



## Legacy polychlorinated organic pollutants in the sediment of the Great Lakes



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### ABSTRACT

Legacy, organic pollutants, including polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), naphthalenes (PCNs), and diphenyl ethers (PCDEs) were quantified in sediments of the Laurentian Great Lakes of North America. A total of 40 cores (939 core segments) and 198 Ponar surface grab samples were collected from the five Great Lakes between 2010 and 2014. Median concentrations in Ponar grab samples were 8.4, 0.27, 0.05, 0.19 and 0.01 ng/g dry weight (dw) for total-PCBs,  $\sum_7$ PCDDs,  $\sum_{10}$ PCDFs,  $\sum_{12}$ PCNs, and  $\sum_7$ PCDEs, respectively. By using Geographic Information Systems Analysis with the inverse distance weight (IDW) interpretation of the spatial distribution of the chemical inventory at coring sites, total mass loads in the five lakes combined were estimated to be 511, 15.3, 5.3, 20.7 and 2.9 t for total-PCBs,  $\sum_7$ PCDDs,  $\sum_{10}$ PCDFs,  $\sum_{12}$ PCNs, and  $\sum_7$ PCDEs, respectively. Patterns of spatial distributions revealed pollution hotspots and provided evidence for historical local sources. Concentrations of residues in Ponar grabs and inventories at coring sites, when normalized to concentrations of organic carbon, exhibited statistically significant correlations with latitude and longitude of the sampling sites for all five chemical groups. At most coring sites, concentrations have been decreasing towards the sediment surface. At locations relatively close to known or suspected sources, estimated half-times for all classes of chemicals were approximately 20 years. The declining trends of PCDDs and PCDFs were unclear at some locations, suggesting the presence of currently active emission sources.

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### Introduction

Many polychlorinated aromatic organic compounds are intrinsically hydrophobic and persistent. In natural waters such as lakes and rivers, such chemicals often accumulate in sediments. Spatial and temporal trends of the chemical inputs to sediment are useful for identifying sources, understanding their transport and fate, and investigating the link between chemical pollution and changes in ecosystems and health of humans.

Since they were first detected in the Great Lakes in 1968 (Veith, 1968), polychlorinated biphenyls (PCBs) have been among chemicals of most concern in terms of potential harm to the ecosystem and people

in the region. Much about PCBs has been learned and summarized (Hornbuckle et al., 2006; MacKay et al., 1983). Sediment was the largest depository of PCBs in the Great Lakes; it was estimated in the 1980s that 53% (in Lake Superior) to 97% (in Lake Erie) of total burdens of PCBs in the Great Lakes, resided in sediments (Eisenreich, 1987).

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) were first reported in the Great Lakes region in the late 1970s. Since then, many studies have been conducted on the occurrence, spatial and temporal trends, and sources of PCDD/Fs in air, water, sediment, biota, and humans in the region (Norstrom, 2006). Sediments of the lakes and their tributaries were investigated for PCDD/Fs over the past several decades (Dahmer et al., 2015; Shen et al., 2009; Richman et al., 2011; C.H. Marvin et al., 2002; C. Marvin et al., 2002; Pearson et al., 1997, 1998; Czuczwa and Hites, 1984, 1985, 1986).

Polychlorinated naphthalenes (PCNs) have been continuously found in the Great Lakes environment (Gewurtz et al., 2009; Helm et al., 2004,

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2006, 2008; Lee et al., 2007; Harner et al., 2006; Hanari et al., 2004; C. Marvin et al., 2002; Kannan et al., 2001; Elder et al., 1981), and appear to be the only widely detected group of halogenated polycyclic aromatic hydrocarbons, although others such as polychlorophenanthrenes are also of concern (Horii et al., 2009; Fu et al., 1999; Elder et al., 1981).

Through the 1980s and 1990s, polychlorinated diphenyl ethers (PCDEs) were found in sediments, and tissues of fishes, birds, and humans from the Great Lakes (Metcalf et al., 1997; Niimi et al., 1994; Chu et al., 1990; Williams et al., 1991; Williams and LeBel, 1988; Jaffe and Hites, 1986; Jaffe et al., 1985; Zenon Environmental Inc., 1985; Coburn and Comba, 1981, 1985). PCDEs were produced as impurities in the manufacturing of other chlorinated organics, and were also generated from combustions of chlorine-containing wastes.

The Great Lakes Sediment Surveillance Program (GLSSP) was established in 2010, with a mission to investigate the presence and reveal the spatial distributions and temporal trends of persistent, bioaccumulative, and toxic chemicals in sediments of the Great Lakes. The results from GLSSP have been published in a number of papers, mostly reporting new discoveries and focusing on chemicals of emerging concern (Cao et al., 2017; Guo et al., 2017, 2016, 2014b; Peng et al., 2016a, 2016b; Codling et al., 2014, 2018). Here we report the findings on five groups of legacy polychlorinated organic pollutants including PCBs, PCDDs, PCDFs, PCNs, and PCDEs. The purpose of this study was to update information and identify recent changes regarding these legacy chemicals in sediments of the Laurentian Great Lakes. For PCBs, the data reported here provides more accurate estimates of mass loadings of chemicals than previous studies, which were based on fewer samples (Li et al., 2009). With the larger database obtained, the dependence of spatial distributions of chemicals on latitude and longitude were assessed and contributions of historical and current hotspots to total mass loads were investigated. Decreases in rates of net mass loading over time were also investigated.

## Methods

### Sampling and sample characterization

Sediments were collected from one lake per year from 2010 through 2014 in the order of Lakes Michigan, Superior, Huron (including the North Channel and Georgian Bay), Ontario, and Erie. All collections were made from the USEPA's *R/V Lake Guardian*. A summary of the samples collected can be found in Electronic Supplementary Material (ESM) Table S1. A total of 1137 samples were collected, including 198 Ponar grabs and 939 core segments from 40 cores. A map of the sampling sites is provided in Fig. 1, and the basic site information in ESM Tables S2a and S2b. A brief description of sampling methods is given in ESM Text S1.

All samples were characterized for basic physicochemical properties including: solid content, bulk density, in-situ density, solid density, porosity, and the contents of organic matter, organic carbon, and soot carbon (Li et al., 2018; Hosseini, 2016; Bonina, 2016; Bonina et al., 2018). Rates of mass sedimentation (MSR) and focusing factors (FF) were determined for locations where cores were collected, by gamma spectrometry measurements of multiple radionuclides including  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , and  $^{226}\text{Ra}$  (Corcoran et al., 2018).

### Chemical analyses

Target analytes of this work are listed in Table 1. Sources and handling of all the chemicals and materials are described in ESM Text S2. Laboratory procedures for identification and quantification of target analytes are described elsewhere (Guo et al., 2014a). Briefly, sediment samples were freeze-dried, and a portion (5 g) of dried sediment was extracted using an accelerated solvent extractor (Dionex ASE350). Extracts were concentrated on a rotary evaporator, then fractionated and cleaned-up using an adsorption chromatographic column filled with

sodium sulfate, activated neutral silica gel and alumina. All analytes reported in this paper were eluted from the column in two fractions with 100 mL hexane (F-1) and 100 mL mixture of hexane and dichloromethane (v/v, 4/1) (F-2).

An Agilent 6890 gas chromatograph (GC) equipped with an Agilent 5973 single quadrupole mass spectrometer with electron capture negative ionization source (ECNI-MS) was used to analyze all PCDDs and PCDFs (except 2,3,7,8-TCDD) in Lake Superior. Agilent 7890 GC coupled with Agilent 7001 triple quadrupole mass spectrometry with electron impact ionization source (EI-QQQMS) was used for identification and quantitation for PCBs, PCNs, and PCDEs in all the lakes, PCDDs and PCDFs in Lakes Michigan, Huron, Erie, and Ontario, plus 2,3,7,8-TCDD in Lake Superior. Different instrumental configurations and/or operational conditions were used for different target chemicals in specific sample fractions or combinations of fractions, as described in ESM Text S2. Mass-to-charge ratios of the analyte homologs as well as the optimized collision energies in EI-QQQMS are summarized in ESM Table S3.

### Quality control

Two or three replicates of field and trip blanks were prepared with samples from each sampling trip. Two laboratory procedural blanks were analyzed along with sediments from each core. All blanks were  $\text{Na}_2\text{SO}_4$  (pre-purified by baking at 500 °C overnight before use). The 75<sup>th</sup>ile (Q3) concentrations found in all blanks were below the method detection limits for PCDDs, PCDFs, PCDEs, and most PCNs. The Q3 value for t-PCBs was 0.19 ng/g dw, which was below the minimum t-PCBs measured in all Ponar grabs. The concentrations reported in this paper were not adjusted by the levels in blanks. Method detection limits (MDLs) were determined for individual congeners as the products of the standard deviation of eight spiked replicated sediment samples and a one-side *t*-value at 0.99 confidence level. Summed MDLs were 0.074, 0.018 and 0.026 ng/g dw for t-PCBs,  $\Sigma_{12}$ PCNs, and  $\Sigma_7$ PCDEs, respectively. Instrument detection limits were 0.028 ng/g dw for  $\Sigma_7$ PCDDs and 0.031 ng/g dw for  $\Sigma_{10}$ PCDFs using GC/EI-QQQMS, and 0.015 ng/g dw for  $\Sigma_7$ PCDDs and 0.006 ng/g dw for  $\Sigma_{10}$ PCDFs using GC/ECNI-MS.

Before extraction,  $^{13}\text{C}$  labeled surrogates PCB52-L and PCB209-L were spiked into all samples ( $N = 926$ ). Median recoveries of these surrogates were 92% (range 33% - 175%) and 85% (range 34% - 158%) for PCB52-L and PCB209-L, respectively.  $^{13}\text{C}$  labeled 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (TCDD-L) and 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (HxCDD-L) were also spiked into some samples ( $N = 68$ ). Median recoveries were 98% (range 55% - 134%) for TCDD-L, and 104% (range 60% - 157%) for HxCDD-L. Concentrations reported were not adjusted for recoveries of surrogates.

One sample from each core and two samples of Ponar grabs for each lake were analyzed in duplicate. A total of 45 samples were analyzed in duplicate for PCBs, PCNs and PCDEs, and 39 samples were analyzed in duplicate for PCDDs and PCDFs. With non-detects (ND) excluded, relative percent difference (RPD) in the concentrations of the duplicates averaged 8.7%, 22%, 20%, 13%, and 20% for t-PCBs,  $\Sigma_7$ PCDDs,  $\Sigma_{10}$ PCDFs,  $\Sigma_{12}$ PCNs, and  $\Sigma_7$ PCDEs, respectively.

A standard reference material (NIST SRM 1941b) of marine sediment was analyzed in triplicate with sediments from Lakes Superior, Michigan, and Huron, and in duplicate with the sediments from Lakes Erie and Ontario. For the 38 PCB congeners with NIST certified or reference concentrations (NIST, 2004), recoveries for individual congeners had an overall mean of 83% and median of 84% (ranging from 30% to 149%), with the exclusion of PCBs 28 and 56, which co-eluted with PCBs 31 and 60, respectively, thus had recoveries of >160%. NIST SRM 1944 (New York / New Jersey waterway sediment) was analyzed in duplicate for the 17 PCDDs and PCDFs with chlorine substitution at 2,3,7,8

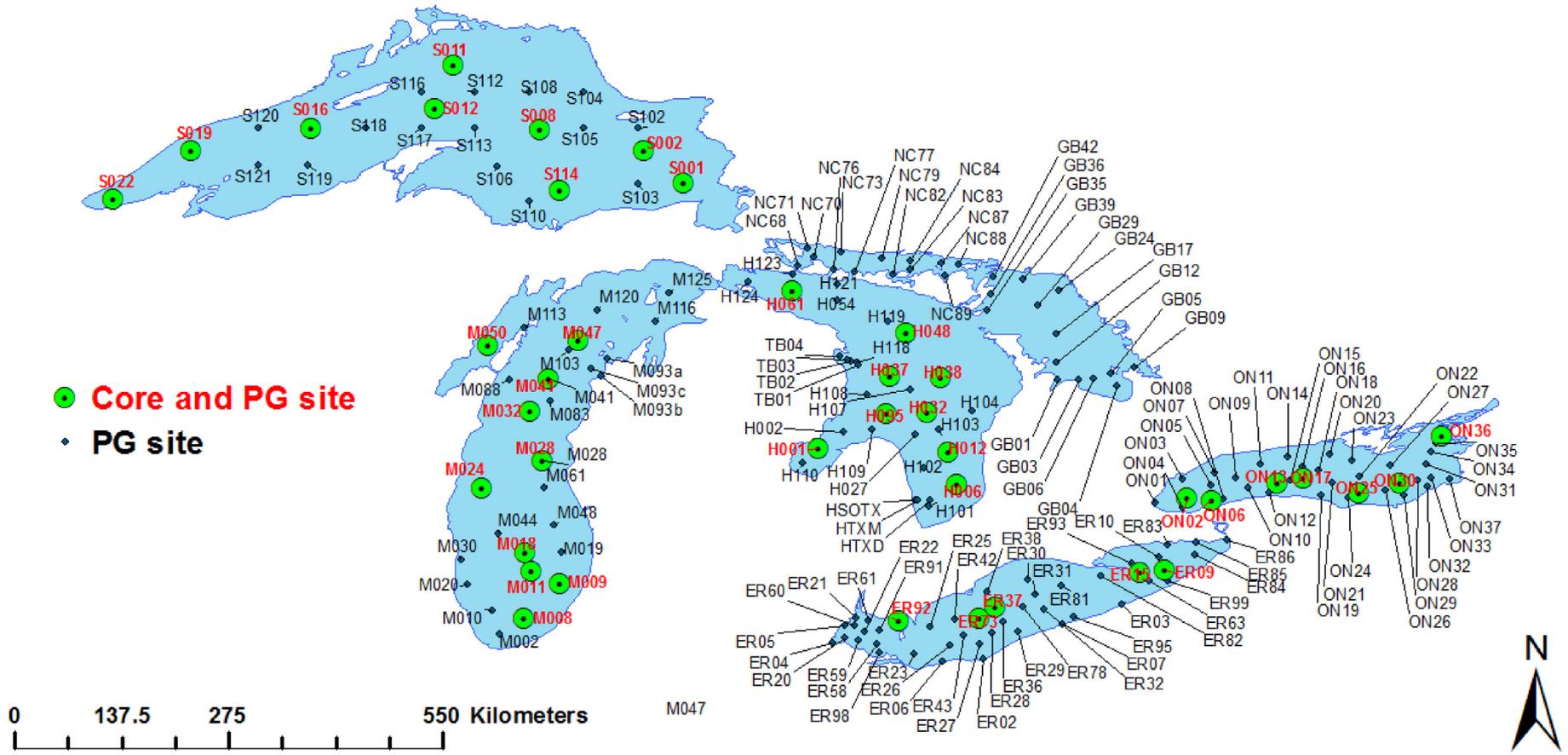


Fig. 1. Sediment sampling locations. PG = Ponar grab. Latitude, longitude and water depth of all the sites are provided in ESM Tables S2a and S2b.

