), copper (50 mesh, granular, reagent grade) and concentrated hydrochloric acid were also from Fisher Scientific. The sorbents silica gel

and alumina as well as Na₂SO₄ were activated at 500 °C for 8 h, stored at 160 °C, and cooled to room temperature in desiccators before use.

Methods. A detailed description of the sample treatment and chemical analysis procedures was published elsewhere (Guo et al., 2014). In brief, about 5 g of freeze-dried sediment of each sample was extracted with an accelerated solvent extraction system (Dionex ASE350, Thermo Fisher Scientific, Inc.). The sediment was extracted for three cycles with hexane and acetone (1:1 v/v) mixture at 100 °C and heating time 5 min and static time 10 min. The extract was concentrated in a rotary evaporator and solvent-exchanged into hexane. A glass column (11 mm id × 40 cm long) was prefilled with dichloromethane (DCM). Then, the column was filled from bottom to top with 1 g granular anhydrous Na₂SO₄, 8 g alumina, 4 g silica gel and 4 g granular anhydrous Na₂SO₄. After the column was packed, DCM was completely replaced by hexane. Concentrated extract was added to the prepared columns and eluted with 100 mL hexane (F-1), 100 mL 4:1 hexane:DCM mixture (F-2), 100 mL DCM (F-3) and 100 mL methanol (F-4). Target analytes were mostly found in F-2. Mirex and Dec602 were found in both F-1 and F-2; EHTBB was found in F-2 and F-3; BTBPE was found in F-2, F-3 and F-4. All the four fractions were solvent exchanged to hexane. An aliquot of each fraction were placed in a 200 µL glass insert of a 2 mL vial for instrumental analysis.

Agilent 7890 gas chromatography (GC) coupled with Agilent 7000 triple quadrupole mass spectrometry (QQMS) with electron impact (EI) ion source was used to analyze PBDEs (except BDE209), and other brominated flame retardants except EHTBB and DBDPE. The multi-mode injection port was operated in solvent vent mode with 60 µL (20 µL × 3) total injection per run. The inlet temperature started at 0 °C, which was held for 2.1 min, then increased to 300 °C at 600 °C/min. The vent flow was 200 mL/min. The purge flow was 60 mL/min at a run time of 3 min. The carrier gas was helium, and the flow was kept constant at 1.2 mL/min. A Restek Rxi-XLB capillary column (30 m × 0.25 mm i.d. × 0.10 µm film thickness) was used for separation. The initial oven temperature was set at 50 °C, which was held for 3 min, then increased to 100 °C at 10 °C/min, then increased to 300°C at 5 °C/min and kept for 5 min until the run was completed. The GC-MS interface temperature was kept at 300 °C. The temperatures of the EI ion source was set at 230 °C, and the temperatures of both quadrupole 1 and quadrupole 2 were set at 150 °C. Data were acquired in multiple reactions monitoring (MRM) mode. Agilent MassHunter program was used for data acquisition and quantification. Identification of the chemicals was based on the GC retention time, precursor to product ions transitions, and the qualifier to quantifier ratio. The transitions of the target analytes, surrogates and internal standards have been previously published (Guo et al., 2014).

Agilent 6890/5973 GC-MS (Agilent Technologies, Santa Clara, CA) equipped with an ion source electron capture negative ionization (ECNI) was used to analyze BDE209, EHTBB, DBDPE, and all the chlorinated flame retardants. The GC was equipped with a programmable temperature vaporization (PTV) injection port, which was operated in solvent vent mode. The inlet temperature started at 40 °C, which was held for 2 mins, and then increased to 300 °C at 600 °C/min. The injection volume was 60 µL (20 µL × 3) for each run. The vent flow was 100 mL/min. The purge flow was 100 mL/min at 2.75 min. The GC was equipped with a Restek Rtx-1614 capillary column (15 m × 0.25 mm ID × 0.10 µm film thickness) for separation. The initial oven temperature was 50 °C, which was held for 3 min, then increased to 300 °C at 10 °C/min and held for 10 mins.

Carrier gas was helium and the flow of carrier gas was kept constant at 1.5 mL/min. In the MS, the reagent gas was methane. Temperatures of the ion source and the quadrupoles were set at 200°C and 150°C, respectively. The interface temperature was kept at 300 °C. Quantification and qualification ions have been previously published (Guo et al., 2014).

Quality Control. Two laboratory procedural blanks (Na₂SO₄) were analyzed along with sediment samples from each core, with one started from the freeze drying (FD) and the other from the extraction (PB). Two FD and two PB were prepared for Ponar grab samples for each lake. Two or three replicates of trip blanks and field blanks from each sampling trips were also analyzed. These blanks were processed using the same laboratory procedures as for sediments. Concentrations of target compounds (except BDE209) in the procedural blanks ranged from below detection limit (N.D.) to 0.12 ng/g dry weight (dw). The concentrations of BDE209 in blanks ranged from N.D. to 1.14 ng/g dw. More than 90% of the sediment samples were higher than the medians of the blanks. Therefore, we did not subtract the concentrations in any blanks from the measured data.

Surrogates F-BDE69 (4 ng), F-BDE154 (8 ng), F-BDE208 (8 ng), Cl-BDE208 (8 ng) were added to each sample before extraction. The average recovery \pm standard deviation (S.D.) for F-BDE69 in GC-ECNI-MS, F-BDE69 in GCQQQ-EI-MS, F-BDE154 in GC-ECNI-MS, F-BDE154 in GCQQQ-EI-MS, F-BDE208 in GC-ECNI-MS, Cl-BDE208 in GC-ECNI-MS were 86 \pm 22% (N=642), 94 \pm 21% (N=612), 103 \pm 12% (N=62), 122 \pm 16% (N=62), 129 \pm 42% (N=393) and 116 \pm 42% (N=581), respectively.

