

Spatial and Temporal Trends of Polyhalogenated Carbazoles in Sediments of Upper Great Lakes: Insights into Their Origin

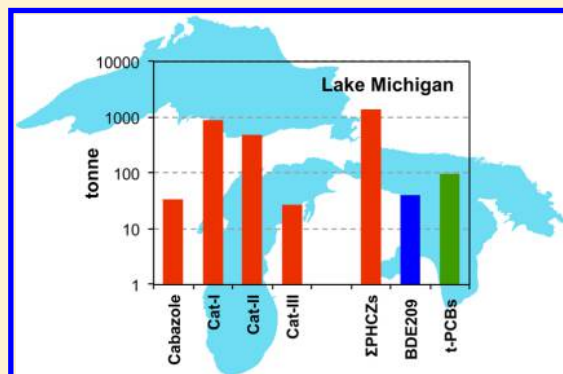
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Supporting Information

ABSTRACT: Polyhalogenated carbazoles (PHCZs) have been increasingly detected in the environment. Their similarities in chemical structure with legacy pollutants and their potential toxicity have caused increasing concern. In this work, 112 Ponar grab and 28 core sediment samples were collected from Lakes Michigan, Superior, and Huron, and a total of 26 PHCZs were analyzed along with unsubstituted carbazole using gas chromatography coupled with single- or triple-quadrupole mass spectrometry. Our results show that the total accumulation of PHCZs in the sediments of the upper Great Lakes is >3000 tonnes, orders of magnitude greater than those of polychlorinated biphenyls (PCBs) and decabromodiphenyl ether (BDE209). The 27 individual analytes differ in spatial distribution and temporal trend. Our results showed that PHCZs with substitution patterns of $-\text{Br}_{2-5}$, $-\text{Cl}_{1-2}\text{Br}_{2-4}$, or having iodine, were more abundant in sediment of Lake Michigan deposited before 1900 than those deposited more recently, implying a natural origin. Some “emerging” PHCZs have been increasingly deposited into the sediment in recent decades, and deserve further environmental monitoring and research. Other PHCZs with low halogen substitution may form from in situ dehalogenation of PHCZs having more halogens. Anthropogenic sources of PHCZs may exist, particularly for the emerging and low molecular mass congeners.



INTRODUCTION

Aromatic organohalogenes may originate from both natural and anthropogenic sources, and can be either detrimental or beneficial to ecosystems and human health. To date, anthropogenic persistent and bioaccumulative organohalogenes have received the most attention in environmental monitoring. However, known anthropogenic organohalogenes comprise only a small fraction of the total organohalogenes found in the environment.¹

Among groups of organohalogenes, polyhalogenated carbazoles (PHCZs) have received little attention since their first detection in the environment in the 1980s.² PHCZs resemble polyhalogenated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in chemical structure with planar molecular conformations that promote toxicity. Indeed, their dioxin-like toxicity to developing zebrafish embryos and rat cells was recently discovered.^{3,4} As such, PHCZs are called nitrogenated dioxins and considered novel persistent organic pollutants.⁵ In our previous study, which focused on the establishment of laboratory methods, 17 PHCZs were detected in sediment cores at two locations in Lake Michigan.⁶ That and other

reports⁷⁻⁹ suggested a distinctly different chronology of deposition and potentially much greater sedimentary load of PHCZs in comparison with known anthropogenic pollutants such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and other organohalogenes in the Great Lakes.¹⁰⁻¹³ Worldwide, the number of studies on the occurrence of PHCZs in the environment is limited,^{2,4,6-8,14-22} and their origin is controversial.²³⁻²⁵ The lack of knowledge on the spatial distribution patterns and temporal trends of PHCZs has made it difficult to speculate on their sources and evaluate their potential impacts on ecosystems and humans.

The objectives of this work were to (1) acquire region-wide data on the concentrations and total accumulations of PHCZs in the sediments of the upper Great Lakes; (2) examine the spatial distribution patterns and temporal trends of PHCZ accumulation; (3) identify the major influencing variables on

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the concentrations and accumulation; and (4) gain insights into the sources of PHCZs observed in the upper Great Lakes.

