



Contents lists available at ScienceDirect

Journal of Great Lakes Research

journal homepage: [www.elsevier.com/locate/jglr](http://www.elsevier.com/locate/jglr)

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

An Li<sup>a,b,c,\*</sup>, Jiehong Guo<sup>a</sup>, Zhuona Li<sup>a</sup>, Tian Lin<sup>a,d</sup>, Shanshan Zhou<sup>a,b</sup>, Huan He<sup>a,e</sup>, Prabha Ranansinghe<sup>a</sup>, Neil C. Sturchio<sup>f</sup>, Karl J. Rockne<sup>g</sup>, John P. Giesy<sup>h</sup>

<sup>a</sup> School of Public Health, University of Illinois at Chicago, Chicago, IL 60612, USA

<sup>b</sup> College of Environment, Zhejiang University of Technology, Hangzhou 310032, China

<sup>c</sup> College of Environmental & Resource Sciences, Zhejiang University, Hangzhou 310000, China

<sup>d</sup> Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

<sup>e</sup> School of Environment, Nanjing Normal University, Nanjing 210023, China

<sup>f</sup> Department of Geological Sciences, University of Delaware, Newark, DE 19716, USA

<sup>g</sup> Department of Civil and Materials Engineering, University of Illinois at Chicago, Chicago, IL 60607, USA

<sup>h</sup> Department of Veterinary Biomedical Sciences and Toxicology Centre, University of Saskatchewan, Saskatoon, Saskatchewan, SK S7N 5B3, Canada

### ARTICLE INFO

#### Article history:

Received 24 September 2017

17 December 2017

Accepted 6 February 2018

Available online xxx

Communicated by Alexander Karatayev

#### Keywords:

Polychlorinated biphenyls

Polychlorinated dibenzo-*p*-dioxins

Polychlorinated dibenzofurans

Polychlorinated naphthalenes

Polychlorinated diphenyl ethers

### 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 American. 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 significantly 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.

© 2018 International Association for Great Lakes Research. Published by Elsevier B.V. All rights reserved.

### 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, 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

\* Corresponding author at: School of Public Health, University of Illinois at Chicago, Chicago, IL 60612, USA.