**Table 1**  
Target analytes.

Abbr'n	Analyte group	N	Compounds
PCBs	Polychlorobiphenyls	39	PCBs 1, 2, 3, 4, 6, 8, 9, 16, 18, 19, 22, 25, 28, 52, 44, 56, 66, 67, 71, 74, 82, 87, 99, 110, 138, 146, 147, 153, 173, 174, 177, 179, 187, 180, 194, 195, 199, 203, and 206 <sup>a</sup>
PCDDs	Polychlorodibenzo- <i>p</i> -dioxins	7	All congeners with 2,3,7,8 chlorine substitutions
PCDFs	Polychlorodibenzofurans	10	All congeners with 2,3,7,8 chlorine substitutions
PCNs	Polychloronaphthalenes	12	PCNs 1, 2, 5, 6, 9, 13, 27, 28, 52, 66, 73, and 75
PCDEs	Polychlorodiphenyl ethers	7	CDEs 3, 7, 15, 77, 105, 118, and 209

<sup>a</sup> PCBs 1, 2, and 3 were not measured for samples from Lake Superior and cores M008, M011, M018, M041 and M047 of Lake Michigan.

positions. Mean recoveries were in the range of 60%–134% compared to the reference values provided by NIST (2011).

### Data analyses

Concentrations measured for sediment cores were used to estimate fluxes of net deposition of chemicals to each segment (*i*) of the cores (Eq. (1)).

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

where  $C_i$  is the chemical concentration (ng/g dw), MSR is in  $\text{g cm}^{-2} \text{ y}^{-1}$  and the FF is dimensionless, both being site-specific. Data for MSR and FF are reported and discussed elsewhere (Corcoran et al., 2018). Different from the flux, which is a vector quantity frequently used to describe transport across phase boundaries, net depositional flux in this work integrated all input and output processes. It is a scalar quantity; as such, its value in surface segments of cores does not indicate whether the sediment is a net sink or source of pollutants to the overlying water. In illustrating site-specific histories of pollutant input, net depositional flux is preferred over measured concentrations because it takes into account the effect of sediment focusing. Sediment focusing is a process that differentially transports fine particulate materials to deeper and more centric locations in lakes and oceans, and alters the actual quantities of substance deposited directly at a particular site.

Chemical inventory represents the total accumulation of the chemical per unit area of the lake bottom at a specified sampling site (Eq. (2)).

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

where  $\rho_{b,i}$  is the dry mass bulk density ( $\text{g cm}^{-3}$ ) and  $d_i$  is the sample thickness (cm) of core segment *i*. The lake-wide annual loading rate was estimated based on median net depositional flux (Eq. (3)):

$$\text{Annual loading rate (kg y}^{-1}) = \text{Average or median net flux} \times \text{Lake water surface area} \times 10^{-3} \quad (3)$$

Surface areas of Lakes Superior, Michigan, Huron, Ontario and Erie are 82,100 km<sup>2</sup>, 57,800 km<sup>2</sup>, 59,600 km<sup>2</sup>, 18,960 km<sup>2</sup>, and 25,700 km<sup>2</sup>, respectively (Quinn, 1992). Of greatest concern are recent net fluxes at each site and associated recent rates of annual loading to each lake. These recent values were estimated from concentrations in the uppermost segments of cores.

Finally, the total lake-wide burdens of chemicals were calculated (Eq. (4)).

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

In Eqs. (3) and (4), the constants are for unit conversions. In previous studies with only a few cores in each lake, means were used in these equations (Li et al., 2006; Song et al., 2004, 2005a, 2005b; Yang et al., 2011, 2012; Guo et al., 2016, 2017). In this work, differences between estimates obtained from using mean and median values were found to be large when there were pollution “hotspots”. For instance, the load of

total PCBs in Lake Huron was estimated to be 160 t using the mean inventory, while only 24 t if the median was used. This was due to the large effect of accumulation of PCBs at site H001. In order to ensure accuracy of lake-wide load estimates, a method using the geostatistical analysis tool of ArcGIS 10.3 was developed (Redlands, CA). Each lake was divided by *N* cells of equal area ( $N = 90,628$  for Lake Superior,  $N = 37,771$  for Lake Michigan,  $N = 38,339$  for Lake Huron,  $N = 59,744$  for Lake Erie, and  $N = 78,604$  for Lake Ontario), inventories of chemicals (ng/cm<sup>2</sup>) in each cell were calculated from inverse distance weight (IDW) interpolation of the spatial distribution of the inventory, based on inventories (Eq. (2)) for all coring sites in the lake. Loads within each cell were the product of the inventory given by GIS and the cell area (Eq. (5)). The total load in each lake is the sum of the loads in all the cells (Eq. (6)).

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

$$\text{Total load (tonnes)} = \sum \text{Cell loads} \quad (6)$$

Descriptive statistics of concentrations, net depositional fluxes and inventories were obtained by use of Microsoft Excel (2010). In calculations of net fluxes and inventories, the “not detected (ND)” data points was treated as zero, and the “less than detection limit (<DL)” data remained as original values. This treatment avoided the possible augmentation of the lake-wide loads when multiplied by the large lake surface areas in Eqs. (3) and (4). For regressions and Pearson correlations, ND and <DL data points were replaced with half of the detection limits, then the data were log transformed and subjected to Excel with StatPlus (version 5 for Mac OS).

## Results and discussion

Mean, median and maximum concentrations of the five chemical groups in the Ponar grab samples of sediments are summarized in Table 2. Concentrations at individual sampling sites are compared in

**Table 2**  
Concentrations in ponar grab sediments (ng/g dw).

	t-PCBs	$\sum_7$ PCDDs	$\sum_{10}$ PCDFs	$\sum_{12}$ PCNs	$\sum_7$ PCDEs
Mean ± Standard Error					
Superior	1.40 ± 0.3	0.12 ± 0.02	0.03 ± 0.01	0.04 ± 0.01	ND
Michigan	32.0 ± 8.6	0.42 ± 0.10	0.10 ± 0.02	0.48 ± 0.12	0.02 ± 0.0
Huron	10.3 ± 4.4	0.40 ± 0.12	0.10 ± 0.05	0.20 ± 0.06	0.02 ± 0.01
Erie	64.3 ± 7.7	1.78 ± 0.30	0.15 ± 0.02	5.16 ± 1.56	0.15 ± 0.01
Ontario	61.2 ± 10	1.10 ± 0.22	2.44 ± 0.85	4.67 ± 0.83	1.30 ± 0.24
All Lakes	33.5 ± 3.5	0.78 ± 0.09	0.53 ± 0.16	2.11 ± 0.38	0.29 ± 0.07
Median/maximum					
Superior	0.99/5.76	0.09/0.43	0.01/0.28	0.03/0.12	ND
Michigan	11.2/183	0.21/2.56	0.08/0.39	0.23/2.45	0.01/0.07
Huron	2.5/246	0.10/6.36	0.02/2.24	0.07/3.27	0.00/0.67
Erie	59.1/146	1.27/8.11	0.12/0.43	1.3/39.0	0.12/0.46
Ontario	47.9/214	0.88/6.54	1.1/26.4	3.37/21.1	0.87/5.54
All Lakes	8.4/246	0.27/8.11	0.05/26.4	0.19/39.0	0.01/5.54

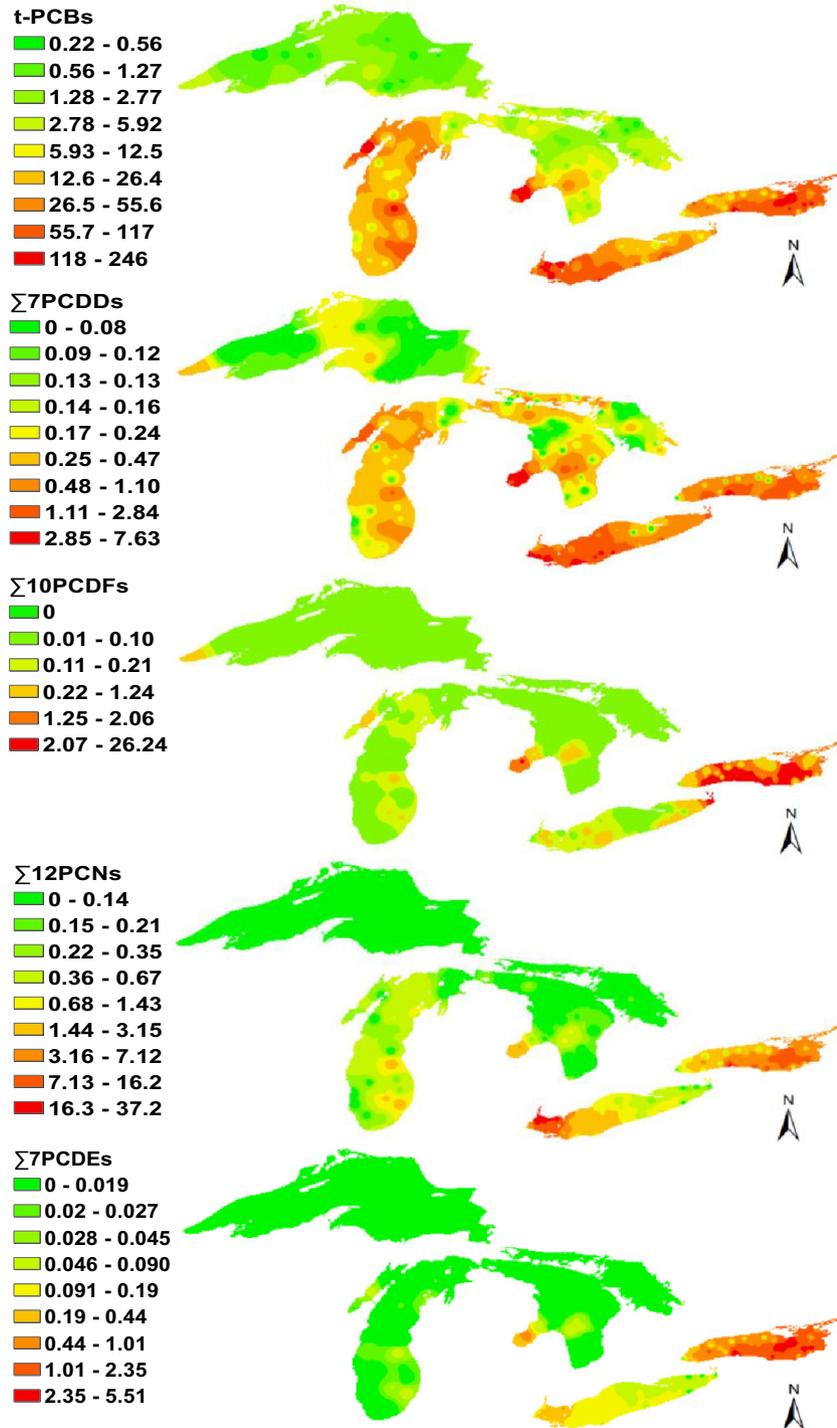
**Table 3**

Total loads (tonnes) of targeted chemical groups in sediment estimated using Eqs. (5) and (6).

	t-PCBs	$\Sigma_7$ PCDDs	$\Sigma_{10}$ PCDFs	$\Sigma_{12}$ PCNs	$\Sigma_7$ PCDEs
Superior	4.4	0.5	0.1	0.1	0
Michigan	123.8	1.3	0.2	1.9	0.1
Huron	105.3	3.8	1.5	1.8	0.3
Erie	143.4	7.8	1.2	10.0	0.5
Ontario	133.8	1.9	2.3	6.9	2.0
All Lakes	510.7	15.3	5.3	20.7	2.9

ESM Fig. S1. Net fluxes and inventories for all the coring sites are summarized in ESM Table S4. Lake-wide total loads of the chemical groups, which were estimated by the ArcGIS method (Eqs. (5) and (6)) are summarized in Table 3. To compare among methods, loads estimated by use of the mean or median (Eq. (4)) are provided in ESM Table S5.

In the discussion of individual chemical groups, spatial distribution patterns across and within the lakes are examined (Fig. 2), regional and within-lake contamination hotspots identified (Tables 4 and ESM Table S6), and dependence of organic carbon normalized concentrations and inventories in cores on the latitude and longitude of the



**Fig. 2.** Spatial distribution of the concentrations of polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), naphthalenes (PCNs), and diphenyl ethers (PCDEs) in Ponar grab samples.