MATERIALS AND METHODS

Sampling. Details of the sampling procedures have been reported elsewhere.²⁶ Briefly, Ponar surface grab and core sediment samples were collected from Lakes Michigan, Superior, and Huron onboard the U.S. EPA Research Vessel (R/V) *Lake Guardian* from 2010 to 2012. A map of sampling sites is given in Supporting Information Figure S1, and related information is given in Tables S1 and S2. A total of 112 surface sediments were collected using a Ponar grab sampler. Sediment cores were collected at 28 locations by using an MC400 multicorer (Ocean Instruments, San Diego, California), except cores collected in 2010 from Lake Michigan, for which either a box corer or an Ekman dredge corer was used. At each coring site, four subcores (10 cm in diameter) were obtained and sectioned using hydraulic extruders. From subcores of the same site, the segments at corresponding depths were combined and homogenized with stainless steel spoons in glass bowls. Well-mixed Ponar grab and composite core segment samples were distributed into precleaned 125-mL amber glass jars with Teflon-lined screw caps, and immediately frozen. Another portion was refrigerated in a 50-mL Falcon tube.

Sediment Characterization and Core Dating. Triplicate subsamples from the 50-mL refrigerated samples were dried to constant mass, and the bulk density, water, and solid contents were determined by mass differences using standard methods.^{27,28} Contents of total organic carbon (TOC) and organic matter (OM) in sediment samples were measured using the procedures previously described.²⁶

Activities of radionuclides ²¹⁰Pb and ¹³⁷Cs in core segments were measured by gamma spectrometry using HPGe well detectors (Ortec) interfaced with DSPEC-Plus digital signal processors, from gamma emissions at 46.5 and 661.6 keV, respectively. Detector efficiencies were calibrated in sample geometry against standard reference materials DL-1a (CANMET U–Th ore) for U- and Th-series radionuclides and NIST-4365 (ocean sediment) for ¹³⁷Cs. The mass sedimentation rates (MSR) and focusing factors (FF) were obtained from cumulative excess ²¹⁰Pb inventories. MSR ranged from <0.01 to 0.16 g/cm² y⁻¹, and FF ranged from <0.1 to 3. Additional description of the procedures and detailed results are given elsewhere.²⁶

Chemicals and Reagents. Chemical standards for 3-monochlorocarbazole (3-CCZ), 3,6-dichlorocarbazole (36-CCZ), 1,3,6,8-tetrachlorocarbazole (1368-CCZ), 2,3,6,7-tetrachlorocarbazole (2367-CCZ), 1-bromo-3,6-dichlorocarbazole (1-B-36-CCZ), 1,8-dibromo-3,6-dichlorocarbazole (18-B-36-CCZ), and 1,3,6-tribromocarbazole (136-BCZ), as well as a surrogate mixture of ¹³C-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). 3-Monobromocarbazole (3-BCZ), 2,7-dibromocarbazole (27-BCZ), and 3,6-dibromocarbazole (36-BCZ) (97%) were purchased from Sigma-Aldrich (St. Louis, MO). 1,3,6,8-Tetrabromocarbazole (1368-BCZ) was purchased from the Florida Center for Heterocyclic Compounds of the University of Florida (Gainesville, FL). Carbazole, polychlorinated biphenyls (PCBs) mixture, decabromodiphenyl ether (BDE209), surrogates 4'-fluoro-2,3',4,6-tetrabromodiphenyl ether (F-BDE69), and 3'-fluoro-2,2',4,4',5,6'-hexabromodiphenyl ether (F-BDE154) were purchased from AccuStandard

(New Haven, CT). Surrogates ¹³C-labeled chlordane, deuterated benzo[*e*]pyrene (BeP-d12), and tributyl phosphate (TBP-d27), and internal standards ¹³C labeled 2,3,3',4,4',5,5',6-octachlorobiphenyl (PCB205L) and ¹³C labeled 2,4,2',4'-tetrachlorobiphenyl (PCB47L) were purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA). No chemical standards were available for 15 “unknown” PHCZs (UNCs), for which molecular formula and general structures were identified⁶ but halogen substitution positions remain unknown.

All solvents were HPLC or Optima grade and purchased from Fisher Scientific (Pittsburgh, PA). Silica gel (100–200 mesh, 75–150 μm, grade 644), alumina (neutral, Brockmann I, 50–200 μm, Acros Organics), granular anhydrous sodium sulfate (Na₂SO₄), copper (50 mesh, granular, reagent grade), and concentrated hydrochloric acid were also purchased from Fisher Scientific. The sorbents silica gel and alumina, as well as Na₂SO₄, were activated at 500 °C for 8 h, stored at 160 °C, and cooled to room temperature in desiccators before use.