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

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

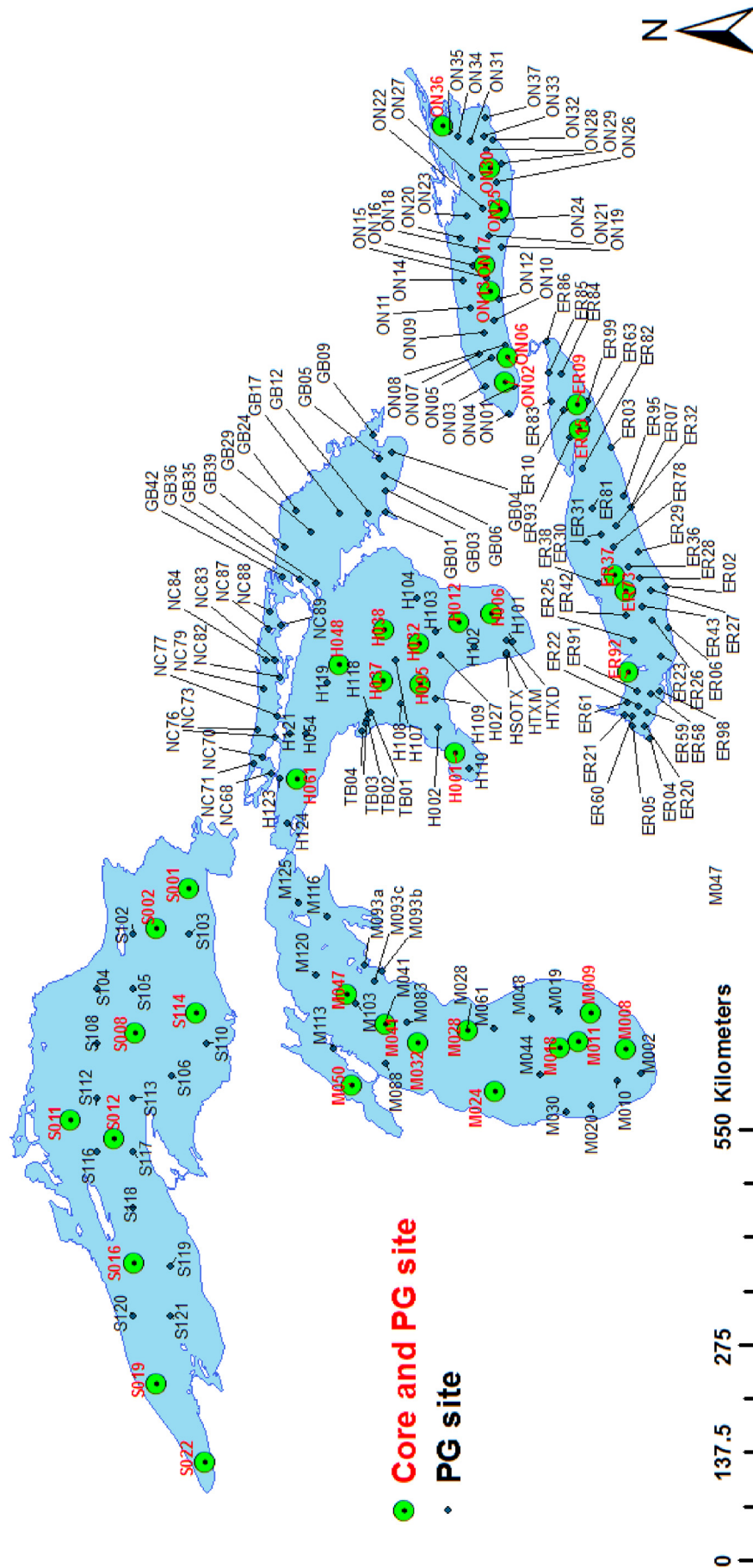


Fig. 1. Sediment sampling locations. PG = Ponar grab. Latitude, longitude and water depth of all the sites are provided in ESM Tables S2a and S2b.

**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.

### 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)).

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

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 overlaying 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)).

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

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)):

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

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 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