One sample from each core and two samples of Ponar grabs for each lake were analyzed in duplicate, and the median relative percentage differences (RPDs) of the duplicate analyses for individual HFRs ranged from 9 to 40%. In addition, duplicate sediment samples were spiked with the target analytes (8 to 24 ng each) and the average recoveries ranged from 60% to 134%. Instrument detection limits (based on three times of signal to noise ratio) ranged from 0.0002 ng/g (0.0005 ng/mL, BDE49) to 0.1061 ng/g (0.2653 ng/mL, DBDPE). Method detection limits (MDL) were determined by spiking previously extracted sediment samples with target analytes. Target analytes (0.02 ng to 4 ng, varied by chemicals) were spiked into each of eight 5 g replicate sediment samples, which were analyzed using the same general procedure described above. The MDLs were calculated as the product of the standard deviation and the one-side t-value at 0.99 confidence level, as described in Standard Method SW846. MDLs ranged from 0.0227 ng/g (BDE28) to 0.7854 ng/g (BDE209).

Table S1. Median and maximum concentrations of individual analytes (ng/g dry weight)*

Comp.	Concentration in Ponar grabs (ng/g dw)				Concentration at core surface (ng/g dw)			
	Michigan (N = 29)	Superior (N = 24)	Huron (N = 59)	All Lakes (N = 112)	Michigan (N = 10) ^a	Superior (N = 9) ^b	Huron (N = 9)	All Lakes (N = 28) ^c
BDE28	0 / 0	0.04 / 0.09	0 / 0.08	0 / 0.09	0 / 0	0 / 0.10	0 / 0	0 / 0.10
BDE47	0.01 / 0.09	0.21 / 0.40	0.03 / 0.5	0.04 / 0.50	0.10 / 0.30	1.10 / 1.70	0.30 / 0.50	0.30 / 1.70
BDE49	0 / 0.01	0.12 / 0.25	0 / 0.26	0 / 0.26	0 / 0	0.10 / 0.20	0 / 0.10	0 / 0.20
BDE99	0 / 0.06	0.32 / 0.51	0.01 / 0.16	0.01 / 0.51	0.10 / 0.10	0.20 / 0.40	0 / 0.20	0.10 / 0.40
BDE100	0.01 / 0.15	0.13 / 0.29	0.01 / 0.16	0.01 / 0.29	0 / 0.10	0.20 / 0.40	0.10 / 0.10	0.10 / 0.40
BDE153	0 / 0.06	0.19 / 0.44	0.01 / 0.16	0.01 / 0.44	0 / 0.10	0.10 / 0.30	0.10 / 0.10	0.10 / 0.30
BDE154	0.02 / 0.05	0.15 / 0.35	0 / 0.15	0.01 / 0.35	0 / 0.10	0.10 / 0.30	0.10 / 0.10	0.10 / 0.30
BDE183	0 / 0.06	0.16 / 0.43	0 / 0.2	0 / 0.43	0.10 / 0.20	0.30 / 1.10	0.10 / 0.10	0.10 / 1.10
BB101	0 / 0	0.08 / 0.09	0 / 0.15	0 / 0.15	0 / 0	0 / 0	0 / 0	0 / 0
BB153	0 / 0.02	0.08 / 0.23	0 / 1.50	0 / 1.50	0 / 0	0.10 / 0.20	0.10 / 0.20	0 / 0.20
BTBPE	0.02 / 0.21	0.34 / 2.18	0.13 / 3.45	0.13 / 3.45	1.10 / 3.90	2.40 / 3.70	0.90 / 3.00	1.10 / 3.90
DBDPE	0 / 0.16	0 / 0.71	0.04 / 0.70	0 / 0.71	1.40 / 2.00	1.10 / 3.80	1.00 / 1.70	1.10 / 3.80
EHTBB	0 / 0	0.12 / 0.51	0.13 / 1.37	0.06 / 1.37	0 / 0	0.40 / 0.80	0.50 / 4.80	0.30 / 4.80
HBBz	0.04 / 0.05	0.06 / 0.10	0.03 / 5.56	0.04 / 5.56	0 / 0	0 / 0.10	0.10 / 3.30	0 / 3.30
PBBz	0 / 0	0 / 0.05	0 / 0.03	0 / 0.05	0 / 0	0 / 0	0 / 0	0 / 0
PBEbz	0 / 0	0 / 0.06	0 / 0	0 / 0.06	0 / 0	0 / 0	0 / 0	0 / 0
PBT	0 / 0	0 / 0.09	0 / 0.01	0 / 0.09	0 / 0	0 / 0	0 / 0	0 / 0
syn-DP	0.01 / 0.06	0.05 / 0.61	0.04 / 0.96	0.03 / 0.96	0.20 / 0.30	0.80 / 2.10	1.00 / 1.40	0.60 / 2.10
anti-DP	0.02 / 0.09	0.19 / 2.61	0.2 / 3.78	0.12 / 3.78	0.40 / 1.10	3.30 / 4.70	3.00 / 4.30	2.20 / 4.70
Cl ₁₁ DP	0 / 0.01	0 / 0.02	0 / 0	0 / 0.02	0 / 0	0 / 0	0 / 0	0 / 0
Cl ₁₀ DP	0 / 0.01	0 / 0	0 / 0	0 / 0.01	0 / 0	0 / 0	0 / 0	0 / 0
DPMA	0 / 0	0 / 0.05	0 / 0.02	0 / 0.05	0 / 0	0 / 1.50	0 / 0.10	0 / 1.50
Mirex	0 / 0.02	0.01 / 0.08	0 / 0.12	0 / 0.12	0 / 0	0 / 0.10	0 / 0.10	0 / 0.10
CP	0 / 0.01	0.01 / 0.06	0 / 0.04	0 / 0.06	0 / 0	0 / 0.10	0 / 0	0 / 0.10
Dec601	0 / 0.01	0 / 0	0 / 0	0 / 0.01	0 / 0	0 / 0	0 / 0	0 / 0
Dec602	0 / 0.03	0.02 / 0.18	0.06 / 2.96	0.02 / 2.96	0.10 / 0.20	0.10 / 0.70	0.40 / 0.90	0.20 / 0.90
Dec603	0.02 / 0.10	0.06 / 0.37	0.01 / 1.70	0.02 / 1.70	0.10 / 0.30	0.30 / 0.90	0.10 / 0.20	0.10 / 0.90
Dec604	0.01 / 0.08	0 / 0.03	0 / 0.03	0 / 0.08	0 / 0	0.10 / 0.10	0.10 / 0.10	0 / 0.10
DEC604 CB	0 / 0	0 / 0	0 / 0.08	0 / 0.08	0 / 0	0 / 0	0 / 0	0 / 0