Sample Pretreatment and Instrumental Analyses. A detailed description of the sample treatment and chemical analysis procedures was published elsewhere.²⁹ In brief, about 5 g of freeze-dried sediment of each sample was extracted with an accelerated solvent extraction system (Dionex ASE350, Thermo Fisher Scientific, Inc.). The sediment was extracted for three cycles with a 1:1 (v/v) hexane/acetone mixture at 100 °C, with heating time 5 min and static time 10 min. The extract was concentrated in a rotary evaporator and solvent-exchanged into hexane. A glass column (11 mm i.d. × 40 cm long) was pre-filled with dichloromethane (DCM). The column was then filled from bottom to top with 1 g of granular anhydrous Na₂SO₄, 8 g of alumina, 4 g of silica gel, and 4 g of granular anhydrous Na₂SO₄. After the column was packed, DCM was completely replaced by hexane. Concentrated extract was added to the prepared columns and eluted with 100 mL of hexane (F-1), 100 mL of 4:1 hexane/DCM mixture (F-2), 100 mL of DCM (F-3), and 100 mL of methanol (F-4). PHCZs were in F-2, F-3, and F-4, which were solvent-exchanged to hexane. An aliquot of F-2 and combination of F-3 and F-4 with equal volume were each placed in a 200-μL glass insert of a 2-mL vial for instrumental analysis.

During sample cleanup and fractionation using silica/alumina chromatography, relatively low molecular weight congeners, including 3-CCZ, 3-BCZ, 36-CCZ, and 1-B-36-CCZ, as well as portions of dibromocarbazole and tribromocarbazole, were more strongly bound to the sorbents than others, and eluted in F-3 and F-4. Although 1368-CCZ and 2367-CCZ have the same formula, 2367-CCZ, which has a highly symmetric molecular structure, was more strongly bound to silica/alumina column and eluted in F-3 and F-4 fractions. UNC-2, UNC-4, UNC-6, UNC-10, and 136-BCZ all have 3 bromines; however, UNC-2 was eluted in F-2 while others mostly eluted in F-3 and F-4 from the cleanup column.

An Agilent 6890/5973 GC-MS (Agilent Technologies, Santa Clara, CA) in electron capture negative ionization (ECNI) mode equipped with an Agilent DB-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) was used for the analysis of all target analytes except carbazole, 3-CCZ, 3-BCZ, and 36-CCZ. An Agilent 7890 gas chromatograph (GC) coupled with an Agilent 7000 triple quadrupole mass spectrometer (QQQMS) with electron impact (EI) ion source was used to analyze carbazole, 3-CCZ, 3-BCZ, and 36-CCZ from a mixture of F-3 and F-4 fractions. The transitions or the