**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

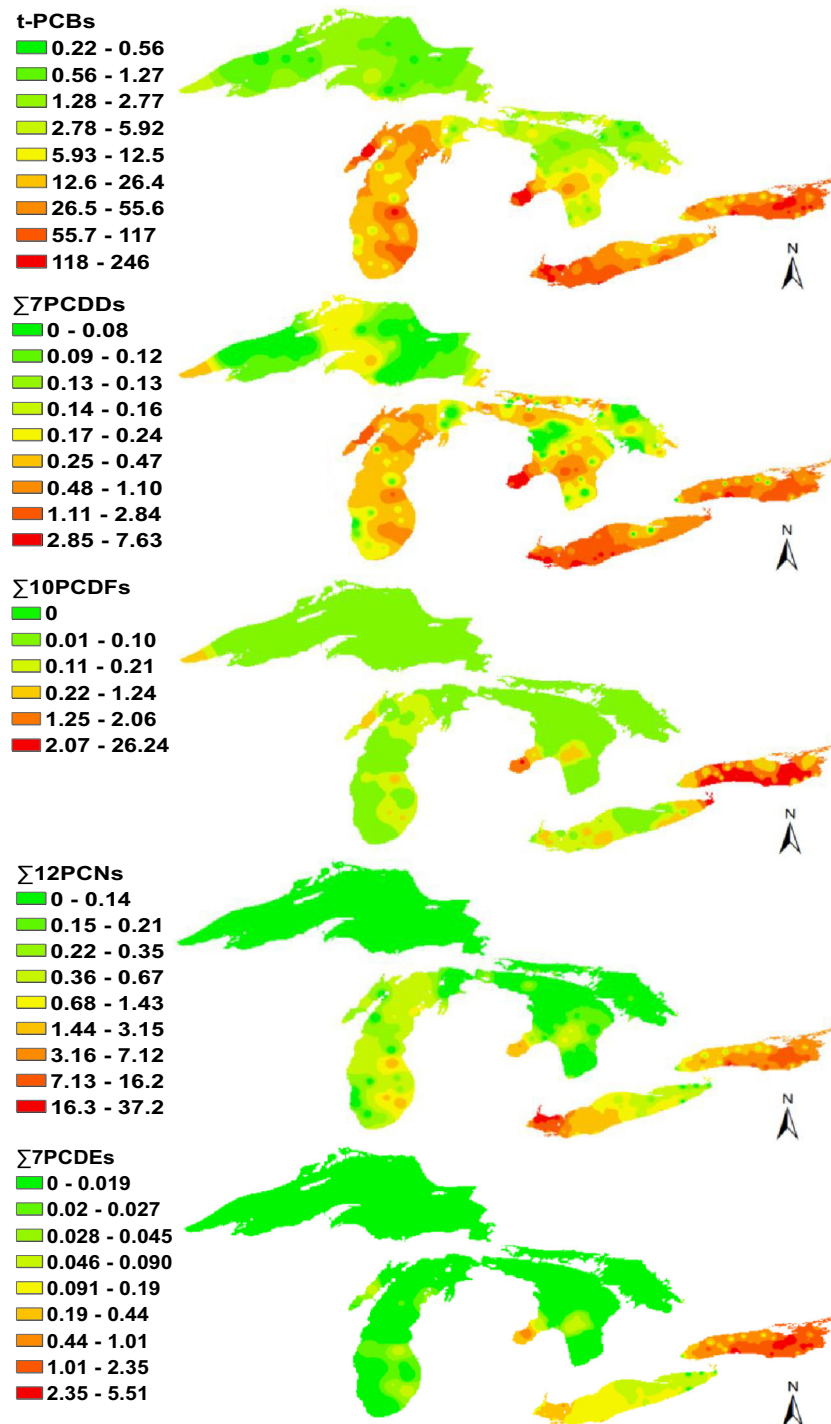
**Table 3**

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

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 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,



**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

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 exceeded 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 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.

**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>2a</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>2a</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.