*0 means the value <0.01; a. N=8 for DPMA, CP and Cl₁₁DP; b. N=2 for Cl₁₁DP; c. N=26 for DPMA and CP and N=19 for Cl₁₁DP.

Table S2. Median and maximum inventories and recent fluxes of individual analytes*

Comp.	Recent net flux (ng/cm ² -y)				Inventory (ng/cm ²)			
	Michigan (N = 10) ^a	Superior (N = 9) ^b	Huron (N = 28) ^c	All Lakes (N = 112)	Michigan (N = 10) ^a	Superior (N = 9) ^b	Huron (N = 9)	All Lakes (N = 28) ^c
BDE28	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0.10	0 / 0.40	0 / 0.40
BDE47	0 / 0.01	0.01 / 0.04	0.01 / 0.02	0.01 / 0.04	0 / 0.20	1.00 / 2.10	0.30 / 1.80	0.30 / 2.10
BDE49	0 / 0	0 / 0	0 / 0.01	0 / 0.01	0 / 0	0.10 / 0.20	0 / 0.90	0 / 0.90
BDE99	0 / 0	0 / 0.01	0 / 0.01	0 / 0.01	0 / 0.10	0.10 / 0.7	0 / 0.70	0.10 / 0.70
BDE100	0 / 0	0 / 0.01	0 / 0	0 / 0.01	0 / 0.10	0.20 / 0.40	0 / 0.30	0.10 / 0.40
BDE153	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0.10 / 0.30	0.10 / 0.90	0 / 0.90
BDE154	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0.10 / 0.20	0 / 0.50	0 / 0.50
BDE183	0 / 0	0 / 0.02	0 / 0	0 / 0.02	0 / 0.10	0.30 / 1.00	0.10 / 0.60	0.10 / 1.00
BB101	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0.60	0 / 0.60
BB153	0 / 0	0 / 0	0 / 0.01	0 / 0.01	0 / 0	0.20 / 0.50	0.10 / 2.00	0.10 / 2.00
BTBPE	0.01 / 0.03	0.03 / 0.05	0.01 / 0.04	0.02 / 0.05	0.30 / 0.90	3.00 / 8.30	1.40 / 6.60	1.30 / 8.30
DBDPE	0.02 / 0.03	0.02 / 0.04	0.02 / 0.05	0.02 / 0.05	0.30 / 0.50	0.60 / 1.70	0.30 / 2.80	0.40 / 2.80
EHTBB	0 / 0	0 / 0.01	0.01 / 0.05	0 / 0.05	0 / 0	0.80 / 3.60	2.00 / 4.60	0.70 / 4.60
HBBz	0 / 0	0 / 0	0 / 0.16	0 / 0.16	0 / 0	0.20 / 0.70	0.20 / 17.8	0.10 / 17.8
PBBz	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0.10	0 / 0.10
PBEbz	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0
PBT	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0.10	0 / 0	0 / 0.10
syn-DP	0 / 0	0.01 / 0.02	0.01 / 0.02	0.01 / 0.02	0.10 / 0.20	1.10 / 6.80	1.40 / 4.60	0.80 / 6.80
anti-DP	0.01 / 0.01	0.04 / 0.07	0.04 / 0.07	0.03 / 0.07	0.20 / 0.60	4.90 / 33.1	4.60 / 14.3	3.10 / 33.1
aCl11DP	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0.10	0 / 0.10	0 / 0.10
aCl10DP	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0
DPMA	0 / 0	0 / 0.01	0 / 0	0 / 0.01	0 / 0	0.10 / 1.80	0.20 / 1.30	0 / 1.80
Mirex	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0.10 / 0.3	0.10 / 0.90	0.10 / 0.90
CP	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0.10 / 0.20	0 / 0.30	0 / 0.30
Dec601	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0
Dec602	0 / 0	0 / 0.01	0.01 / 0.01	0 / 0.01	0.10 / 0.10	0.30 / 1.00	1.10 / 2.20	0.30 / 2.20
Dec603	0 / 0	0 / 0.01	0 / 0	0 / 0.01	0.10 / 0.20	1.00 / 4.60	0.40 / 0.90	0.30 / 4.60
Dec604	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0.10 / 0.20	0 / 0.40	0 / 0.40
DEC604 CB	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0

*0 means the value <0.01; a. N=8 for DPMA, CP and aCl₁₁DP; b. N=2 for aCl₁₁DP; c. N=26 for DPMA and CP and N=19 for aCl₁₁DP.