**Table 4**

Top ten most contaminated sites among the five Great Lakes.

	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
By concentrations in Ponar grab sediment samples										
t-PCBs	H001	ON22	ON12	M050	ON27	ON33	ON28	M061	ER61	ER02
$\sum_7$ PCDDs	ER04	ON12	H001	ER06	ER58	ER59	ER98	ER20	ER28	ER29
$\sum_{10}$ PCDFs	ON12	ON08	ON28	ON33	ON26	ON24	ON15	ON27	ON19	ON17
$\sum_{12}$ PCNs	ER60	ER61	ER21	ON12	ER92	ER91	ON33	ER22	ON28	ON27
$\sum_7$ PCDEs	ON12	ON22	ON33	ON28	ON27	ON24	ON26	ON30	ON19	ON15
By inventories of the cores										
t-PCBs	ON06	H001	ER92	M009	M050	ER37	ER09	ON36	ON25	ON30
$\sum_7$ PCDDs	H001	ER09	ER73	ER37	ER92	ER15	ON06	ON30	M050	ON17
$\sum_{10}$ PCDF	ON06	H001	ON30	ON36	ON02	ON13	ON17	ER92	ON25	ER73
$\sum_{12}$ PCNs	ON06	ER92	ON30	H001	ER73	ON25	ON17	ER37	ON13	ON36
$\sum_7$ PCDEs	ON06	ON30	ON25	ON17	ON13	ER92	ON36	H001	ON02	ER73

sampling sites and the urban impact investigated (Table 5). Temporal trends of net depositional fluxes at two selected coring sites (one near potential sources and the other in open water location away from shore, when possible) in each lake are presented in Fig. 3. Half-times of post-peak decline in net depositional flux were estimated by use of pseudo first-order kinetics for these selected sites (Table 6). Finally, correlations among chemical groups are presented in ESM Table S7.

#### Polychlorinated biphenyls

Total concentrations of PCBs (t-PCBs) were estimated to be twice the sum of concentrations of 39 individual congeners ( $\sum_{39}$ PCBs), which are those included in the AccuStandard Mix-1 (catalog numbers C-CS-01). This approach of estimating t-PCBs was developed by Li et al. (2009), based on the concentration ratio of  $\sum_{39}$ PCBs to total PCBs in Aroclors A1016, A1242, A1248, A1254, and A1260 (USEPA, 2007) weighted by the reported percentages of individual Aroclors in total production of PCBs in the U.S. during 1957–1977 (Brown, 1994). Total accumulation (load) of t-PCBs in sediments of all five Great Lakes was estimated to be 510 metric tonnes (Table 3). If the top five hotspots ON06, H001, ER92, M009, M050 (Table 4, lower part), where t-PCB inventories

exceed 300 ng/cm<sup>2</sup>, were excluded, the total load of PCBs in all five lakes was estimated to be 270 metric tonnes. This represents a 10% reduction from the estimate of 304 metric tonnes in the early 2000s (Li et al., 2009), and about 40% reduction from the sedimentary load of 393–441 t estimated in the 1980s (Eisenreich, 1987).

Based on results of one-way ANOVA on t-PCB concentrations in Ponar grabs, decreasing order of PCB contamination is: Lake Erie  $\approx$  Lake Ontario > Lake Michigan > Lake Huron > Lake Superior ( $p < 0.05$ ). Lake-wide loads are in the same rank order (Table 3). In Lake Erie, median concentration of t-PCBs in Ponar grabs was 59 ng/g dw (range 2.4–146 ng/g dw), which is less than the previously reported 96.5 ng/g dw (C.H. Marvin et al., 2002; C. Marvin et al., 2002). The western basin of Lake Erie is the region-wide “hot” area of pollution by PCBs (Fig. 2), where t-PCBs exceeded 100 ng/g dw in Ponar grabs at most sites. The only core taken from the western basin (ER92) had an inventory of >1200 ng/cm<sup>2</sup>, which was more than twice those at other coring sites in the lake (ESM Table S4). These observations support the conclusion that the Detroit River is a primary vector of PCBs into western Lake Erie (Lu et al., 2015; Marvin et al., 2004; Painter et al., 2001). In cores from sites ER09 and ER15, PCB concentrations were greatest in bottom segments deposited in 1981 and 1982, respectively, which suggest

**Table 5**

Multi-variate regression equations.

	N	Intercept	a	b	R <sup>2</sup>	F	p-level
Ln concentration (ng/g OC, Ponar grabs) = intercept + a × latitude + b × longitude							
t-PCBs	185	33.07 ± 2.28	−0.515 ± 0.049	0.045 ± 0.027	0.474	81.88	0.00E + 00
$\sum_7$ PCDDs	186	14.78 ± 2.54	−0.213 ± 0.055	0.028 ± 0.03	0.118	12.21	1.06E-05
$\sum_{10}$ PCDFs	186	18.69 ± 2.63	−0.119 ± 0.057	0.139 ± 0.031	0.188	21.12	5.60E-09
$\sum_{12}$ PCNs	185	32.78 ± 2.32	−0.360 ± 0.050	0.160 ± 0.03	0.468	80.08	0.00E + 00
$\sum_7$ PCDEs	185	34.24 ± 2.67	−0.251 ± 0.058	0.264 ± 0.032	0.464	78.84	0.00E + 00
Ln Inventory (ng/cm <sup>2</sup> , cores) = intercept + a × latitude + b × longitude							
t-PCBs	40	46.02 ± 5.17	−0.803 ± 0.126	0.071 ± 0.06	0.654	34.93	3.01E-09
$\sum_7$ PCDDs	37	28.72 ± 6.44	−0.250 ± 0.149	0.196 ± 0.082	0.354	9.31	5.95E-04
$\sum_{10}$ PCDF	37	38.73 ± 7.66	−0.382 ± 0.177	0.262 ± 0.097	0.435	13.10	6.04E-05
$\sum_{12}$ PCNs	39	48.34 ± 5.03	−0.754 ± 0.122	0.167 ± 0.058	0.710	45.28	1.14E-10
$\sum_7$ PCDEs	39	61.61 ± 6.21	−0.723 ± 0.151	0.374 ± 0.072	0.742	53.30	1.27E-11
Ln Concentration (ng/g OC, Ponar grabs) = intercept + a × UDF <sup>a</sup>							
t-PCBs	185	0.31 ± 0.56	0.014 ± 0.001	–	0.412	128.21	0.00E + 00
$\sum_7$ PCDDs	186	0.28 ± 0.6	0.006 ± 0.001	–	0.108	22.28	4.66E-06
$\sum_{10}$ PCDFs	186	−1.67 ± 0.63	0.008 ± 0.001	–	0.153	33.25	3.37E-08
$\sum_{12}$ PCNs	185	−2.79 ± 0.57	0.010 ± 0.000	–	0.403	123.65	0.00E + 00
$\sum_7$ PCDEs	185	−5.62 ± 0.68	0.015 ± 0.001	–	0.361	103.47	0.00E + 00
Ln Inventory (ng/cm <sup>2</sup> , cores) = intercept + a × UDF <sup>a</sup>							
t-PCBs	40	−5.94 ± 1.3	0.023 ± 0.003	–	0.627	63.98	1.14E-09
$\sum_7$ PCDDs	37	−4.68 ± 1.52	0.013 ± 0.003	–	0.289	14.23	6.00E-04
$\sum_{10}$ PCDFs	37	−8.89 ± 1.79	0.019 ± 0.004	–	0.397	23.02	2.95E-05
$\sum_{12}$ PCNs	39	−10.79 ± 1.22	0.026 ± 0.003	–	0.707	91.91	1.09E-11
$\sum_7$ PCDEs	39	−16.77 ± 1.68	0.033 ± 0.004	–	0.678	79.99	6.91E-11

<sup>a</sup> UDF = Unban Distance Factor. The derivation of UDF is provided in Text S3 of the Electronic Supplementary Materials.

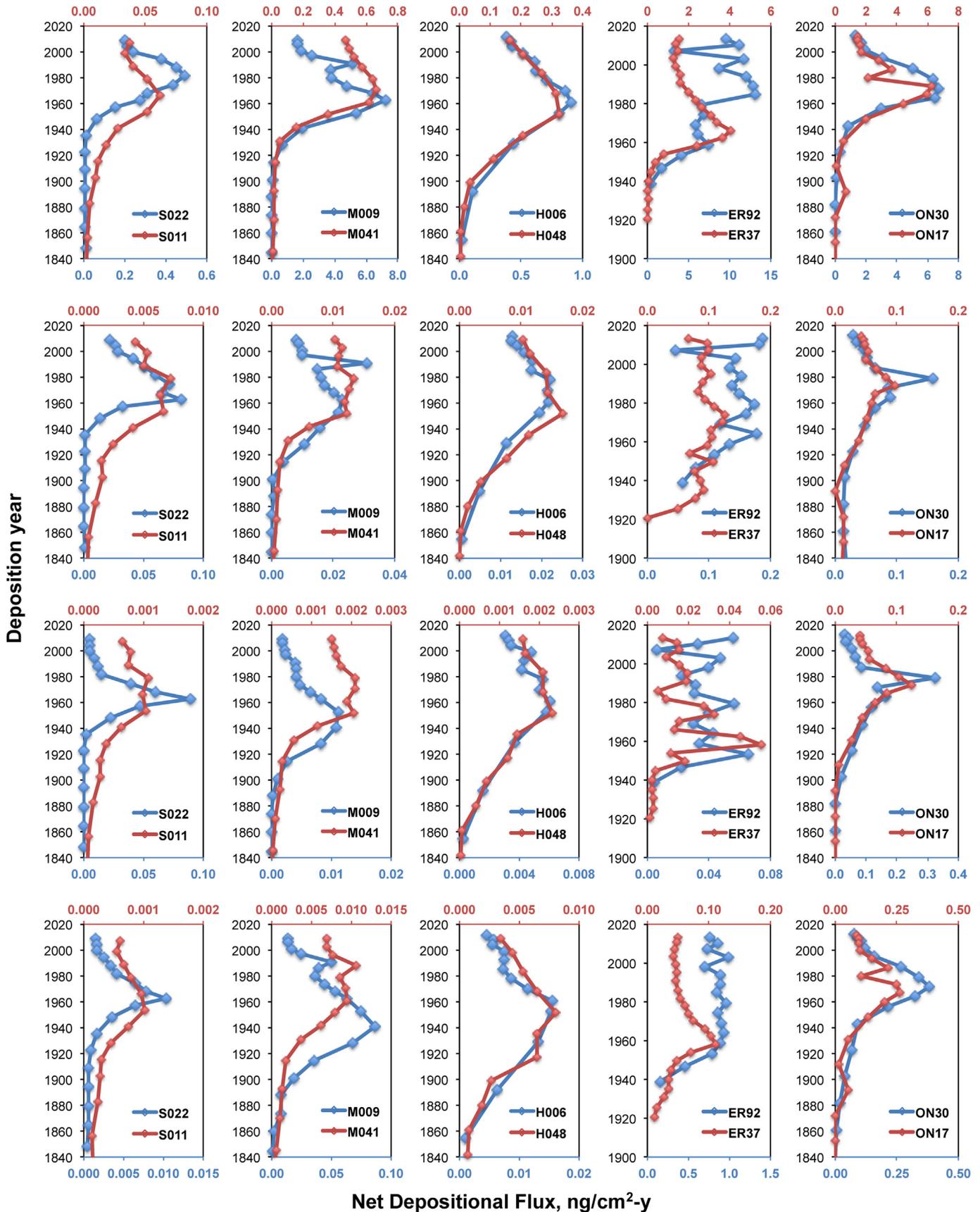


Fig. 3. Temporal trends of net depositional fluxes at selected coring sites. From top to bottom rows are t-PCBs, Σ<sub>7</sub>PCDDs, Σ<sub>10</sub>PCDFs, and Σ<sub>12</sub>PCNs. From left to right columns are for Lakes Superior, Michigan, Huron, Erie, and Ontario.

**Table 6**  
Estimated half-time ( $t_{1/2}$ , y) of depositional flux declining since peaking at selected coring sites.

	S022	S011	M009	M041	H006	H048	ER15	ER37	ON30	ON17
t-PCBs	19	48	21	72	39	57	22	30	16	22
$\sum_7$ PCDDs	18	45	33	234	58	85	422	95	16	35
$\sum_{10}$ PCDFs	15	45	21	118	55	100	20	33	11	23
$\sum_{12}$ PCNs	17	58	22	99	34	48	34	55	17	29

that more PCBs were buried below 35 cm, which was the length of the core. Thus, greater inventories than reported in ESM Table S4 are likely to exist at these sites.

Another hotspot of contamination with PCBs was ON06, which is near the mouth of the Niagara River in Lake Ontario. Greatest concentrations of t-PCB measured in this work were observed in deeper segments (34–36 cm deep) of this core at 856 ng/g dw, which is only one fifth of >4000 ng/g previously reported in the lower portions of a core collected at this site in 1995 (Swart et al., 1996). However, the Ponar grab at ON06 had t-PCBs of only 27 ng/g dw, which suggested the lack of significant recent input and the quick removal from this site by movement of water. A cluster of chlorine chemical industries was located near the Niagara River and is likely to be the source of PCBs (Shen et al., 2008). Site ON12, downstream from ON06 near the south shore of the Mississauga Basin, has accumulated PCBs to almost 200 ng/g dw in the Ponar grab sample. The mean concentration of t-PCBs in Ponar grabs of Lake Ontario is 62 ng/g dw (median 44 ng/g dw, Table 2), which is less than the mean of 100 ng/g dw measured in samples collected in the late 1990s (C.H. Marvin et al., 2002; C. Marvin et al., 2002). In general, the Rochester Basin in eastern Lake Ontario is relatively more contaminated than the other two main basins, Mississauga and Niagara Basins, to the west.