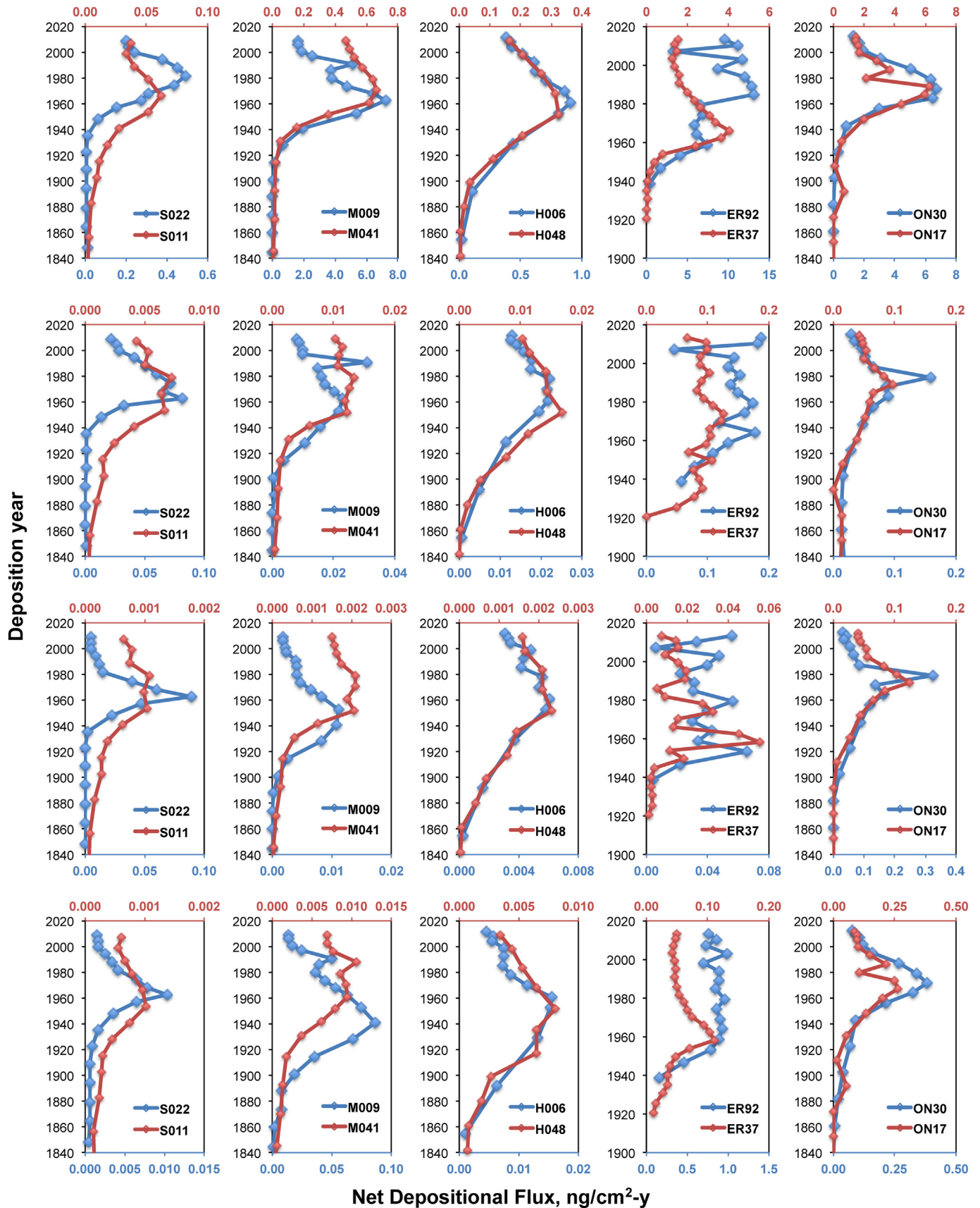


Fig. 3. Temporal trends of net depositional fluxes at selected coring sites. From top to bottom rows are t-PCBs, Σ<sub>7</sub>PCDDs, Σ<sub>10</sub>PCDFs, and Σ<sub>12</sub>PCNs. From left to right columns are for Lakes Superior, Michigan, Huron, Erie, and Ontario.

**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

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  $\sum_7$ PCDDs and  $\sum_{10}$ 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.

## Acknowledgments

This research was funded by a Cooperative Agreement from the U.S. EPA Great Lakes Restoration Initiative with Assistance No. GL-OOE00538 (EPA Program Officers Todd Nettesheim and Elizabeth Murphy). Matching funds have been provided by the University of Illinois at Chicago (UIC). Partial student supports were provided by a Predoctoral Fellowship from the UIC Institute for Environmental Science and Policy (IESP). Prof. Giesy was supported by the Canada Research Chair program, the 2012 “High Level Foreign Experts” (#GDT20143200016) program, funded by the State Administration of Foreign Experts Affairs, the P.R. China to Nanjing University, the Einstein Professor Program of the Chinese Academy of Sciences and a Distinguished Visiting Professorship in the School of Biological Sciences of the University of Hong Kong. We thank the crew of *R/V Lake Guardian* for their assistance during sediment sampling.