Table S3. Recent annual loading rate and total load of individual analytes*

Comp.	Recent annual loading rate (kg/y)				Total load (tonnes)			
	Michigan (N = 10) ^a	Superior (N = 9) ^b	Huron (N = 9)	All Lakes (N = 28) ^c	Michigan (N = 10) ^a	Superior (N = 9) ^b	Huron (N = 9)	All Lakes (N = 28) ^c
BDE28	0.06	0.26	0.17	0.49	0.01	0.02	0.03	0.06
BDE47	1.05	8.65	3.13	12.83	0.05	0.58	0.25	0.88
BDE49	0.12	0.75	0.52	1.39	0	0.04	0.05	0.09
BDE99	0.64	1.50	0.79	2.93	0.02	0.10	0.05	0.17
BDE100	0.45	1.79	0.71	2.95	0.02	0.11	0.04	0.17
BDE153	0.20	1.08	0.59	1.87	0.01	0.08	0.07	0.16
BDE154	0.45	1.10	0.64	2.19	0.01	0.07	0.04	0.12
BDE183	0.59	2.26	0.65	3.50	0.02	0.19	0.09	0.30
BB101	0.02	0.07	0.14	0.23	0	0.01	0.03	0.04
BB153	0.15	0.85	0.84	1.84	0.01	0.12	0.13	0.26
BTBPE	11.22	16.70	9.11	37.03	0.35	1.70	1.18	3.23
DBDPE	10.86	9.63	9.79	30.28	0.28	0.4	0.33	1.01
EHTBB	0	2.69	7.51	10.20	0	0.63	1.24	1.87
HBBz	0.13	0.37	8.15	8.65	0.01	0.13	0.84	0.98
PBBz	0.01	0.04	0.06	0.11	0	0.01	0.01	0.02
PBEBz	0	0.01	0.01	0.02	0	0	0	0
PBT	0.01	0.04	0.03	0.08	0	0.02	0.01	0.03
<i>syn</i> -DP	1.58	6.67	8.04	16.29	0.07	0.96	0.92	1.95
<i>anti</i> -DP	5.04	22.13	25.53	52.70	0.21	3.87	2.80	6.88
aCl ₁₁ DP	0.01	0.13	0.14	0.28	0	0.01	0.02	0.03
aCl ₁₀ DP	0	0	0	0	0	0	0	0
DPMA	0	1.22	0.30	1.52	0	0.23	0.18	0.41
Mirex	0.19	0.35	0.26	0.80	0.02	0.08	0.08	0.18
CP	0.17	0.27	0.18	0.62	0.01	0.04	0.04	0.09
Dec601	0	0	0	0	0	0	0	0
Dec602	0.88	1.55	3.88	6.31	0.05	0.23	0.64	0.92
Dec603	1.08	2.50	1.18	4.76	0.09	0.71	0.21	1.01
Dec604	0.11	0.54	0.47	1.12	0	0.04	0.04	0.08
DEC604 CB								

*0 means the value <0.01; a. N=8 for DPMA, CP and Cl₁₁DP; b. N=2 for aCl₁₁DP; c. N=26 for DPMA and CP and N=19 for aCl₁₁DP.

Table S4. Top three most contaminated sites in individual lakes

	Lake Superior			Lake Michigan			Lake Huron		
	#1	#2	#3	#1	#2	#3	#1	#2	#3
	<u>by concentrations in Ponar grab sediment samples</u>								
Σ_8 PBDEs	S022	S016	S019	M020	M093a	M093c	H001	NC71	GB42
BDE209	S002	S011	S001	M093b	M061	M011	H001	NC71	NC76
Σ_9 BFRs	S117	S116	S011	M061	M093c	M093b	H001	NC71	NC76
Σ_2 DPs	S117	S011	S116	M093b	M061	M009	NC76	GB42	H103
Σ_{10} CFRs	S011	S106	S001	M009	M061	M093b	H002	H027	NC76
	<u>by inventories of the cores</u>								
Σ_8 PBDEs	S022	S011	S019	M009	M011	M008	H001	H012	H032
BDE209	S011	S016	S002	M011	M008	M047	H001	H006	H032
Σ_9 BFRs	S011	S002	S022	M011	M008	M024	H001	H012	H006
Σ_2 DPs	S011	S012	S008	M009	M011	M024	H001	H012	H006
Σ_{10} CFRs	S011	S012	S008	M009	M024	M032	H001	H012	H048

*NC = North Channel, GB = Georgian Bay.

Table S5. Half-life ($t_{1/2}$) and doubling time (t_2) of target compounds in the sediment cores deposited after 1900s (unit: years; if one core has both $t_{1/2}$ and t_2 , the estimation of $t_{1/2}$ used data from the topmost layers and t_2 were got based on the layers underneath.)