Green Bay in Lake Michigan is known to be contaminated with PCBs due to industrial pollution of the lower Fox River and other tributaries (ATSDR, 2006). As expected, site M050, located near the Sturgeon Bay Ship Canal in Green Bay, exhibited the greatest concentrations of PCBs in Ponar grabs and second greatest concentrations in core inventory among sites in Lake Michigan. In the main lake, an obvious hotspot area is on the southeast side, including sites M009, M011, and M061. This area receives inputs from the heavily polluted Grand, Kalamazoo, St. Joseph, and Muskegon Rivers. An unexpected hotspot was M093 near the Sleeping Bear Dunes, which is not near populated areas, heavy industry, or other major sources (Sun et al., 2007). Relatively low concentrations of chemicals were found at sites near Chicago, Milwaukee, and the Indiana Harbor (M008, M010, M020, and M030). These sites are in a non-depositional zone of Lake Michigan, and sediments had lesser contents of organic carbon (<2.5 mg/g dw). Pollutants entering the lake from these source areas tend to be carried by the counterclockwise gyre to the depositional area on the southeast side of the lake.

Over the entire region, the “hottest” spot of PCB contamination was H001 in Saginaw Bay, Lake Huron. Concentrations in sediments from deeper segments (33–35 cm deep) of core H001 were as high as 480 ng/g dw, which suggested historical input from the Saginaw River. Except for H001, no sites in Lake Huron were in the top-ten greatest for the region (Table 4). In the main lake, sediments from sites H027, H032 and H103 had t-PCBs >20 ng/g dw. Given its downstream location, this area is influenced by Saginaw Bay.

In Lake Superior, concentrations of PCBs were significantly lower than those in the other Great Lakes (Tables 2 and 3). Site S022 near the cities of Duluth, MN and Superior, WI, had greater concentrations of t-PCBs in both Ponar grab and the core compared with other sites in the lake. S022 was followed by S106 located east of the Keweenaw Peninsula, MI, and by S011 near Thunder Bay and Marathon Bay, ON. The greatest concentration of t-PCBs in the 0–0.5 cm of sediment (surface segments of the cores) was 16 ng/g dw, which is small compared

with the corresponding value of 220 ng/g dw measured in the 1980s (Eisenreich, 1987). The range of concentrations of t-PCBs measured in the Ponar grabs of this work for Lake Superior was 0.21 to 5.8 ng/g dw, which is less than the range of 0.38 to 15 ng/g dw reported ten years earlier (Gewurtz et al., 2008).

Results of multivariate regressions against latitude and longitude of the sampling locations revealed a general trend of exponential decreases in concentrations and inventories of t-PCBs from south to north and from east to west in the region (Table 5). Comparatively, the dependence on latitude appears to be stronger for t-PCBs than for other classes of chemicals, with slopes being  $-0.515$  and  $-0.803$  for concentration in the Ponar grabs and inventory of the cores, respectively. The inventory often performs better than surface concentration in such regressions, since it is a measure of longer-term accumulations (Li et al., 2009). As shown by the  $R^2$ , about 82% of the variation in inventory of t-PCBs is accounted for by latitude and longitude together; and, as can be seen by comparing a and b values, latitude outweighs longitude in describing the spatial pattern (Table 5). This was expected given that the general south-to-north direction of long-range atmosphere transport in the northern hemisphere, and that the population density in the region declines in the same general direction. To assess effects of urban areas, an Urban Distance Factor (UDF) was previously developed and used as an independent variable in similar regressions (Cao et al., 2017; Li et al., 2006). In this work, regressions against UDF as a single independent variable were comparable in statistical significance with those using latitude and longitude (Table 5). These observations indicate that spatial distributions of PCBs in sediments of the Great Lakes are influenced by both the locations of population centers and the long-range atmospheric transport over the region.

Net depositional fluxes of target, legacy pollutants have been declining from their respective peak values in almost all cores (Fig. 3). The half-time for decreases in concentrations of t-PCBs in sediments was about 20 years at sites near potential source tributaries, such as S022, M009, and others (Table 6). At relatively central locations such as M041 and H048, the half-time tended to be longer, reflecting slower response to the reduction in input at relatively more remote locations. In Lake Ontario, the half-time for t-PCBs at all coring sites including the center locations ranged from 8 to 22 y, shorter than the other lakes. In Lake Erie, the declining trend is discernible in most cores, despite the scatter of data points due to sediment mixing (Fig. 3).

#### Polychlorinated dibenzo-p-dioxins and dibenzofurans

2,3,7,8-Tetrachloro-p-dioxin Equivalents (TEQ) based on measured concentrations of PCDD/Fs were calculated using U.S. EPA recommended Toxicity Equivalency Factors (TEF) (USEPA, 2010). The median concentration of  $\sum_{17}$ PCDD/Fs (sum of all 17 congeners) in the Ponar grab sediment of individual lakes ranged from 0.10 ng/g dw (1.1 pg/g TEQ) for Lake Superior to 2.0 ng/g dw (98 pg/g TEQ) for Lake Ontario (Table 2). The mean concentration of  $\sum_{17}$ PCDD/Fs in Lake Ontario was 3.2 ng/g dw, which is similar to the previously reported 2.8 ng/g dw (C.H. Marvin et al., 2002; C. Marvin et al., 2002). Among Ponar grabs taken in this study, the highest concentration of  $\sum_{17}$ PCDD/Fs was 33 ng/g dw (261 pg/g TEQ), found at site ON12. Based on data

from sediment cores, total loads of  $\sum_{17}$ PCDD/Fs in sediments of all five Great Lakes were estimated to be about 20 metric tonnes (Table 3).

Patterns of spatial distributions of concentrations of  $\Sigma_7$ PCDDs and  $\Sigma_{10}$ PCDFs differed, particularly between Lakes Erie and Ontario. Lake Erie is more contaminated by PCDDs than is Lake Ontario, while the opposite is true for PCDFs. Most hotspots of contamination with PCDDs are in Lake Erie (besides the “super hot” spot of H001 near the mouth of the Saginaw River in Lake Huron), while all hotspots for PCDFs were observed in Lake Ontario (Table 4). In sediments collected by Ponar grabs, greater concentrations of PCDFs in Lake Ontario resulted in concentrations of TEQ that were 4.3-fold greater than those in Lake Erie. These results are consistent with those reported previously (C.H. Marvin et al., 2002; C. Marvin et al., 2002; Shen et al., 2008). These observations suggest that significant discharges of PCDFs exist in the area from eastern Lake Erie to western Lake Ontario. In sediments from Pettit Flume, a storm sewer in North Tonawanda, NY, concentrations of  $\Sigma$ PCDF as great as 1810 ng/g dw were observed (Norstrom, 2006). The more contaminated sediment in the Pettit Flume could have migrated into the Niagara River and Lake Ontario.

Site H001 in Lake Huron is no doubt the most contaminated site by PCDD/Fs in the Upper Great Lakes. At this site, inventories were 79 ng/cm<sup>2</sup> for  $\Sigma_7$ PCDDs, the greatest among all cores taken during this study, and 34 ng/cm<sup>2</sup> for  $\Sigma_{10}$ PCDFs, the second greatest. The Saginaw Bay watershed has been known to be contaminated by PCDD/Fs, as some of its tributaries flow through a chemical manufacturing site where numerous organochlorine chemicals were made and PCDD/Fs were produced as by-products (Norstrom, 2006). In the 1990s, 5000 ng/g dw of  $\Sigma$ PCDDs and 4100 ng/g dw of  $\Sigma$ PCDFs were reported in sediments of the Saginaw River at Bay City, where the river enters Saginaw Bay (Gale et al., 1997). A study conducted in the mid 2000s found 55 ng/g dw of total PCDD/Fs at the river mouth (Kannan et al., 2008). In this work, concentrations of  $\Sigma_7$ PCDDs and  $\Sigma_{10}$ PCDFs in sediments collected by Ponar grab from H001 were 6.4 ng/g dw and 2.2 ng/g dw, respectively. Closer to the mouth of the Saginaw River at site H110, concentrations of  $\Sigma_7$ PCDDs and  $\Sigma_{10}$ PCDFs were 2.7 ng/g dw and 1.5 ng/g dw, respectively (Fig. S1-b). These results are in good alignment with the 6.1 ng/g dw of  $\Sigma$ PCDD/Fs in sediment at this site in 2002 (Shen et al., 2009). After normalization to organic carbon content of sediments, concentrations at H001 and H110 were effectively the same.

In Lakes Michigan and Superior, patterns of spatial distributions of  $\Sigma_7$ PCDDs and  $\Sigma_{10}$ PCDFs were similar to those of t-PCBs (ESM Fig. S1-a). In Lake Superior, sites S022 and S106 were the most contaminated, and site M050 in Green Bay exhibited the greatest concentrations in Lake Michigan. In the watersheds of these lakes, historical releases of PCDD/Fs from wood treatment, pulp and paper mills, mining operations, and chlorine-based chemical manufacturing have been reported (Dahmer et al., 2015; Shen et al., 2009).

Similar to PCBs, concentrations and inventories of  $\Sigma_7$ PCDDs and  $\Sigma_{10}$ PCDFs decreased exponentially as a function of increasing latitude and decreasing longitude ( $p < 0.05$ , Table 5). However, variations with latitude were less for PCDDs and PCDFs, as can be seen from the less steep slopes (the “a” values), and the regressions are weaker compared with those of other classes of target chemicals based on  $R^2$  (Table 5). At most locations, PCDD/Fs appeared in sediment slightly earlier than did PCBs, accelerated in the 1940s, and peaked between 1960 and 1980. However, decreases in net deposition after their peaks were inconsistent among sites. At most sites, decreases were clearly observed. However, decreases were not observed at sites S008, S012, M008 and ER09, and the declining trends at M024, M047, ER92, ON02, and ON06 appear to have changed in recent years. Overall, relative to PCBs, PCDD/Fs are decreasing more slowly. Given that the releases from known industrial sources have ceased or been largely reduced for decades, fugitive emissions from various combustion sources may have been dominating the environmental presence of PCDD/Fs in most parts of the Great Lakes region.

### Polychlorinated naphthalenes

From core inventories, a total load of about 20 t of PCNs in sediments among the five lakes was estimated (Table 3). Lakes Erie and Ontario were loaded with a total of 17 t. Among Ponar grab samples, concentrations of  $\Sigma_{12}$ PCNs >10 ng/g dw were observed in western Lake Erie near the input of the Detroit River (ER60, ER61, ER21, ER92, ER91, and ER20). The St. Clair River, Lake St Clair, and the Detroit River form the connecting waterway between Lake Huron and Lake Erie. Since concentrations of PCNs in the southern end of Lake Huron (H006, H102, HSOX) are generally low (ESM Fig. S1-b), it is clear that the primary sources of PCNs reside within the heavily industrialized and populated area along the connecting waterway, most likely the Detroit River. Concentrations of PCNs as great as 61,000 ng/g dw were measured in sediments in this area (Furlong et al., 1988).

Other sites where concentrations of  $\Sigma_{12}$ PCNs >10 ng/g dw in sediments collected by Ponar grabs were all in Lake Ontario, with the maximum of 21 ng/g dw at ON12. To compare, a range from 21 to 38 ng/g dw was reported for the sum of ~35 PCN congeners with three to eight chlorines in the sediment collected across Lake Ontario in 1998 (Helm et al., 2008). Core ON06 had the greatest inventory (185 ng/cm<sup>2</sup>) among all coring sites, followed by core ER92 (ESM Table S4). Other cores in Lake Ontario had  $\Sigma_{12}$ PCNs inventories ranging from 10 to 24 ng/cm<sup>2</sup>, which indicated relatively even accumulation of PCNs in off-shore depositional areas across the lake.

As expected, greater concentrations of  $\Sigma_{12}$ PCNs were found in sediments collected by both Ponar grab and cores at sites H001 (3.3 ng/g dw) and H110 (2.2 ng/g dw) than other sites in Lake Huron (ESM Fig. S1-b). In Lake Michigan,  $\Sigma_{12}$ PCNs ranged from 0.01 to 2.5 ng/g dw in Ponar grabs, with southeastern sites M061, M009, and M011 being more contaminated. Previously, 0.3 to 0.8 ng/g dw were reported from a site in Lake Michigan (Kannan et al., 2001). In Lake Superior, site S022 and S106 were the most contaminated, where  $\Sigma_{12}$ PCNs was about 0.1 ng/g dw. Temporal trends in concentrations of cores of sediments were similar to those of t-PCBs, with slightly earlier peaking years at most locations. Half-times for decreases in net deposition fluxes were similar to those of PCBs (Table 6).

### Polychlorinated diphenyl ethers

Patterns of spatial distributions of  $\Sigma_7$ PCDEs (Fig. 2) clearly indicates that Lake Ontario is more contaminated than all other lakes. Median and mean concentrations of  $\Sigma_7$ PCDEs in sediments collected by Ponar grabs from Lake Ontario were 0.87 and 1.30 ng/g dw, respectively, which are similar to those of  $\Sigma_7$ PCDDs in Lake Ontario, and 6 and 9 times greater than concentrations of  $\Sigma_7$ PCDE in sediments from Lake Erie. In cores, sediments have accumulated 6 to 22 ng/cm<sup>2</sup> of  $\Sigma_7$ PCDEs, resulting in a lake-wide load of approximately 2 t in Lake Ontario. From the upper Great Lakes, PCDEs in >90% of sediments in Ponar grabs were either not detected or less than the MDL. Among the five lakes, the total load was estimated to be 3 t, which is less than those of other classes of target chemicals (Table 3).