## Appendix A. Supplementary data

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

## References

- ATSDR, 2006. PCB contaminated sediment in the lower Fox River and Green Bay north-eastern Wisconsin. EPA Facility ID: WI0001954841. March 14, 2006. [https://www.atsdr.cdc.gov/hac/pha/foxriver/pcbinfoxriver\\_greenbaypha031406.pdf](https://www.atsdr.cdc.gov/hac/pha/foxriver/pcbinfoxriver_greenbaypha031406.pdf), Accessed date: 12 September 2017.
- Bonina, S.M.C., 2016. (PhD. Dissertation). Carbon Loading to Lake Michigan Sediments. University of Illinois at Chicago.
- 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.* (this issue).
- Brown Jr., J.F., 1994. Determination of PCB metabolic, excretion, and accumulation rates for use as indicators of biological responses and relative risk. *Environ. Sci. Technol.* 28, 2295–2305.
- 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.B., 2017. Organophosphate esters in sediment of the Great Lakes. *Environ. Sci. Technol.* 51 (3), 1441–1449.
- Chu, I., Villeneuve, D.C., Secours, V., Valli, V.E., 1990. Toxicological assessment of chlorinated diphenyl ethers in the rat, part II. *J. Environ. Sci. Health Part B* 25 (2), 225–241.
- Coburn, J.A., Comba, M., 1981. Identification of polychlorinated diphenyl ethers in Whitby Harbour sediments. Association of Analytical Chemist's, Spring Workshop, Ottawa, Ontario.
- Coburn, J.A., Comba, M., 1985. The Development of an Analytical Method for Polychlorinated Diphenylethers in Fish, Final Contract Report. National Water Research Institute, Burlington, Ontario.
- Codling, G., Vogt, A., Jones, P.D., Wang, T.Y., 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.
- Codling, G., Hosseini, S., Corcoran, M.B., Bonina, S.M.C., Lin, T., Li, A., Sturchio, N.C., Rockne, K.J., Ji, K., Peng, H., Giesy, J.P., 2018. 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.
- Corcoran, M., Smalley, C., Poghosyan, A., Sherif, M., Li, A., Rockne, K.J., Giesy, J.P., Sturchio, N.C., 2018. Sedimentation rates in the Great Lakes from core profiles of <sup>210</sup>Pb and <sup>137</sup>Cs. *J. Great Lakes Res.* (this issue).
- Czuczwa, J.M., Hites, R.A., 1984. Environmental fate of combustion-generated polychlorinated dioxins and furans. *Environ. Sci. Technol.* 18, 444–450.
- Czuczwa, J.M., Hites, R.A., 1985. Historical record of polychlorinated dioxins, furans in Lake Huron sediments. In: Keith, L.H., Rappe, C., Choudhary, G. (Eds.), *Chlorinated Dioxins and Dibenzofurans in the Total Environment II*. Butterworth, Toronto, p. 59.
- Czuczwa, J.M., Hites, R.A., 1986. Airborne dioxins and dibenzofurans: sources and fates. *Environ. Sci. Technol.* 20, 195–200.
- Dahmer, S., Tetreault, G.R., Hall, R.L., Munkittrick, K.R., McMaster, M.E., Servos, M.R., 2015. Historical decline and altered congener patterns of polychlorinated dibenzo-p-dioxins and dibenzofurans in fish and sediment in response to process changes at a pulp mill discharging into Jackfish Bay, Lake superior. *Environ. Toxicol. Chem.* 34 (11), 2489–2502.
- Eisenreich, S.J., 1987. The chemical limnology of nonpolar organic contaminants: polychlorinated biphenyls in Lake Superior. In: Hites, R.A., Eisenreich, S.J. (Eds.), *Source and Fate of Aquatic Pollutants*. American Chemical Society (Chapter 13).
- Elder, V.A., Procter, B.L., Hites, R.A., 1981. Organic compounds found near dump sites in Niagara Falls, New York. *Environ. Sci. Technol.* 15 (10), 1237–1243.