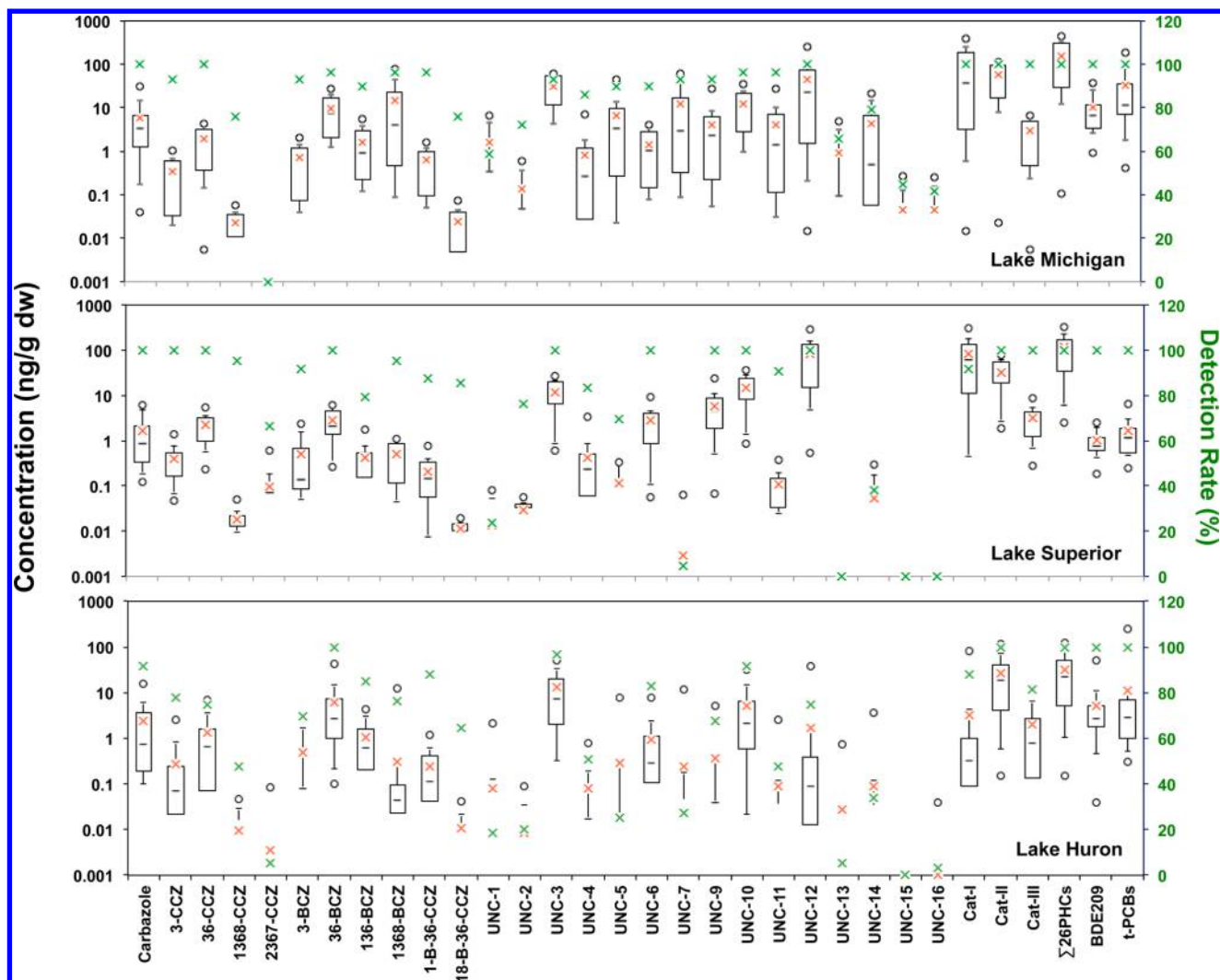


Figure 1. Box and whisker plots of concentrations of PHCZs in Ponar grab sediment samples from Lakes Michigan, Superior, and Huron. Concentrations of carbazole, t-PCBs, and BDE209 in the same samples are included for comparison. Shown are average (red cross), median (lines inside the box), 25th–75th percentiles (box), 10th and 90th percentiles (whiskers), minimum and maximum (circles), and detection rate (green cross).

mass-to-charge ratios (m/z) of the target analytes, surrogates, and internal standards are summarized in Table S3. Detailed operational conditions of the instruments, chromatograms, and mass spectra of most PHCZs have been published elsewhere.⁶

Among the 27 analytes, 17 were previously detected in sediments of Lake Michigan.⁶ The previously observed UNC-8 was identified to be 136-BCZ by matching mass spectra and retention times with the now available authentic standard. UNC-16 was detected for the first time. On the basis of its mass spectrum, UNC-16 has a molecular ion cluster centered at m/z 402, and ions $[\text{Br}]^-$ (m/z 79) and $[\text{I}]^-$ (m/z 127); its most probable formula is $\text{C}_{12}\text{H}_6\text{NCIBrI}$.

Carbazole, 3-CCZ, 36-CCZ, 1368-CCZ, 2367-CCZ, 3-BCZ, 27-BCZ, 36-BCZ, 136-BCZ, 1368-BCZ, 1-B-36-CCZ, and 18-B-36-CCZ were quantified using an internal standard method. The UNCs were semiquantified based on the calibration curves of their analogues. Specifically, 27-BCZ was used for the quantification of UNC-3, 1-B-36-CCZ was used for UNC-1, UNC-5, and UNC-7; 136-BCZ was used for UNC-2, UNC-4, UNC-6, and UNC-10; and 1368-BCZ was used for UNC-9 and UNC-11 through UNC-16. All the Ponar grab samples, but not all core samples, were analyzed for all target PHCZs. In

addition, BDE209 and a suite of 39 PCBs were analyzed. Concentrations of “total PCBs” (t-PCBs) were estimated by doubling the sum of the 39 PCB congeners, based on the fractions of individual PCB congeners in Aroclors and the production volumes of individual Aroclors in the U.S. during 1957–1977.¹¹ These data are included in this paper wherever possible for comparison purposes. Detailed data for PBDEs and PCBs are to be reported elsewhere.