### Conclusions

Correlations between t-PCBs,  $\Sigma_7$ PCDDs,  $\Sigma_{10}$ PCDFs,  $\Sigma_{12}$ PCNs and  $\Sigma_7$ PCDEs are statistically significant ( $p < 0.05$ , ESM Table S7), which is attributable to the similar time horizons of their appearance, peaking, and rate of decline in most cases. With regard to spatial distribution patterns, proximity to point discharge sources is the most determinative factor within a lake as well as among lakes. All hotspots are near known or potential local sources which are mostly the discharge points of chemical industries and their wastewaters, often through tributaries. However, at far-from-shore open water locations, the input from air deposition may outweigh that from local discharge, and this is reflected in the latitudinal and longitudinal dependence of pollutant concentrations

and inventories. Other factors influencing the spatial distributions within a lake are the directions of water flow and circulation as well as the lateral movement of sediment. Given that finer sediment particles tend to sorb more hydrophobic compounds and that they also transport over longer distance during sediment focusing, it is not surprising to see that depositional zones accumulate these chemicals much more than the non-depositional zones.

Vertical profiles of concentrations measured in sediment cores reflect the combined impacts of input history, post-depositional diffusive and advective transport within the sediment, re-entering water due to sediment resuspension, and degradation over time. In this work, the temporal trends of net depositional fluxes reflect mostly the input history, but could have been altered to some degree by diffusive transport causing the widening of the peaks. Continuous declines from their peaks are observed for all the target chemical groups. The decreases are generally faster at locations closer to input sources than in relatively remote locations in the lakes, supporting the above statement on the dominant impact of local sources. Decreases in concentrations of PCDDs and PCDFs are slower than other chemical groups, and inconsistent or uncertain at a number of coring locations across the region. The presence of currently active sources of PCDDs and PCDFs are implied by these findings.

For legacy pollutants that were phased out decades ago, contaminated sediments could now act as a secondary source of emissions to the overlying water. This is the case with PCBs in Lake Michigan (McCarty et al., 2004), and likely in other natural waters as well. Future research is needed to assess the strength and impact that sediment exerts on the water and biota, and the associated risks to human. The data set obtained from this work will be examined further on homolog and congener bases and by the use of various environmental source identification and fate assessment models, in order to gain scientific insights that are generalizable beyond the Great Lakes region.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jglr.2018.02.002>.

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## Supplementary Materials

### **Legacy Polychlorinated Organic Pollutants in the Sediment of the Great Lakes**

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#### Table of Content

(in the order of citing in the main text)

Table S1	Sediment samples collected from the Great Lakes
Table S2-a	Location and water depth (m) of the sampling sites in Lakes Superior, Michigan and Huron
Table S2-b	Location and water depth (m) of the sampling sites in Lakes Erie and Ontario
Text S1	Sampling Method
Text S2	Method of Chemical Analyses
Table S3	The mass-to-charge ratios ( $m/z$ ) and optimized collision energy (CE, in volts) in EI-QQQMS or $m/z$ in ECNI for target analytes of this work
Figure S1	Comparison in concentrations (ng/g dw) in Ponar grab sediment samples among sampling sites
Table S4	Data summary for sediment cores
Table S5	Estimated total load (tonnes) of targeted chemical groups in sediment using equation [4]
Table S6	Top three most contaminated sites in individual lakes
Table S7	Pearson linear correlation matrix among analyte groups
Text S3	Urban Distance Factor (UDF)

Table S1. Sediment samples collected from the Great Lakes

<b>Lakes</b>	<b>Sampling Date</b>	<b>Cores</b>	<b>Core Segments</b>	<b>Ponar Grabs</b>	<b>Sum</b>
Michigan	Sept. 17-20, 2010	8	159	28	187
Michigan	May 23-29, 2011	2	37	4	41
Superior	May 23-29, 2011	9	226	24	250
Huron	Sept. 15-18, 2012	9	224	27	251
Huron <sup>a</sup>	Oct. 4-7, 2012	0	0	32	32
Ontario	July 23-25, 2013	7	173	37	210
Erie	May 27-30, 2014	5	120	46	166
All	-	40	939	198	1137

- a. This trip was for the North Channel (NC) and Georgian Bay (GB), located north of the main Lake Huron.

Table S2-a. Location and water depth (m) of the sampling sites in Lakes Michigan (M), Superior (S), and Huron (H) including Georgian Bay (GB), the North Channel (NC), Thunder Bay (TB), and special sites (SOTX's).<sup>a</sup>

Site	Latitude	Longitude	Depth	Site	Latitude	Longitude	Depth	Site	Latitude	Longitude	Depth	Site	Latitude	Longitude	Depth
<b>M008</b>	<b>41.9842</b>	<b>- 87.0142</b>	<b>64</b>	M125	45.7228	- 85.3314	16	<b>H012</b>	<b>43.9007</b>	<b>- 82.1130</b>	<b>99</b>	GB12	44.9202	- 80.8748	91
<b>M009</b>	<b>42.3850</b>	<b>- 86.5915</b>	<b>60</b>	<b>S001</b>	<b>46.9930</b>	<b>- 85.1612</b>	<b>98</b>	H027	44.0999	- 82.5025	65	GB17	45.2449	- 80.8742	80
M010	42.0662	- 87.3792	50	<b>S002</b>	<b>47.3603</b>	<b>- 85.6208</b>	<b>158</b>	<b>H032</b>	<b>44.3542</b>	<b>- 82.3596</b>	<b>94</b>	GB24	45.7457	- 80.8394	31
<b>M011</b>	<b>42.5283</b>	<b>- 86.9220</b>	<b>160</b>	<b>S008</b>	<b>47.6058</b>	<b>- 86.8177</b>	<b>309</b>	<b>H037</b>	<b>44.7619</b>	<b>- 82.7836</b>	<b>76</b>	GB29	45.5836	- 81.0830	44
<b>M018</b>	<b>42.7338</b>	<b>- 86.9995</b>	<b>161</b>	<b>S011</b>	<b>48.3438</b>	<b>- 87.8250</b>	<b>236</b>	<b>H038</b>	<b>44.7507</b>	<b>- 82.2024</b>	<b>166</b>	GB35	45.5257	- 81.6705	37
M019	42.7335	- 86.5833	90	<b>S012</b>	<b>47.8553</b>	<b>- 88.0418</b>	<b>245</b>	<b>H048</b>	<b>45.2614</b>	<b>- 82.5912</b>	<b>183</b>	GB36	45.7082	- 81.6201	54
M020	42.3665	- 87.6672	45	<b>S016</b>	<b>47.6212</b>	<b>- 89.4633</b>	<b>185</b>	H054	45.6338	- 83.4028	142	GB39	45.8729	- 81.2584	27
<b>M024</b>	<b>43.4830</b>	<b>- 87.4882</b>	<b>146</b>	<b>S019</b>	<b>47.3703</b>	<b>- 90.8535</b>	<b>193</b>	<b>H061</b>	<b>45.7498</b>	<b>- 83.9164</b>	<b>122</b>	GB42	45.9125	- 81.5954	26
M028 <sup>b</sup>	43.8003	- 86.7998	133	<b>S022</b>	<b>46.8002</b>	<b>- 91.7508</b>	<b>56</b>	<b>H095</b>	<b>44.3328</b>	<b>- 82.8326</b>	<b>70</b>	NC68	46.0413	- 83.8536	16
<b>M028<sup>b</sup></b>	<b>43.7998</b>	<b>- 86.7997</b>	<b>133</b>	S102	47.6173	- 85.6973	95	H101	43.2690	- 82.3349	31	NC70	46.1365	- 83.6720	22
M030	42.6600	- 87.7382	18	S103	46.9838	- 85.6972	169	H102	43.7059	- 82.4039	53	NC71	46.2335	- 83.7462	36
<b>M032</b>	<b>44.3715</b>	<b>- 86.9333</b>	<b>250</b>	S104	48.0382	- 86.3217	194	H103	44.1449	- 82.2209	99	NC73	46.1869	- 83.3552	19
M041 <sup>b</sup>	44.7367	- 86.7215	265	S105	47.6177	- 86.3217	83	H104	44.3720	- 81.8380	132	NC76	46.0003	- 83.4329	60
<b>M041<sup>b</sup></b>	<b>44.7375</b>	<b>- 86.7221</b>	<b>266</b>	S106	47.1807	- 87.3183	225	H107	44.6154	- 82.5541	66	NC77	45.9704	- 83.1977	80
M044	42.9528	- 87.3155	90	S108	48.0392	- 86.9493	233	H108	44.5574	- 83.0502	55	NC79	46.1230	- 82.8867	26
<b>M047</b>	<b>45.1783</b>	<b>- 86.3745</b>	<b>195</b>	S110	46.7735	- 86.9495	142	H109	44.1502	- 83.0000	35	NC82	45.9369	- 82.7588	28
M048	43.0585	- 86.6630	104	S112	48.0393	- 87.5733	222	H110	43.7723	- 83.8037	7	NC83	46.0000	- 82.5497	31
<b>M050</b>	<b>45.1165</b>	<b>- 87.4165</b>	<b>32</b>	S113	47.6177	- 87.5730	176	H118	44.9168	- 83.1660	46	NC84	46.0917	- 82.5564	36
M061	43.4742	- 86.7847	133	S114	46.9095	- 86.5980	409	H119	45.3977	- 82.8107	135	NC87	46.0611	- 82.1971	41
M083	44.4737	- 86.7060	263	S116	48.0392	- 88.2007	261	H121	45.8189	- 83.4039	45	NC88	46.0553	- 81.9998	37
M088	44.7187	- 87.1740	92	S117	47.6175	- 88.2007	277	H123	45.9365	- 83.9059	30	NC89	45.9165	- 82.1617	39
M093a	44.9622	- 86.0552	97	S118	47.6175	- 88.8420	194	H124	45.8512	- 84.4216	57	TB01	44.8996	- 83.1496	50
M093b	44.7712	- 86.1168	58	S119	47.1955	- 89.5048	202	GB01	44.7178	- 80.8564	93	TB02	44.9387	- 83.2405	31
M093c	44.8562	- 86.2430	126	S120	47.6185	- 90.0712	183	GB03	44.7253	- 80.6170	34	TB03	44.9552	- 83.2770	19
M103	45.0623	- 86.4918	201	S121	47.1955	- 90.0727	150	GB04	44.6457	- 80.1673	59	TB04	44.9997	- 83.3742	10
M113	45.3267	- 87.0090	36	<b>H001</b>	<b>43.9374</b>	<b>- 83.6142</b>	12.7	GB05	44.7969	- 80.2431	60	SOTXD	43.3399	- 82.3335	37
M116	45.4014	- 85.4997	36	H002	44.1249	- 83.3324	18.8	GB06	44.7382	- 80.4360	88	SOTXM	43.3398	- 82.4668	20
M120	45.5288	- 86.1708	136	<b>H006</b>	<b>43.5265</b>	<b>- 82.0185</b>	62	GB09	44.8716	- 79.9675	30	SOTXS	43.3397	- 82.4991	12

a. Bold fonts indicate the sites where both sediment core and Ponar grab samples were collected. b. Ponar grabs of M028 and M041 were sampled in both 2010 and 2011.

Table S2-b. Location and water depth (m) of the sampling sites in Lakes Ontario (ON) and Erie (ER).<sup>a</sup>

Site	Latitude	Longitude	Depth	Site	Latitude	Longitude	Depth	Site	Latitude	Longitude	Depth	Site	Latitude	Longitude	Depth
ON01	43.3039	- 79.7340	25	ON28	43.5638	- 76.7081	208	ER02	41.5091	- 81.7135	8	ER59	41.7269	- 83.1494	8
<b>ON02</b>	<b>43.3713</b>	<b>- 79.3533</b>	<b>101</b>	ON29	43.3952	- 76.8645	73	ER03	42.1357	- 80.1106	8	ER60	41.8922	- 83.1959	9
ON03	43.5829	- 79.4167	52	<b>ON30</b>	<b>43.5429</b>	<b>- 76.9066</b>	<b>220</b>	ER04	41.7019	- 83.4488	10	ER61	41.9466	- 83.0454	9
ON04	43.2478	- 79.4188	NA	ON31	43.7474	- 76.6018	80	ER05	41.8915	- 83.3074	6	ER63	42.4173	- 79.7991	49
ON05	43.5166	- 79.0803	136	ON32	43.4921	- 76.5820	61	ER06	41.4762	- 82.1842	7	<b>ER73</b>	<b>41.9778</b>	<b>- 81.7571</b>	<b>25</b>
<b>ON06</b>	<b>43.3360</b>	<b>- 79.0700</b>	<b>69</b>	ON33	43.5982	- 76.5484	156	ER07	41.9126	- 80.7964	8	ER78	42.1168	- 81.2501	24
ON07	43.6486	- 79.0407	114	ON34	43.8958	- 76.5487	56	<b>ER09</b>	<b>42.5387</b>	<b>- 79.6163</b>	<b>51</b>	ER81	42.3542	- 80.8079	22
ON08	43.3575	- 78.9396	79	ON35	43.9926	- 76.4901	49	ER10	42.6803	- 79.6922	34	ER82	42.4648	- 80.3604	20
ON09	43.5975	- 78.8016	137	<b>ON36</b>	<b>44.0780</b>	<b>- 76.4125</b>	<b>26</b>	<b>ER15</b>	<b>42.5171</b>	<b>- 79.8930</b>	<b>65</b>	ER83	42.8236	- 79.5808	17
ON10	43.4856	- 78.6554	155	ON37	43.5832	- 76.3334	46	ER20	41.7604	- 83.3065	7	ER84	42.7052	- 79.2665	23
ON11	43.7587	- 78.5158	84					ER21	41.9783	- 83.1879	6	ER85	42.8499	- 79.2503	16
ON12	43.4306	- 78.4144	86					ER22	41.8210	- 83.0769	10	ER86	42.8787	- 78.9037	7
<b>ON13</b>	<b>43.5414</b>	<b>- 78.3143</b>	<b>181</b>					ER23	41.5746	- 82.5184	14	ER91	41.8418	- 82.9163	11
ON14	43.8342	- 78.2063	82					ER25	41.8760	- 82.3292	17	<b>ER92</b>	<b>41.9506</b>	<b>- 82.6867</b>	<b>12</b>
ON15	43.5598	- 78.1656	186					ER26	41.6729	- 82.1004	20	ER93	42.6164	- 80.0002	43
ON16	43.7172	- 78.0267	128					ER27	41.6756	- 81.7518	21	ER95	42.0000	- 80.6666	18
<b>ON17</b>	<b>43.5902</b>	<b>- 78.0111</b>	<b>183</b>					ER28	41.8061	- 81.6075	23	ER98	41.5833	- 82.9163	8
ON18	43.6819	- 77.8487	146					ER29	41.8237	- 81.3076	19	ER99	42.4170	- 79.5834	33
ON19	43.3993	- 77.8194	73					ER30	42.4298	- 81.2055	22				
ON20	43.8722	- 77.7130	52					ER31	42.2536	- 81.1075	23				
ON21	43.5414	- 77.6859	173					ER32	42.0817	- 81.0113	23				
ON22	43.6093	- 77.3759	149					ER36	41.9353	- 81.4779	24				
ON23	43.7938	- 77.4648	57					<b>ER37</b>	<b>42.1097</b>	<b>- 81.5748</b>	<b>25</b>				
ON24	43.3621	- 77.5008	121					ER38	42.2820	- 81.6717	23				
<b>ON25</b>	<b>43.4180</b>	<b>- 77.3762</b>	<b>200</b>					ER42	41.9654	- 82.0410	23				
ON26	43.4583	- 77.0697	230					ER43	41.7885	- 81.9461	23				
ON27	43.7312	- 77.0169	88					ER58	41.6847	- 82.9335	10				