		M008	M009	M011	M018	M024	M032	M041	M047	M050	S002	S008	S011	S012	S016	S019	S022	H001	H006	H012	H032	H038	H048	H061	H095
BDE28	$t_{1/2}$	18*					54	126		8*								20*	19	10	23*				
	t_2	14*	10*	27*	13*	37*	16*	16*	15*	13*	69	42*	13*	55*	57*	16*	15*	66*	18*	15*	22*	37*	56*	35*	27*
BDE47	$t_{1/2}$	76*					87	72		7			22	10				4	19	14	25	63			
	t_2	13*	7*	11*	11*	21*	11*	11*	7*	12*	38	33*	15*	20*	24*	12*	7*	11*	11*	7*	15*	24*	17*	19*	20*
BDE49	$t_{1/2}$	89*				60	192			6			120					16*	15	21*	14	99			
	t_2	13*	6*	11*	7*	18*	9*	9*	6*	7*	31*	11*	12*	13*	14*	6	6*	8*	10*	5*	8*	13*	12*	21*	14*
BDE99	$t_{1/2}$	87	6	320			123			8			71	11				3	13	48		56			
	t_2	13*	7*	5*	14*	24*	9*	10*	7*	12*	20*	14*	10*	14*	19*	11*	7*	9*	8*	4*	9*	10*	13*	11*	13*
BDE100	$t_{1/2}$	98	11			50	158	141		9			55	4				4	23	15	54	55			
	t_2	17*	8*	10*	11*	16*	12*	10*	7*	9*	15*	15	10*	5	24*	9*	7*	7*	10*	5*	8*	14*	10*	16*	20*
BDE153	$t_{1/2}$	97	12		31		9		42	9		89		7		4		12		6	81	54	45		35
	t_2	27*	9*	17*	11*	20*	13*	12*	5*	10*	17*	13	17*	10*	29*	2	8*	18*	12*	10*	2*	24*	8*	18*	22
BDE154	$t_{1/2}$	206			92		129			11				21		117		11	268	13		33			
	t_2	16*	10*	12*	10*	19*	13*	10*	8*	10*	13*	12*	10*	13*	20*	6*	8*	23*	11*	6*	13*	24*	16*	18*	23*
BDE183	$t_{1/2}$	32	21			44*	7	213	11	7			21			3	7	5	11	7	588	6	103		9
	t_2	24	7*	17*	15*	10	24*	9*	5*	11*	16*	19	14*	22*	31*	4	2	45	13*	10*	1	30*	18*	26*	29
BDE209	$t_{1/2}$	42	142	79	127		95*	119	286	10			197					70	13*		57	14	34		
	t_2	49*	4*	10*	9*	18*	9*	10*	7*	10*	19*	13*	8*	20*	35*	11*	5*	17*	11*	8*	7*	25*	11*	22*	20*
CP	$t_{1/2}$	67	27*		126*	570	16	9*	46*				52	102	57		23*		8	22*	28*	10	6		364
	t_2	41*	8*		10*	16*	20*	10*	11		28*	24*	16*	13*	38*	13*	7	29	2	6	9*	21*	166		22*
aCl ₁₁ DP	$t_{1/2}$		25*		17			53	26									40*	47	41	39	3946	207	49	
	t_2	65	4		13	16*	11	9*	6					22*	36*			17	5*	12*	10	10	9	12*	20*
mirex	$t_{1/2}$	58*	2	141	63*	53	170	6	17*	10		5	22	52*		31	8	67	2	1	26		7	7	3
	t_2		7	13*		30*	11*	13*	3*	36	19	21*	19*	26	136	10*	9		24	3	2		15*	33	5
Dec 602	$t_{1/2}$	32	51	131	47*	87	72*	26*	36*	5		43	8	27	4	14	38	35*	20*	28*	10	10	21	89	
	t_2	26*	4	7*	5	14*	7*	8*	8	11*	17*	12*	10*	24	63	5	3*	2	7*	2*	3*	50*	11*	57	30*
Dec 603	$t_{1/2}$	42*	12*	85*	241	73*	50	55*	23*	7*	129	29	7	50	82	19	9	14*	2	22*	48*	13	58	20	14
	t_2		6*	8	7*	6*	10*	7*	6*	46	12*	19*	13*	11*	9	7	8*	73	63	8*	5*	23*	22	41*	28*
Dec 604	$t_{1/2}$	47	43	175			155	11	10									14	46	133	3	12	17		49
	t_2	17*	16*	13*	15*	27	9	8	17*	5	21			12	9	6		14*	9*	1	20*	6	4	18*	16
syn-DP	$t_{1/2}$		18*	69			109	157		7*		37		95			30	16*	8	56*	157	8	80	174	11
	t_2	41*	2	10*	13*	29*	9*	9*	13*	10*	18*	12*	21*	18*	63	11*	5*	29*	10*	4*	2*	34*	9*	28*	21*
anti-DP	$t_{1/2}$		13*		58		37	148	33*	21			145	149*	26		31	17*	205	47*	524	85	68		
	t_2	55*	2*	17*	6*	30*	9*	7*	5*	6*	19*	12*	11*	12*	18*	9*	8*	31*	7	4*	3*	25*	9*	29*	28*
BB 101	$t_{1/2}$	138	36*			128	254	159	77*	10*			151	57				28	24*	30*	31*	112	76	161	
	t_2	35*	6*	28*	21*	9*	19*	11*	9*	21*	17	18	7	22	40*			14	13*	8*	6*	83*	17*	35*	36*
BB 153	$t_{1/2}$	14	45*	27	89*	94	37	49*	77	7			9			4	45	23	24	22*	32*	278	50	71	
	t_2	12*	5*	14*	10	8*	19*	8*	6	19*	17	21	16		9	5	8	28	8*	5*	5*	45*	17	32	40*
BTBPE	$t_{1/2}$		35*	42	57		26	144	19	16			12	64				12*	1	7*	3	6	78	5	9
	t_2	70*	3	4*	6*	22*	8*	7*	6*	7*	9*	15*	7*	19*	10*	12*	4*	33*	5*	5*	5	18*	7*	12*	20*
DBDPE	$t_{1/2}$		17		40	31				49			5					50	38	6					
	t_2	13*	3	11*	11	18*	18*	6	7*	8	15*	11*	9	12*	16*	6	7*	6*	4*	4*	6*	22*	10	18*	14*
EHTBB	$t_{1/2}$	783		22	36					9*									37	38*	5*	66	10		
	t_2			28*	32	81*	67*	38*	19*	40*									15*	4	8*	22	20	25*	31
HBBz	$t_{1/2}$	13	14	8	12		45	50	105			9	180						20		1				6
	t_2	9	4	113	42	97	70*	17	89		72*		9		20*		3	88	14*	19*	23*	39*	60*	95	25
PBBz	$t_{1/2}$	98			74				56									204	7	35					7
	t_2	40	26*	76*	16*	86	19	24*	20*										18*	9*		4			9
PBEBz	$t_{1/2}$	82	35	23	14				27									50							
	t_2	17	9*	68*	21				14																
PBT	$t_{1/2}$		175	8																					
	t_2		27*	53*	202						13								<1				7		

*Significant at 95% confidence interval.