- Fu, P.P., Von Tungeln, L.S., Chiu, L.-H., Own, Z.Y., 1999. Halogenated-polycyclic aromatic hydrocarbons: a class of genotoxic environmental pollutants. *Environ. Carcinog. Ecotoxicol. Rev.* C17 (2), 71–109.
- Furlong, E.T., Carter, D.S., Hites, R.A., 1988. Organic contaminants in sediments from the Trenton Channel of the Detroit River, Michigan. *J. Great Lakes Res.* 14, 489–501.
- Gale, R.W., Huckins, J.N., Petty, J.D., Peterman, P.H., Williams, L.L., Morse, D., Schwartz, T.R., Tillitt, D.E., 1997. Comparison of the uptake of dioxin-like compounds by Caged Channel catfish and semipermeable membrane devices in the Saginaw River, Michigan. *Environ. Sci. Technol.* 31, 178.
- Gewurtz, S.B., Shen, L., Helm, 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 (1), 153–168.
- Gewurtz, S.B., Lega, R., Crozier, P.W., Whittle, D.M., Fayed, L., Reiner, E.J., Helm, P.A., Marvin, C.H., Tomy, G.T., 2009. Factors influencing trends of polychlorinated naphthalenes and other dioxin-like compounds in lake trout (Salvelinus Namaycush) from Lake Ontario, North America (1979–2004). *Environ. Toxicol. Chem.* 28 (5), 921–930.
- Guo, J., Li, Z., Sandy, A.L., Li, A., 2014a. Method development for simultaneous analyses of multiple legacy and emerging organic chemicals in sediments. *J. Chromatogr. A* 1370, 1–8.
- Guo, J., Chen, D., Potter, D., Rockne, K.J., Sturchio, N.C., Giesy, J.P., Li, A., 2014b. Polyhalogenated carbazoles in sediments of Lake Michigan: a new discovery. *Environ. Sci. Technol.* 48 (21), 12807–12815.
- 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 (14), 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., 2017. Spatial and temporal trends of polyhalogenated carbazoles in sediments of upper Great Lakes – insights into their origin. *Environ. Sci. Technol.* 51, 89–97.
- Hanari, N., Kannan, K., Horii, Y., Taniyasu, S., Yamashita, N., Jude, D.J., Berg, M.B., 2004. Polychlorinated naphthalenes and polychlorinated biphenyls in benthic organisms of a Great Lakes food chain. *Arch. Environ. Contam. Toxicol.* 47 (1), 84–93.
- Harner, T., Shoeib, M.A., Gouin, T., Blanchard, P., 2006. Polychlorinated naphthalenes in Great Lakes air: assessing spatial trends and combustion inputs using PUF disk passive air samplers. *Environ. Sci. Technol.* 40, 5333–5339.
- Helm, P.A., Bidleman, T.F., Li, H.H., Fellin, P., 2004. Seasonal and spatial variation of polychlorinated naphthalenes and non-mono-ortho-substituted polychlorinated biphenyls in Arctic Air. *Environ. Sci. Technol.* 38 (21), 5514–5521.
- Helm, P.A., Kannan, K., Bidleman, T.F., 2006. Polychlorinated Naphthalenes in the Great Lakes. In: Hites, R.A. (Ed.), *Persistent Organic Pollutants in the Great Lakes*. Handbook of Environmental Chemistry Vol. 5, Part N. Springer-Verlag, Berlin Heidelberg, pp. 267–306.
- Helm, P.A., Gewurtz, S.B., Whittle, D.M., Marvin, C.H., Fisk, A.T., Tomy, G.T., 2008. Occurrence and biomagnification of polychlorinated naphthalenes and non- and mono-ortho PCBs in Lake Ontario sediment and biota. *Environ. Sci. Technol.* 42 (4), 1024–1031.
- Horii, Y., Ohura, T., Yamashita, N., Kannan, K., 2009. Chlorinated polycyclic aromatic hydrocarbons in sediments from industrial areas in Japan and the United States. *Arch. Environ. Contam. Toxicol.* 57, 651–660.
- Hornbuckle, K.C., Carlson, D.L., Swackhamer, D.L., Baker, J.E., Eisenreich, S.C., 2006. Polychlorinated Biphenyls in the Great Lakes. In: Hites, R.A. (Ed.), *Persistent Organic*