a. Bold fonts indicate the sites where both sediment core and Ponar grab samples were collected.

## **Text S1. Sampling Methods**

All samplings were conducted onboard EPA's *R/V Lake Guardian*, with the sampling equipment operated by the ship's crew. Different sampling operations were carried out without overlap in time, to avoid mutual impact that may affect the integrity of the collected samples.

Surface sediment grab samples were collected at all stations. Upon retrieving the Ponar sampler onto the deck, the overlaying water was dumped. The sediment was collected in a bucket (Lake Michigan) or a stainless steel flat tray (other lakes), and homogenized using a drill-driven paint mixer. The well mixed Ponar grab sample was subsampled into amber glass jars. A separate portion of the same sample was placed in a 50 mL Falcon tube.

For sediment core collection, a box or Ekman corer was used during sampling on Lake Michigan in 2010. In later years, a multi-corer MC400 (Ocean Instrument, San Diego, CA) was used, which collects four subcores in each deployment. At each site, the corer was deployed no less than twice, resulting in at least 8 subcores. Five to seven cores at each location were extruded and sectioned using hydraulic extruders. A stainless steel trimmer was designed and used to trim off a 2 mm rind of sediment that touched the tube. This was done for all core segments except the top layers that were often too watery to trim. Core sectioning was performed using stainless scrapers. Core sectioning schemes varied among lakes and sites. All cores from Lake Superior were cut with 0.5 cm until 5 cm, then 1 cm until 15 cm, and 2 cm to 25 cm or 27 cm. All cores from Lake Michigan were sectioned into 1 cm intervals until 10 cm, then 2 cm intervals to a depth of 30 cm or the end. In Lake Huron, cores from sampling sites H038 and H061 were sectioned with the same cutting scheme as cores from Lake Superior (see above); other cores from Lake Huron were cut into 1 cm intervals until 15 cm and then 2 cm intervals to 35 cm or the end of the cores. Cores collected from Lake Erie were sectioned in 2 cm intervals throughout the core length. In Lake Ontario, the core segment thickness was 1 cm for depth 0 – 10 cm followed by 2 cm to the bottoms of cores. Segments from the same depth of cores were combined into a Pyrex mixing bowls, homogenized using stainless steel spoons, and placed into amber glass jars. A separate portion of each sample was placed in a 50 mL Falcon tube.

All the Falcon tubes were immediately refrigerated in an onboard cool room. All amber glass jars were immediately placed into the onboard freezer room. After each trip, the samples were transferred in coolers to laboratories at University of Illinois at Chicago. The samples in Falcon tubes were used for sediment characterization. The glass jars remained frozen at -16 °C before being processed for chemical analyses.

## **Text S2. Method of Chemical Analyses**

### *Chemicals*

Chemical standards of PCB mix #1 including 39 congeners (PCBs 1, 2, 3, 4, 6, 8, 9, 16, 18, 19, 22, 25, 28, 44, 52, 56, 66, 67, 71, 74, 82, 87, 99, 110, 138, 146, 147, 153, 173, 174, 177, 179, 180, 187, 194, 195, 199, 203, 206), PCDD/F mixture (M-1613-CAL-SET-05), which contained all the 17 congeners with chlorines at 2,3,7,8 substitution positions, individual standards PCDEs 3, 7, 15, 77, 105, 118 and 209, and PCNs 1 and 5, were purchased from AccuStandard (New Haven, CT). PCN mixture (PCN-MXA) including PCNs 2, 6, 13, 28, 52, 66, 73 and 75, surrogate mixture of <sup>13</sup>C labeled 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (TCDD-L) and 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (HxCDD-L) were purchased from Wellington Laboratories (Ontario, Canada). Internal standards <sup>13</sup>C labeled PCB-205 (PCB205L) and <sup>13</sup>C labeled PCB-47 (PCB47L), and surrogate <sup>13</sup>C labeled PCB-52 (PCB52L) were purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA). Individual standards of PCN-9 and PCN-75 were purchased from Sigma-Aldrich (St. Louis, MO).

All solvents were HPLC or Optima grade and purchased from Fisher Scientific (Pittsburgh, PA). Silica gel (Davisil, grade 644, 100-200 mesh), alumina (Brockmann I, neutral, 50-200 μm), copper (50 mesh, granular, reagent grade), sodium hydroxide, anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), and concentrated hydrochloric acid were also from Fisher Scientific. Alumina was activated at 500 °C for 8 h. Silica gel was activated at either 160 °C for at least 16 h or 500 °C for 8 h. Both sorbents were stored at 160 °C, and cooled to room temperature in desiccators before use.

### *Instrumental Analyses*

Agilent 7890 gas chromatography (GC) equipped with Agilent 7001B electron impact triple quadrupole mass spectrometry (EI-QQQMS) was used to analyze most targeted analytes. The multi-mode injection port was operated in solvent vent mode with 60 μL (20 μL × 3) total injection per run. PCBs, PCDEs and PCNs were analyzed in the same run. The inlet temperature started at 40 °C, which was held for 2.1 min, then increased to 300 °C at 600 °C/min. The vent flow was 50 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. Two types of column were used for the separation. Lake Michigan Ponar grab and core M009, M024, M028, M032 and M050, and all Lakes Huron and Superior samples were separated with a 60 m J&W DB-5MS capillary column (0.25 mm i.d. × 0.10 μm film thickness), The initial oven temperature was 35 °C, which was held for 3 min, then increased to 140 °C at 15 °C/min, then increased to 284 °C at 1.5 °C/min, then increased to 300°C at 16 °C/min and kept for 5 min until the run was completed. Samples in the other cores from Lake Michigan were analyzed with a 30 m J&W DB-5MS capillary column (0.25 mm i.d. × 0.10 μm film thickness). The initial oven temperature was 35 °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 was kept at 300 °C.

PCDDs and PCDFs in all samples except those from Lake Superior were analyzed on the 7890/7001B GC-QQQMS with the same 30 m column described above but different inlet and oven programs. The inlet temperature started at 0 °C, which was held for 2.1 min, then increased to 300 °C at 600 °C/min. The initial oven temperature was 50 °C, which was held for 3 min, then increased to 210 °C at 10 °C/min, then increased to 250 °C at 5 °C/min, then increased to 275 °C at 2 °C/min, then increased to 300 °C at 10 °C/min and kept for 5 min until the run was completed. The temperature of the 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. The transitions of all target analytes, surrogates and internal standards are summarized in Table S3.

Agilent 6890/5973 GC/MS with electron capture negative ionization source (ECNI) was used for the analyses of PCDDs (except 2,3,7,8-TCDD) and PCDFs in Lake Superior samples. The instrument was equipped with a Gerstel programmable temperature vaporization (PTV) injection port, which was operated in solvent vent mode. The inlet temperature started at 20 °C, which was held for 2 min, and then increased to 300 °C at 600 °C/min. The vent flow was 100 mL/min. The purge flow was 50 mL/min at 3 min. A same 30 m J&W DB-5MS capillary column (0.25 mm i.d. × 0.10 µm film thickness) was used for separation. The initial oven temperature was 80 °C, which was held for 3 min, then increased to 230 °C at 10 °C/min, then increased to 241 °C at 0.5 °C/min, then increased to 272 °C at 2 °C/min, then increased to 300 °C at 10 °C/min and kept for 4 min until the run was completed. The carrier gas flow was kept constant at 1.2 mL/min. The ECNI-MS was operated in selective ion monitoring (SIM) mode, with the temperatures of the ion source and the quadrupoles set at 200 °C and 150 °C, respectively. The m/z values of the quantitation and qualification ions for target analytes, surrogates and internal standards are given in Table S3. The ECNI-MS was found not sensitive to 2,3,7,8-TCDD. Therefore, GC-EIQQQMS as described above was also used to analyze 2,3,7,8-TCDD for samples from Lake Superior.

Agilent MassHunter software was used for data acquisition and quantification. Before injection, internal standards PCB205L and PCB47L were added to all samples. Quantification of concentrations used either the isotope dilution or the internal standard methods. Calibration curves were made from running 7 to 9 level of standard solutions, based on linear or quadratic regressions with 1/x weighing factor. All calibration curves had  $R^2 > 0.99$ .

**Table S3.** The mass-to-charge ratios (m/z) and optimized collision energy (CE, in volts) in EI-QQQMS or m/z in ECNI for target analytes of this work

Name	Type	Precursor	Quantification		Qualification	
			Ion	CE	Ion	CE
PCBs						
Monochlorobiphenyl		187.8	152	25	153	9
Dichlorobiphenyl		221.8	152	31	196	25
Trichlorobiphenyl		255.8	186	31	221	15
Tetrachlorobiphenyl		291.7	222	31	257	13
Pentachlorobiphenyl		325.7	256	31	291	15
Hexachlorobiphenyl		359.6	290	33	325	15
Heptachlorobiphenyl		393.6	324	33	359	15
Octachlorobiphenyl		429.6	360	35	395	17
Nonachlorobiphenyl		463.5	394	35	392	35
Decachlorobiphenyl		497.6	428	33	426	33
Monochlorobiphenyl		187.8	152	25	153	9
Dichlorobiphenyl		221.8	152	31	196	25
PCDDS						
Tetrachlorodibenzo-p-dioxin	EIQQQ	321.8	259	25	257	25
	ECNI		319.9		321.9	
Pentachlorodibenzo-p-dioxin	EIQQQ	355.7	293	25	291	25
	ECNI		355.8		357.8	
Hexachlorodibenzo-p-dioxin	EIQQQ	389.7	327	25	325	25
	ECNI		389.8		391.8	
Heptachlorodibenzo-p-dioxin	EIQQQ	425.6	363	27	361	25
	ECNI		388.7		390.7	
Octachlorodibenzo-p-dioxin	EIQQQ	459.6	397	25	395	25
	ECNI		422.7		424.7	
PCDFs						
Tetrachlorodibenzofuran	EIQQQ	305.8	243	35	241	37
	ECNI		305.9		303.9	
Pentachlorodibenzofuran	EIQQQ	339.8	277	35	275	35
	ECNI		339.8		341.8	
Hexachlorodibenzofuran	EIQQQ	373.7	311	37	309	37
	ECNI		373.8		375.8	
Heptachlorodibenzofuran	EIQQQ	407.7	345	35	343	35
	ECNI		407.7		409.7	
Octachlorodibenzofuran	EIQQQ	443.7	381	35	379	35
	ECNI		443.7		441.7	

PCNs						
Monochloronaphthalene		161.9	127	23	101	39
Dichloronaphthalene		195.8	126	39	161	19
Trichloronaphthalene		229.9	160	35	195	21
Tetrachloronaphthalene		265.1	195	37	230	21
Pentachloronaphthalene		299.9	230	37	228	37
Hexachloronaphthalene		333.9	264	37	262	37
Heptachloronaphthalene		367.8	298	37	296	37
Octachloronaphthalene		403.6	334	37	332	37
PCDEs						
Monochlorodiphenyl ether		203.8	176	11	169	13
Dichlorodiphenyl ether		237.8	203	13	210	9
Tetrachlorodiphenyl ether		307.7	245	21	243	21
Pentachlorodiphenyl ether		341.7	272	23	307	9
Decachlorodiphenyl ether		513.6	444	23	442	23
Internal Standards and Surrogates						
PCB47L	2,4,2',4'-tetrachlorobiphenyl, <sup>13</sup> C12	303.8	234	31	269	13
PCB52L	2,2',5,5'-tetrachlorobiphenyl, <sup>13</sup> C12	303.8	234	31	269	13
PCB205L	2,3,3',4,4',5,5',6-octachlorobiphenyl, <sup>13</sup> C12	439.7	370	33	405	17
			441.7		439.7	
PCB209L	decachlorobiphenyl, <sup>13</sup> C12	509.6	440	35	438	35
TCDDL	1,2,3,4-tetrachloro[ <sup>13</sup> C <sub>12</sub> ]dibenzo-p-dioxin	333.8	270	21	204	47
			333.9		331.9	
HxCDDL	1,2,3,7,8,9-hexachloro[ <sup>13</sup> C <sub>12</sub> ]dibenzo-p-dioxin	401.8	338	25	274	47
			366.8		401.9	