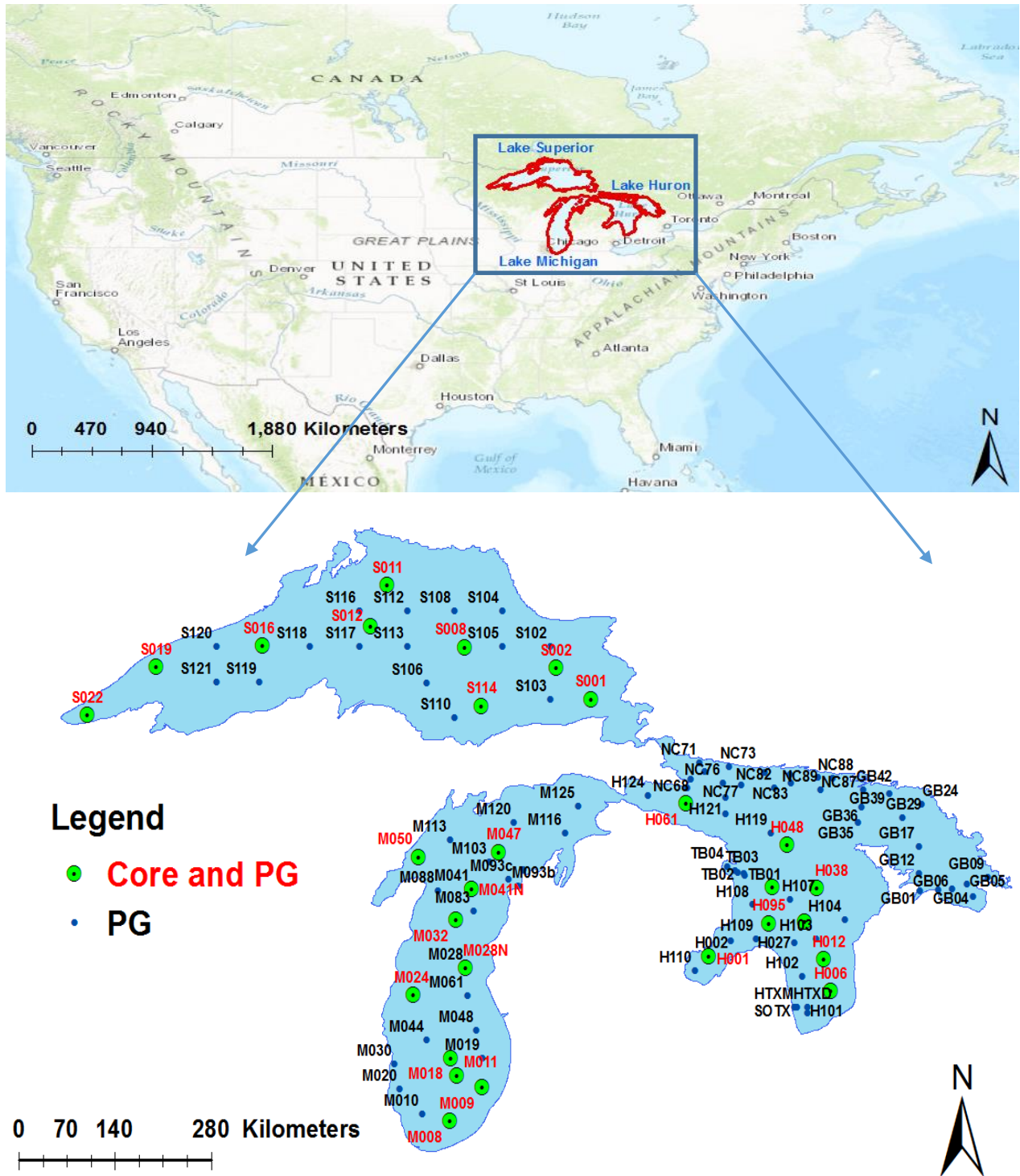


Figure S1. Sampling sites. PG = Ponar grab; labels for the Ponar grab sites are not all shown. The shape file for the lakes was made by extracting the Electronic Navigational Chart (ENC) data from the NOAA Office of Coast Survey. This figure has been previously published (Cao et al., 2017).