- Pollutants in the Great Lakes. Handbook of Environmental Chemistry Vol. 5, Part N. Springer-Verlag, Berlin Heidelberg, pp. 13–70.
- Hosseini, S., 2016. (PhD. Dissertation). Implications of Carbon Deposition on the Fate of Semi-Volatile Organic Pollutants in the Great Lakes. University of Illinois at Chicago.
- Jaffe, R., Hites, R.A., 1986. Anthropogenic, polyhalogenated organic compounds in non-migratory fish from the Niagara River area and tributaries to Lake Ontario. *J. Great Lakes Res.* 12, 63–71.
- Jaffe, R., Stemmler, E.A., Eitzer, B.D., Hites, R.A., 1985. Anthropogenic, polyhalogenated organic compounds in sedentary fish from Lake Huron and Lake superior tributaries and embay- ments. *J. Great Lakes Res.* 11, 156–162.
- Kannan, K., Kober, J.L., Kang, Y.-S., Masunaga, S., Nakanishi, J., Ostaszewski, A., Giesy, J.P., 2001. Polychlorinated naphthalenes, biphenyls, dibenzo-p-dioxins, and dibenzofurans as well as polycyclic aromatic hydrocarbons and alkylphenols in sediments from the Detroit and Rouge rivers, Michigan, USA. *Environ. Toxicol. Chem.* 20, 1878–1889.
- Kannan, K., Yun, S.H., Ostaszewski, A., McCabe, J.M., Mackenzie-Taylor, D., Taylor, A.B., 2008. Dioxin-like toxicity in the Saginaw River watershed: polychlorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls in sediments and floodplain soils from the Saginaw and Shiawassee rivers and Saginaw Bay, Michigan, USA. *Arch. Environ. Contam. Toxicol.* 54 (1), 9–19.
- Lee, S.C., Harnner, T., Pozo, K., Shoenib, M., Wania, F., Muir, D.C.G., Barrie, L.A., Jones, K.C., 2007. Polychlorinated naphthalenes in the global atmospheric passive sampling (GAPS) study. *Environ. Sci. Technol.* 41, 2680–2687.
- Li, A., Rockne, K.J., Sturchio, N., Song, W., Ford, J.C., Buckley, D.R., Mills, W.J., 2006. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 4. Influencing factors, trends, and implications. *Environ. Sci. Technol.* 40 (24), 7528–7534.
- Li, A., Rockne, K.J., Sturchio, N., Song, W., Ford, J.C., Wei, H., 2009. PCBs in sediments of the Great Lakes – distribution and trends, homolog and chlorine patterns, and in situ degradation. *Environ. Pollut.* 157 (1), 141–147.
- Li, A., Giesy, J.P., Rockne, K.J., Sturchio, N., 2018. Great Lakes Sediment Surveillance Program (GLSSP) Final Report (in preparation).
- Lu, Z., Letcher, R.J., Chu, S., Ciborowski, J.J.H., Haffner, G.D., Drouillard, K.G., MacLeod, S.L., Marvin, C.H., 2015. Spatial distributions of polychlorinated biphenyls, polybrominated diphenyl ethers, tetrabromobisphenol A and bisphenol A in Lake Erie sediment. *J. Great Lakes Res.* 41 (3), 808–817.
- MacKay, D., Eisenreich, S.J., Patterson, S., Simmons, M.S., 1983. Physical Behavior of PCBs in the Great Lakes. Butterworth Publishers, Stoneham, MA, USA.
- Marvin, C.H., Howell, E.T., Kolic, T.M., Reiner, E.J., 2002a. Polychlorinated dibenzo-p-dioxins and dibenzofurans and dioxin-like polychlorinated biphenyls in sediments and mussels at three sites in the lower Great Lakes, North America. *Environ. Toxicol. Chem.* 21 (9), 1908–1921.
- Marvin, C., Alae, M., Painter, S., Charlton, M., Kauss, P., Kolic, T., MacPherson, K., Takeuchi, D., Reiner, E., 2002b. Persistent organic pollutants in Detroit River suspended sediments: polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like polychlorinated biphenyls and polychlorinated naphthalenes. *Chemosphere* 49, 111–120.
- Marvin, C.H., Painter, S., Charlton, M.N., Fox, M.E., Thiessen, P.A.L., 2004. Trends in spatial and temporal levels of persistent organic pollutants in Lake Erie sediments. *Chemosphere* 54 (1), 33–40.
- McCarty, H.B., Schofield, J., Miller, K., Brent, R.N., van Hoof, P., Eadie, B., April 2004. Results of the Lake Michigan Mass Balance Study Polychlorinated Biphenyls and Trans-Nonachlor Data Report. Great Lakes Environmental Research Laboratory National Oceanic and Atmospheric Administration <https://www.epa.gov/sites/production/files/2015-08/documents/lmmbpcb.pdf>, Accessed date: 17 May 2010.
- Metcalfe, C.D., Metcalfe, T.L., Cormier, J.A., Huestis, S.Y., Niimi, A.J., 1997. Early life-stage mortalities of Japanese medaka (*Oryzias latipes*) exposed to polychlorinated diphenyl ethers. *Environ. Toxicol. Chem.* 16 (8), 1749–1754.
- Niimi, A.J., Metcalfe, C.D., Huestis, S.Y., 1994. Chlorinated diphenyl ethers in Great Lakes fish and their environmental implication. *Environ. Toxicol. Chem.* 13, 1133–1138.
- NIST, August 16, 2004. Certificate of Analysis: Standard Reference Material 1941b – Organics in Marine Sediment. National Institute of Standards and Technology.
- NIST, September 27, 2011. Certificate of Analysis: Standard Reference Material 1944 – New York/New Jersey Waterway Sediment. National Institute of Standards and Technology.