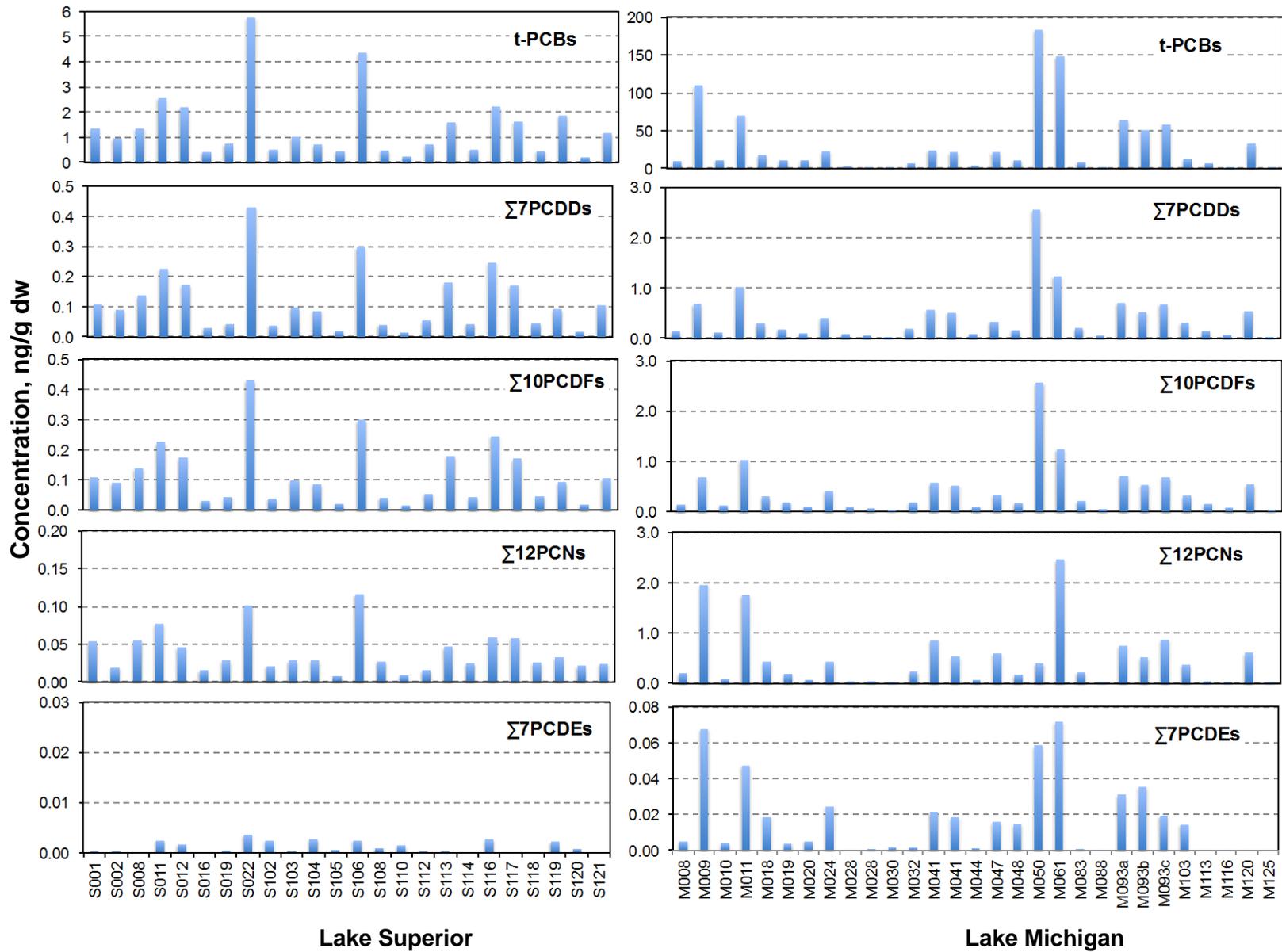
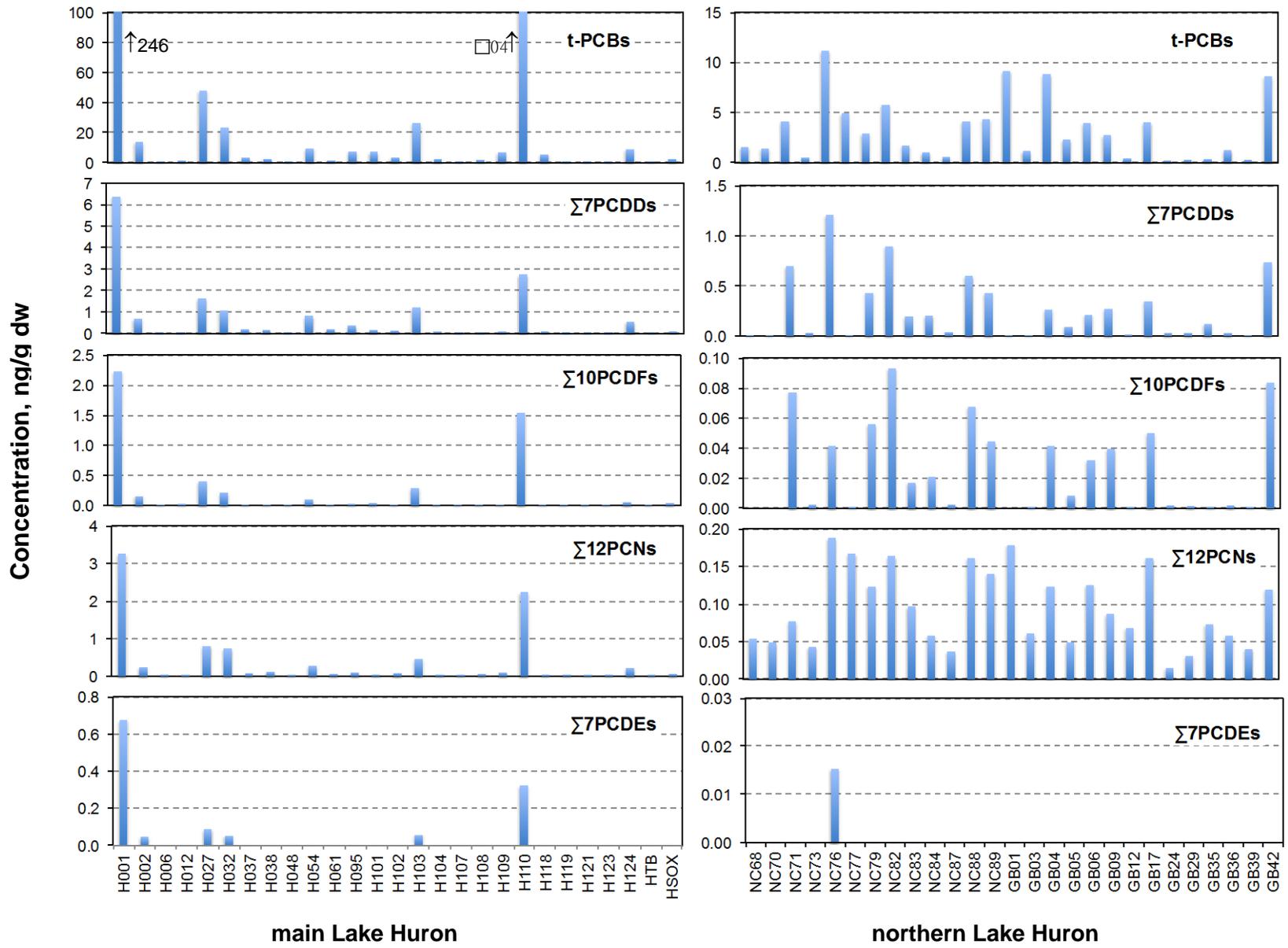


Figure S1-a. Comparison of concentrations in Ponar grab sediment samples among sampling sites in Lakes Superior and Michigan.



**Figure S1-b.** Comparison of concentrations (ng/g dw) in Ponar grab sediment samples among sampling sites in Lake Huron.

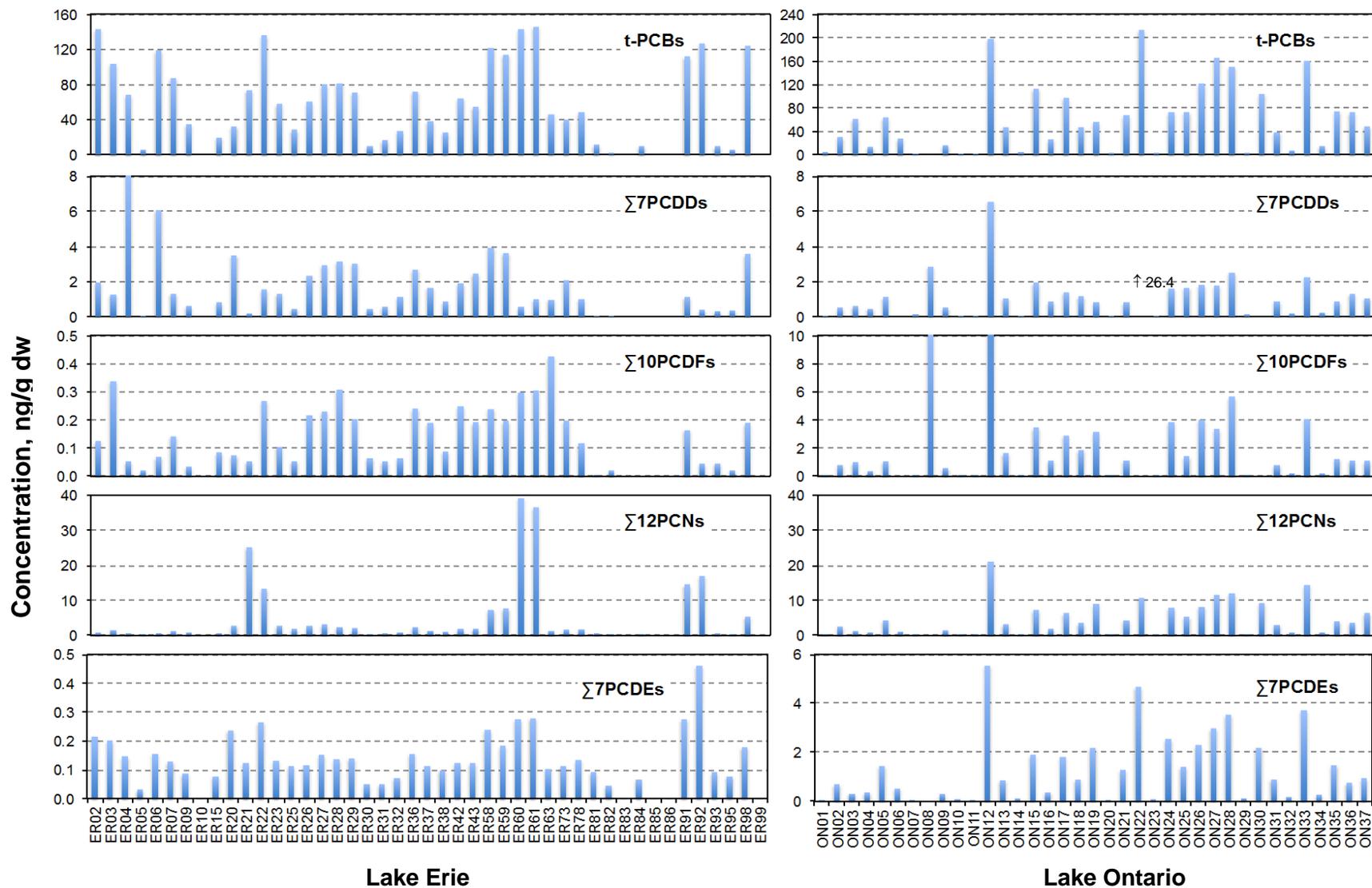


Figure S1-c. Comparison of concentrations in Ponar grab sediment samples among sampling sites in Lakes Erie and Ontario.