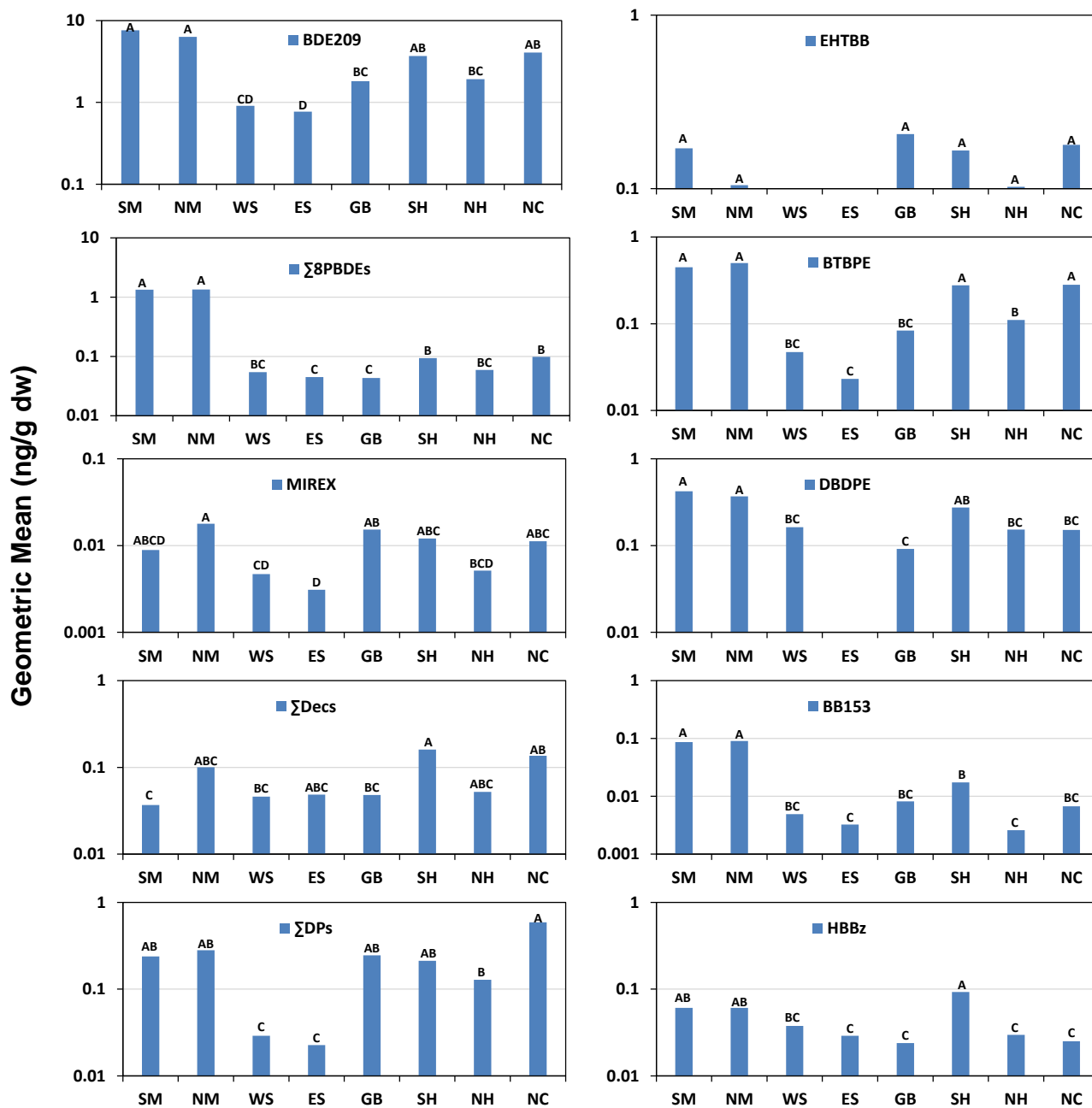


Figure S2. Comparison in geometric mean concentrations of selected HFRs among geographic areas. Southern (SM) and northern (NM) Lake Michigan were divided at latitude 44°N; Western (WS) and eastern (ES) Lake Superior were divided at longitude 87.573°W; Southern (SH) and northern (NH) main Lake Huron were divided at latitude 44.4°N; Georgian Bay (GB) and North Channel (NC) are commonly considered as parts of Lake Huron. Fisher's exact test was used to compare every pair of two areas and areas that do not share a letter on top of bar are significantly different at 95% confidence interval.