Quality Control. Two laboratory procedural blanks (Na_2SO_4) were analyzed along with sediment samples from each core, with one started from the freeze-drying (FD) and the other started from the extraction (PB). Two FD and two PB blanks were prepared for Ponar grab samples for each lake. Two or three replicates of trip blanks and field blanks from each sampling trip were also analyzed. More than 50 blanks were processed using the same laboratory procedures as for sediments. Concentrations of 27 individual target compounds in the blanks ranged from below detection limit (ND) to 0.38 ng/g (UNC-10 in a single blank sample) dry mass (dw), which were much lower than measured concentrations in the samples. No blank corrections were made. Surrogates chlordane-L (8 ng), F-BDE69 (4 ng), HxCDD-L (0.6 ng), F-BDE154 (8 ng),

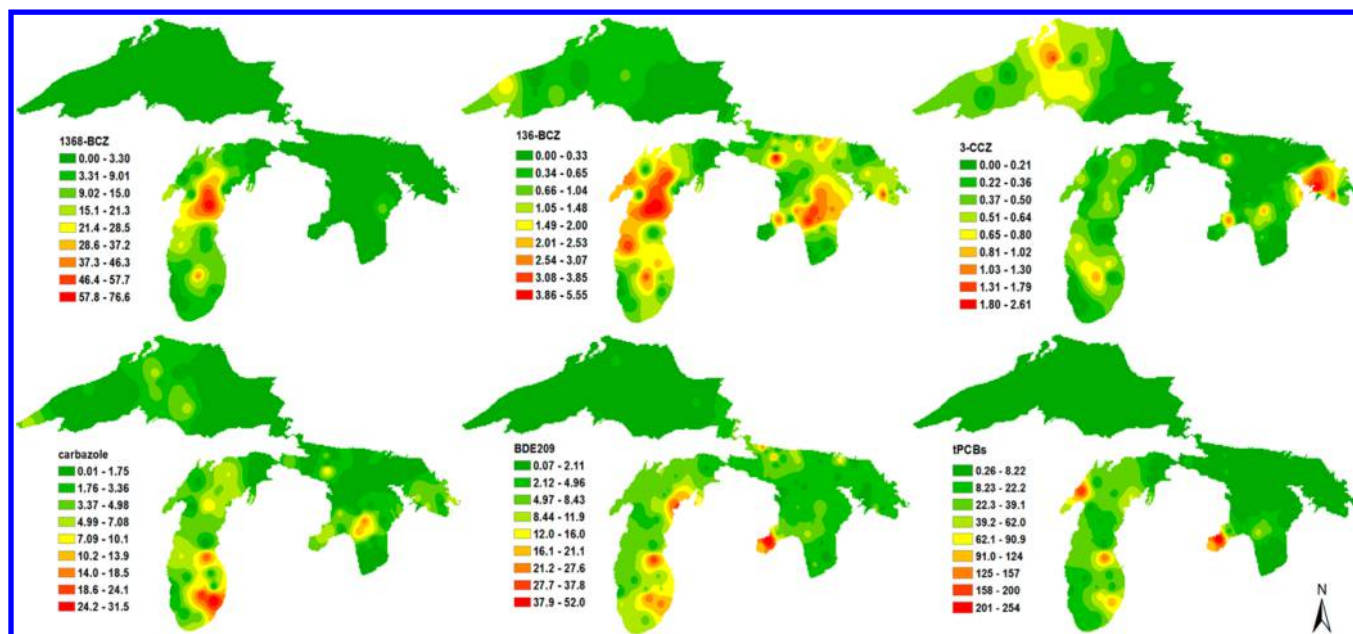


Figure 2. Spatial distribution of concentrations of selected PHCZ (ng/g dw) in Ponar grab samples of sediments from Lakes Michigan, Superior, and Huron. The three individual PHCZs were selected from Categories I, II, and III, respectively. Carbazole, BDE209, and t-PCBs are included for comparison. Maps were drawn using inverse distance weight (IDW) interpretation in the geostatistical analysis tool of ArcGIS 10.3 and the shapefile was made by extracting the Electronic Navigational Chart (ENC) data from the NOAA Office of Coast Survey.