**Table S4.** Data summary for sediment cores <sup>a</sup>

Site ID	MSR <sup>b</sup>	FF <sup>c</sup>	Recent net depositional flux (ng/cm <sup>2</sup> -y)					Inventory (ng/cm <sup>2</sup> )				
			t-PCBs	∑ <sub>12</sub> PCNs	∑ <sub>7</sub> PCDEs	∑ <sub>7</sub> PCDDs	∑ <sub>10</sub> PCDFs	t-PCBs	∑ <sub>12</sub> PCNs	∑ <sub>7</sub> PCDEs	∑ <sub>7</sub> PCDDs	∑ <sub>10</sub> PCDFs
S001	NA	0.09	NA	NA	NA	NA	NA	1.2	0.01	0.00	0.11	0.02
S002	0.007	0.82	0.059	0.051	0.000	0.004	0.000	2.8	0.49	0.00	0.32	0.04
S008	0.007	0.76	0.142	0.001	0.000	0.008	0.001	8.1	0.13	0.00	0.49	0.07
S011	0.015	2.45	0.038	0.001	0.000	0.004	0.001	8.2	0.23	0.01	1.12	0.18
S012	0.010	1.84	0.032	0.001	0.000	0.004	0.001	5.5	0.13	0.00	0.62	0.08
S016	0.007	1.01	0.045	0.001	0.000	0.006	0.001	4.0	0.08	0.00	0.46	0.07
S019	0.009	0.62	0.080	0.001	0.000	0.008	0.001	3.9	0.14	0.00	0.41	0.09
S022 <sup>d</sup>	0.017	0.60	0.205	0.002	0.000	0.022	0.005	20.4	0.37	0.01	3.06	1.87
S114	NA	0.63	NA	NA	NA	NA	NA	2.1	0.06	0.00	0.24	0.03
M008	0.021	2.58	0.394	0.008	0.000	0.006	0.001	120.0	2.74	0.05	1.01	0.16
M009	0.065	2.20	1.659	0.014	0.001	0.008	0.002	698.7	13.02	0.46	3.38	1.43
M011	0.041	2.76	0.640	0.010	0.000	0.011	0.002	177.4	3.18	0.02	2.36	0.45
M018	0.018	1.52	1.140	0.016	0.000	0.007	0.001	160.2	2.58	0.04	1.42	0.25
M024	0.019	1.98	0.448	0.007	0.001	0.007	0.001	151.0	3.18	0.24	1.76	0.27
M028	NA	0.30	NA	NA	NA	NA	NA	13.1	0.51	0.22	0.08	0.01
M032	0.018	2.09	0.456	0.008	0.000	0.003	0.001	101.3	1.71	0.14	1.43	0.23
M041	0.022	2.11	3.833	0.036	0.002	0.016	0.004	82.8	1.64	0.01	2.00	0.34
M047	0.031	2.64	0.753	0.012	0.000	0.014	0.003	185.8	4.74	0.11	2.11	0.37
M050 <sup>d</sup>	0.043	2.85	0.589	0.014	0.000	0.007	0.001	672.2	1.61	0.13	8.60	0.94
H001	0.155	>3.24	0.779	0.011	0.001	0.008	0.001	1910.1	22.92	4.90	79.45	34.00
H006	0.032	2.17	0.382	0.005	0.001	0.013	0.003	109.5	1.89	0.24	3.00	0.81

<b>H012</b>	0.057	>3.49	0.285	0.007	0.001	n.a.	n.a.	181.9	5.25	0.68		
<b>H032</b>	0.044	3.16	0.239	0.004	0.000	0.010	0.002	109.2	3.10	0.06	4.18	0.95
<b>H037</b>	NA	0.87	NA	NA	NA	NA	NA	11.9	0.63	0.06	0.37	0.05
<b>H038</b>	0.009	0.89	0.129	0.004	0.001	n.a.	n.a.	14.2	0.86	0.14		
<b>H048</b>	0.017	1.60	0.164	0.003	0.000	0.010	0.002	40.2	1.31	0.04	2.20	0.33
<b>H061</b>	0.006	0.60	0.107	0.003	0.000	0.012	0.002	5.7	0.15	0.02	0.51	0.07
<b>H095</b>	0.014	1.13	0.176	0.004	0.001	n.a.	n.a.	16.3	0.47	0.12		
<b>ER09</b>	0.452	>5.34	1.837	0.035	0.002	0.291	0.028	418.0	8.02	0.63	40.42	3.16
<b>ER15</b>	0.591	>4.67	1.269	0.030	0.004	0.203	0.020	266.4	5.76	0.58	24.48	2.51
<b>ER37</b>	0.141	>3.63	1.514	0.049	0.003	0.067	0.008	505.7	18.05	1.03	30.42	5.17
<b>ER73</b>	0.155	>3.44	1.009	0.053	0.007	0.110	0.008	336.7	22.75	2.18	32.78	5.71
<b>ER92</b>	0.205	2.28	9.600	0.763	0.014	0.187	0.056	1230.4	134.50	5.13	25.03	6.14
<b>ON02</b>	0.018	0.92	1.768	0.109	0.036	0.112	0.184	163.7	10.39	3.27	6.19	6.74
<b>ON06</b>	0.237	>3.83	1.071	0.037	0.012	0.049	0.023	3812.0	185.08	48.80	21.66	47.12
<b>ON13</b>	0.018	1.11	1.585	0.106	0.036	0.042	0.048	315.8	17.61	5.53	8.44	6.53
<b>ON17</b>	0.032	1.36	1.628	0.100	0.039	0.049	0.047	354.5	19.94	6.73	8.45	6.19
<b>ON25</b>	0.026	1.44	1.279	0.083	0.033	0.033	0.027	357.1	20.65	7.18	8.06	5.99
<b>ON30</b>	0.025	1.37	1.159	0.070	0.039	0.026	0.027	354.8	23.55	7.64	10.69	13.29
<b>ON36</b>	0.033	1.65	0.124	0.002	0.008	0.010	0.009	369.6	14.23	4.94	8.29	6.84

- a. n.a. = not analyzed. NA = not available due to unavailable mass sedimentation rate and focusing factor (Corcoran et al., 2017).
- b. MSR = mass sedimentation rate, g/cm<sup>2</sup>-y. FF = focusing factor, dimensionless. Red indicates high uncertainties. (Data are from Corcoran et al., 2017).
- c. The MSR shown here for S022 and M050 are those in upper sections of the cores with depositional years after 1975 and 1998, respectively. The MSR values for deeper sediments were 0.025 g/cm<sup>2</sup>-y for S022 and 0.020 g/cm<sup>2</sup>-y for M050.

**Table S5.** Estimated total load (tonnes) of targeted chemical groups in sediment using equation [4]

	t-PCBs	$\Sigma_7$ PCDDs	$\Sigma_{10}$ PCDFs	$\Sigma_{12}$ PCNs	$\Sigma_7$ PCDEs
<u>Based on core average inventory</u>					
Superior	5.1	0.6	0.2	0.1	0
Michigan	136.6	1.4	0.3	2.0	0.1
Huron	158.9	5.9	2.4	2.4	0.4
Erie	141.7	7.9	1.2	9.7	0.5
Ontario	155.1	1.9	2.5	7.9	2.3
All Lakes	597.4	17.8	6.6	22.2	3.3
<u>Based on core median inventory</u>					
Superior	3.3	0.4	0.1	0.1	0
Michigan	90.0	1.1	0.2	1.2	0
Huron	24.0	0.3	0.04	0.8	0.1
Erie	107.4	7.9	1.1	3.6	0.3
Ontario	67.3	1.6	1.4	3.9	1.3
All Lakes	291.9	11.3	2.8	9.6	1.6

**Table S6.** Top three most contaminated sites in individual lakes

	Lake Superior			Lake Michigan			Lake Huron			Lake Erie			Lake Ontario		
	#1	#2	#3	#1	#2	#3	#1	#2	#3	#1	#2	#3	#1	#2	#3
<u>by concentrations in Ponar grab sediment samples</u>															
t-PCBs	S022	S106	S011	M050	M061	M009	H001	H110	H027	ER61	ER02	ER60	ON22	ON12	ON27
$\sum_7$ PCDDs	S022	S106	S116	M050	M061	M011	H001	H110	H027	ER04	ER06	ER58	ON12	ON08	ON28
$\sum_{10}$ PCDFs	S022	S106	S116	M050	M061	M011	H001	H110	H027	ER63	ER03	ER28	ON12	ON08	ON28
$\sum_{12}$ PCNs	S106	S022	S011	M061	M009	M011	H001	H110	H027	ER60	ER61	ER21	ON12	ON33	ON28
$\sum_7$ PCDEs	S022	S104	S116	M061	M009	M050	H001	H110	H027	ER92	ER61	ER91	ON12	ON22	ON33
<u>by inventories of the cores</u>															
t-PCBs	S022	S011	S008	M009	M050	M047	H001	H012	H006	ER92	ER37	ER09	ON06	ON36	ON25
$\sum_7$ PCDDs	S022	S011	S012	M050	M009	M011	H001	H032	H006	ER09	ER73	ER37	ON06	ON30	ON17
$\sum_{10}$ PCDFs	S022	S011	S019	M009	M050	M011	H001	H032	H006	ER92	ER73	ER37	ON06	ON30	ON36
$\sum_{12}$ PCNs	S002	S022	S011	M009	M047	M024	H001	H012	H037	ER92	ER73	ER37	ON06	ON30	ON25
$\sum_7$ PCDEs	S022	S011	S002	M009	M024	M028	H001	H012	H006	ER92	ER73	ER37	ON06	ON30	ON25

**Table S7.** Pearson linear correlation matrix among analyte groups

		Ln Concentration, ng/g dw in Ponar grab sediments				Ln Inventory, ng/cm <sup>2</sup> in sediment cores			
		<i>N</i> = 186, Critical value (5%) = 1.97294				<i>N</i> = 37, Critical value (5%) = 2.03010			
		t-PCBs	∑12PCNs	∑7PCDEs	∑7PCDDs	t-PCBs	∑12PCNs	∑7PCDEs	∑7PCDDs
∑ <sub>12</sub> PCNs	Pearson Coefficient	<b>0.8987</b>				<b>0.9415</b>			
	<i>R Standard Error</i>	0.0011				0.0032			
	<i>t</i>	27.6408				16.5293			
	<i>p-value</i>	0.0E+00				0.0E+00			
	<i>H0 (5%)</i>	<i>rejected</i>				<i>rejected</i>			
∑ <sub>7</sub> PCDEs	Pearson Coefficient	<b>0.8020</b>	<b>0.9032</b>			<b>0.8637</b>	<b>0.9243</b>		
	<i>R Standard Error</i>	0.002	0.001			0.0073	0.0042		
	<i>t</i>	18.1129	28.3959			10.1366	14.3222		
	<i>p-value</i>	0.0E+00	0.0E+00			5.9E-12	2.2E-16		
	<i>H0 (5%)</i>	<i>rejected</i>	<i>rejected</i>			<i>rejected</i>	<i>rejected</i>		
∑ <sub>7</sub> PCDDs	Pearson Coefficient	<b>0.6035</b>	<b>0.5628</b>	<b>0.5175</b>		<b>0.6355</b>	<b>0.6068</b>	<b>0.6440</b>	
	<i>R Standard Error</i>	0.0035	0.0038	0.004		0.0170	0.0181	0.0167	
	<i>t</i>	10.2097	9.1863	8.1586		4.8700	4.5162	4.9796	
	<i>p-value</i>	0.0E+00	0.0E+00	5.4E-14		2.4E-05	6.9E-05	1.7E-05	
	<i>H0 (5%)</i>	<i>rejected</i>	<i>rejected</i>	<i>rejected</i>		<i>rejected</i>	<i>rejected</i>	<i>rejected</i>	
∑ <sub>10</sub> PCDFs	Pearson Coefficient	<b>0.6120</b>	<b>0.6453</b>	<b>0.7195</b>	<b>0.7669</b>	<b>0.7055</b>	<b>0.7179</b>	<b>0.7493</b>	<b>0.9419</b>
	<i>R Standard Error</i>	0.0034	0.0032	0.0027	0.0023	0.0144	0.0138	0.0125	0.0032
	<i>t</i>	10.4409	11.3952	13.9750	16.1209	5.8891	6.1008	6.6947	16.5888
	<i>p-value</i>	0.0E+00	0.0E+00	0.0E+00	0.0E+00	1.1E-06	5.7E-07	9.5E-08	0.0E+00
	<i>H0 (5%)</i>	<i>rejected</i>	<i>rejected</i>	<i>rejected</i>	<i>rejected</i>	<i>rejected</i>	<i>rejected</i>	<i>rejected</i>	<i>rejected</i>

### Text S3. Urban Distance Factor (UDF)

Urban Distance Factor (UDF) was initially developed by Li et al. (2006), and expanded by Cao et al. (2017). Seven different forms of UDF, as defined below, have been defined and compared. UDF2 has shown better performance than others, thus the regression statistics using UDF2 are included in Table 5 of the main text. The description of UDFs below is from Cao et al. (2017):

	UDF1	UDF2	UDF3	UDF4	UDF5	UDF6	UDF7
Definition	$\sqrt{P} / D$	$P / \sqrt{D}$	$\sqrt{P} / \sqrt{D}$	$P / D$	$P / D^2$	$\sqrt{P} / D^2$	$\text{Ln } P / D^2$

where P = population, D = distance (km) between city and sampling locations.

A total of 210 potential source areas in the Great Lakes region were included based on the 2010 U.S. Census and 2011 Canadian Census. These include all 96 metropolitan statistical areas (MSAs) in the States of Minnesota, Wisconsin, Illinois, Indiana, Michigan, Ohio, Pennsylvania, and New York, of the United States, as well as 16 of the census metropolitan areas (CMA) and census agglomerations (CA) in the Province of Ontario, Canada with population greater than 100,000. Additionally, the Washington-Arlington-Alexandria MSA is included due to its large population although it is not in the eight Great Lakes states. All cities “on the Great Lakes” in both countries ([https://en.wikipedia.org/wiki/List\\_of\\_cities\\_on\\_the\\_Great\\_Lakes](https://en.wikipedia.org/wiki/List_of_cities_on_the_Great_Lakes)) are included regardless their populations, unless they are part of an MSA, CMA or CA. The latitude and longitude of these areas and cities are from their web sites in Wikipedia.

The distance (D) between each sampling location (lat1, lon1) and each potential source area (lat2, lon2) was calculated based on the Haversine formula:

$$D = 6378.7 \times \arccos [\sin(\text{lat}1/57.2958) \times \sin(\text{lat}2/57.2958) + \cos(\text{lat}1/57.2958) \times \cos(\text{lat}2/57.2958) \times \cos(\text{lon}1/57.2958 - \text{lon}2/57.2958)]$$

where 6378.7 is the radius of the Earth in km; and  $57.2958 = 180/\pi$ , which converts latitude and longitude in degrees to radians.

### References

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