- Norstrom, R.J., 2006. Polychlorinated Dibenzo-p-dioxins and dibenzofurans in the Great Lakes. In: Hites, R.A. (Ed.), Persistent Organic Pollutants in the Great Lakes. Handbook of Environmental Chemistry Vol. 5, Part N. Springer-Verlag, Berlin Heidelberg, pp. 71–150.
- Painter, S., Marvin, C., Rosa, F., Reynoldson, Trefor B., Charlton, M.N., Fox, M., Thiessen, P.A. L., Estenik, J.F., 2001. Sediment contamination in Lake Erie: a 25-year retrospective analysis. *J. Great Lakes Res.* 27 (4), 434–448.
- Pearson, R.F., Swackhamer, D.L., Eisenreich, S.J., Long, D.T., 1997. Concentrations, accumulations, and inventories of polychlorinated dibenzo-p-dioxins and dibenzofurans in sediments of the Great Lakes. *Environ. Sci. Technol.* 31, 2903–2909.
- Pearson, R.F., Swackhamer, D.L., Eisenreich, S.J., Long, D.T., 1998. Atmospheric inputs of polychlorinated dibenzo-p-dioxins and dibenzofurans to the Great Lakes: compositional comparison of PCDD and PCDF in sediments. *J. Great Lakes Res.* 24, 65–82.
- Peng, H., Chen, C., Cantin, J., Saunders, D.M.V., Sun, J., Tang, S., Codling, G., Hecker, M., Wiseman, S., Jones, P.D., Li, A., Rockne, K.J., Sturchio, N.C., Giesy, J.P., 2016a. Untargeted screening and distribution of organo-bromine compounds in sediments of Lake Michigan. *Environ. Sci. Technol.* 50 (1), 321–330.
- Peng, H., Chen, C., Cantin, J., Saunders, D.M.V., Sun, J., Tang, S., Codling, G., Hecker, M., Wiseman, S., Jones, P.D., Li, A., Rockne, K.J., Sturchio, N.C., Cai, M., Giesy, J.P., 2016b. Untargeted screening and distribution of organo-iodine compounds in sediments from Lake Michigan and the Arctic Ocean. *Environ. Sci. Technol.* 50 (18), 10097–10105.
- Quinn, F.H., 1992. Hydraulic residence times for the Laurentian Great Lakes. *J. Great Lakes Res.* 18, 22–28.
- Richman, L.A., Hobson, G., Williams, D.J., Reiner, E., 2011. The Niagara River mussel bio-monitoring program (*Elliptio complanata*): 1983–2009. *J. Great Lakes Res.* 37, 213–225.
- Shen, L., Gewurtz, S.B., Reiner, E.J., MacPherson, K.A., Kolic, T.M., Helm, P.A., Brindle, I.D., Marvin, C.H., 2008. Patterns and sources of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in surficial sediments of Lakes Erie and Ontario. *Environ. Pollut.* 156 (2), 515–525.
- Shen, L., Gewurtz, S.B., Reiner, E.J., MacPherson, K.A., Kolic, T.M., Khurana, V., Helm, P.A., Howell, E.T., Burniston, D.A., Brindle, I.D., et al., 2009. Occurrence and sources of polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like polychlorinated biphenyls in surficial sediments of lakes superior and Huron. *Environ. Pollut.* 157 (4), 1210–1218.
- Song, W.L., 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 (12), 3286–3293.
- Song, W.L., Li, A., Ford, J.C., Sturchio, N.C., Rockne, K.J., Buckley, D.R., Mills, W.J., 2005a. Polybrominated diphenyl ethers in the sediments of the great lakes. 2. Lakes Michigan and Huron. *Environ. Sci. Technol.* 39 (10), 3474–3479.
- Song, W.L., Ford, J.C., Li, A., Sturchio, N.C., Rockne, K.J., Buckley, D.R., Mills, W.J., 2005b. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 3. Lakes Ontario and Erie. *Environ. Sci. Technol.* 39 (15), 5600–5605.
- Sun, P., Basu, I., Blanchard, P., Brice, K.A., Hites, R.A., 2007. Temporal and spatial trends of atmospheric polychlorinated biphenyl concentrations near the Great Lakes. *Environ. Sci. Technol.* 41, 1131–1136.
- Swart, J., Estabrooks, F., Bopp, R., November 1996. Lake Ontario Sediment Survey: 1995 Sediment Coring Results. New York State Department of Environmental Conservation, Division of Water, Bureau of Watershed Assessment and Research, 50 Wolf Road, Room 305, Albany, New York, p. 12233-3502 (43pp).
- USEPA, 2007. PCB ID – composition of PCB (Aroclor) mixtures. [http://www.epa.gov/toxteam/pcb/aroclor\\_comp.htm](http://www.epa.gov/toxteam/pcb/aroclor_comp.htm), Accessed date: 3 January 2007.
- USEPA, December 2010. Recommended Toxicity Equivalence Factors (TEFs) for Human Health Risk Assessments of 2,3,7,8-Tetrachlorodibenzo-P-Dioxin and Dioxin-like Compounds. United States Environmental Protection Agency. EPA/100/R 10/005.
- Veith, G., 1968. Environmental Chemistry of the Chlorobiphenyls in the Milwaukee River. (PhD Dissertation). Water Chemistry Program, University of Wisconsin, Madison, Wisconsin.
- Williams, D.T., LeBel, G.L., 1988. Chlorinated diphenyl ethers in human adipose tissue. *Chemosphere* 17, 2349–2354.
- Williams, D.T., Kennedy, B., LeBel, G.L., 1991. Chlorinated diphenyl ethers in human adipose tissue. Part 2. *Chemosphere* 23, 601–608.
- 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 (12), 5156–5163.
- Yang, R., Wei, H., Guo, J., Li, A., 2012. Emerging brominated flame retardants in the sediment of the Great Lakes. *Environ. Sci. Technol.* 46 (6), 3119–3126.
- Zenon Environmental Inc, 1985. The Development of an Analytical Method for Polychlorinated Diphenyl Ethers in Fish, Final Report, Prepared for Departments of Fisheries and Oceans, Canada, Contract No. IS282–00108.