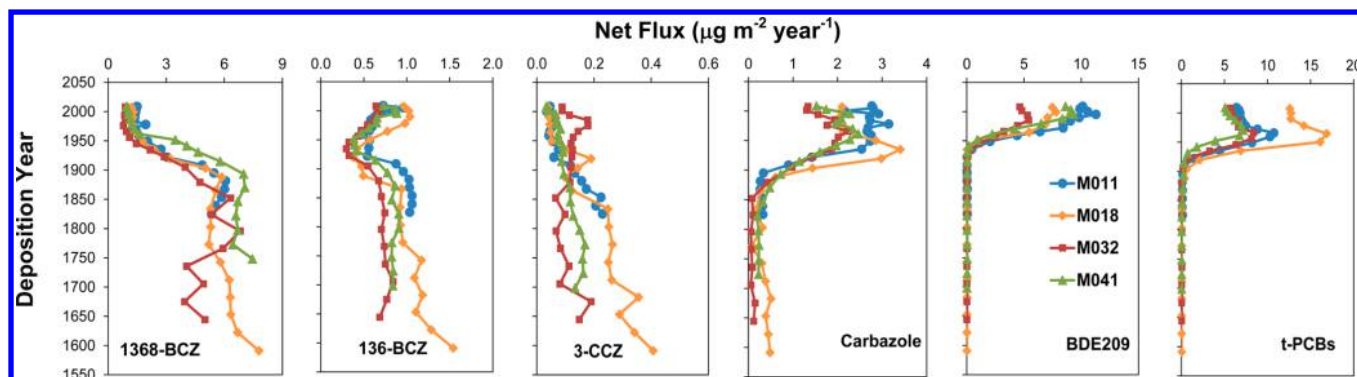


Figure 3. Temporal trends in net fluxes at four coring sites in Lake Michigan. The fluxes were estimated using eq 1 in Materials and Methods. Three individual PHCZs were selected from Categories I, II, and III, respectively. Carbazole, BDE209, and t-PCBs are included for comparison.

BeP-d12 (8 ng), and TBP-d27 (8 ng) were added to each sample before extraction, and their average recoveries \pm standard deviations were $87 \pm 13\%$ ($N = 157$), $96 \pm 24\%$ ($N = 469$), $116 \pm 58\%$ ($N = 92$), $108 \pm 9\%$ ($N = 39$), $95 \pm 40\%$ ($N = 538$), and $84 \pm 45\%$ ($N = 561$), respectively. One sample from each core and two samples from Ponar grabs for each lake were analyzed in duplicate, and the median relative percentage differences (RPDs) of the duplicate analyses for individual PHCZs ranged from 0 to 20%. In addition, two blanks (Na_2SO_4) were spiked with the 12 analytes for which chemical standards were available (8–32 ng each); and the average recoveries ranged from 55% to 123%. Instrument detection limits (based on three times the signal-to-noise ratio) ranged from 0.0017 ng/g (18-B-36-CCZ) to 0.0741 ng/g (carbazole) (Table S3).

Data Analysis. In data analysis, “non detect” data points were replaced with half of the detection limits for statistical calculations. Concentrations measured for sediment cores were used to estimate the following:

$$\text{Net flux}_i (\mu\text{g m}^{-2}\text{y}^{-1}) = C_i \times \text{MSR}/\text{FF} \times 10 \quad (1)$$

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

$$\begin{aligned} \text{Annual loading rate} (\text{kg y}^{-1}) \\ = \text{Median net flux} \times \text{Lake water surface area} \times 10^{-3} \end{aligned} \quad (3)$$

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

where C_i is the chemical concentration (ng g^{-1} dw), $\rho_{b,i}$ is the dry mass bulk density (g cm^{-3}), and d_i is the thickness (cm) of segment i . The MSR is in $\text{g cm}^{-2} \text{y}^{-1}$ and the FF is dimensionless. Recent net fluxes were estimated from concentrations in the uppermost segments of cores. The water surface areas of Lakes Michigan, Superior, and Huron are 57 800, 82 100, and 59 600 km^2 , respectively. Other constants are for unit conversions.