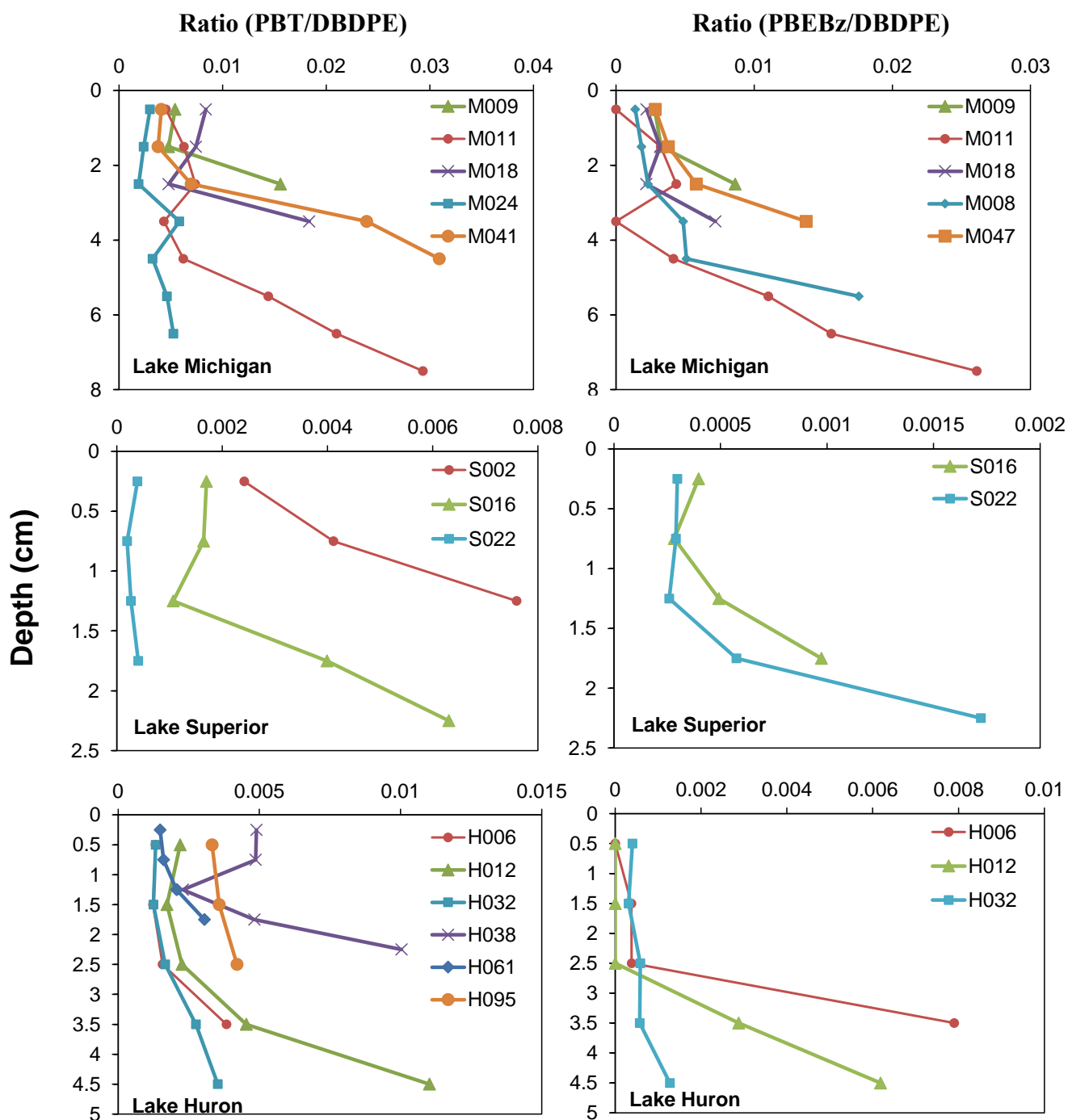


Figure S3. The variation in concentration ratios of PBT over DBDPE and PBEBz over DBDPE with depth in selected sediment cores.

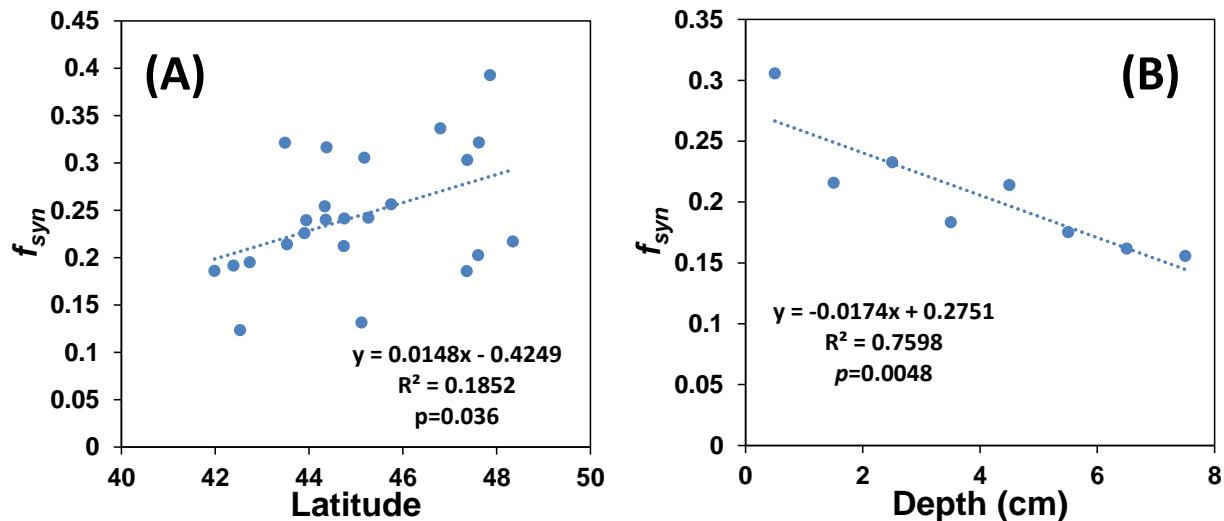


Figure S4. The correlations of f_{syn} (A) in surface sediment with latitude of the coring sites, and (B) in sediment core with depth at site M047.

References

- Cao, D., Guo, J., Wang, Y., Li, Z., Liang, K., Corcoran, M.B., Hosseini, S., Bonina, S.M.C., Rockne, K.J., Sturchio, N.C., Giesy, J.P., Liu, J., Li, A., Jiang, G., 2017. Organophosphate Esters in Sediment of the Great Lakes. *Environ. Sci. Technol.* 51, 1441-1449.
- Corcoran, M., Sherif, M.I., Smalley, C., Li, A., Rockne, K.J., Giesy, J.P., Sturchio, N.C., 2018. Accumulation Rates, Focusing Factors, and Chronologies from Depth Profiles of 210pb and 137cs in Sediments of the Laurentian Great Lakes. *J. Great Lakes Res.* 44, 693-704.
- Guo, J., Li, Z., Ranasinghe, P., Bonina, S., Hosseini, S., Corcoran, M.B., Smalley, C., Kaliappan, R., Wu, Y., Chen, D., Sandy, A.L., Wang, Y., Rockne, K.J., Sturchio, N.C., Giesy, J.P., Li, A., 2016. Occurrence of Atrazine and Related Compounds in Sediments of Upper Great Lakes. *Environ. Sci. Technol.* 50, 7335-7343.
- Guo, J., Li, Z., Sandy, A.L., Li, A., 2014. Method Development for Simultaneous Analyses of Multiple Legacy and Emerging Organic Chemicals in Sediments. *J. Chromatogr. A* 1370, 1-8.