Statistical analyses were conducted using Microsoft Excel (2010) with StatPlus (version 5 for Mac OS). Pearson correlations were examined for log transformed concentrations in Ponar grabs and for estimated surface fluxes or inventories at the coring sites, with site- or sample-specific variables. Principal component analysis (PCA) from Minitab 17 (State College, PA) was used to examine the clustering of PHCZs. The inverse distance weight (IDW) interpretation in the geostatistical analysis tool of ArcGIS 10.3 (Redlands, CA) was used to illustrate the spatial distribution of PHCZs based on measured concentrations.

RESULTS AND DISCUSSION

Carbazole and 26 PHCZs were detected in the sediments of the upper Great Lakes (Table S3). In Ponar grab samples collected from 112 locations, the total concentrations of the 26 PHCZs (Σ_{26} PHCZs) ranged from <1 to 440 ng/g dry weight (dw) (Figure 1 and Table S4). From the measured concentrations in sediment cores, the net fluxes of individual and Σ_{26} PHCZs in each core segment and the inventories at each coring locations were calculated (Table S5). On the basis of these data, the total accumulation of Σ_{26} PHCZs in sediments of all three lakes was estimated to be 3200 tonnes, exceeding those of PCBs and PBDEs by orders of magnitude (Table S6). On the basis of the estimated total load in all three lakes (Table S6), the most abundant PHCZ congeners are UNC-12, UNC-3, UNC-10, 1368-BCZ, UNC-7, 36-BCZ, and UNC-9 (>100 tonnes each), followed by UNC-5, UNC-6, UNC-14, and UNC-11 (>50 tonnes each).

Representative spatial and temporal distribution patterns of selected PHCZs are illustrated in Figures 2 and 3, respectively. The results of PCA (Figure 4) showed that the first two

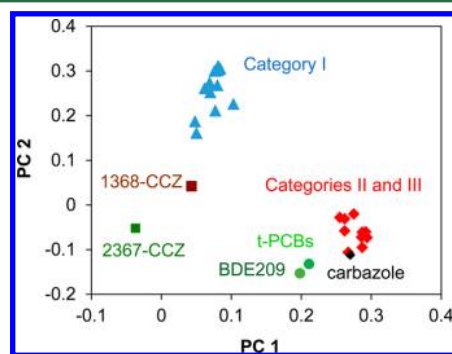


Figure 4. Principal component analysis. Loading plot of principal component (PC) scores for organic matter normalized concentrations of PHCZs in all samples (including both core and Ponar grab sediment, $N = 280$) from Lakes Michigan, Superior, and Huron. PC1 and PC2 account for 38% and 32% of the total variance, respectively.

principal components explained 70% of the total variance in the data (PC1:38%; PC2:32%). On the basis of the observations of the spatial and temporal patterns, as well as the PCA results, we classified PHCZs into three categories (Table S4) as discussed below.

Category I. Category I includes 13 PHCZs and these are 1368-BCZ and UNC-2, -4, -9, and -12 (containing only Br), plus UNC-1, -5, -7, and -11 (containing both Br and Cl), as well as UNC-13, -14, -15, and -16 (all containing iodine). The concentration range for 1368-BCZ in sediments of Lake Michigan (as high as 112 ng/g dw) was similar to that measured previously.⁷ Concentrations of all Category I PHCZs

are strongly correlated with each other by Pearson and Spearman correlation analyses, and are clustered on the PCA plot (Figure 4). Together, the load of this category comprises 64% of the Σ_{26} PHCZ load. In Lake Michigan, almost all Category I compounds were detected in the bottom segments of the 30-cm cores deposited around the 1600s (Figure 3), suggesting the estimated inventory of 886 tonnes (Table S4) could be a lower limit.

Concentrations of most Category I PHCZs were higher in Lake Michigan than in the other lakes, as shown by the spatial distribution of 1368-BCZ (Figure 2). For example, UNC-7 had a median concentration of 4 ng/g dw and a detection rate of nearly 100% in Lake Michigan, but it was barely detected in Lakes Superior and Huron. UNC-12 is an exception—it had a median concentration of 79 ng/g dw in Ponar grabs and its load accounted for >60% of the total load of Σ_{26} PHCZs in Lake Superior, while its median concentration in Lake Michigan was much lower (23 ng/g dw). In samples from Lake Huron, Category I PHCZs were detected less frequently and at lower concentrations than in those from Lakes Michigan and Superior. These differences may not be surprising given that biogeochemical conditions differ among the lakes, and most naturally occurring organohalogenes are unique to individual organisms which tend to be regiospecific.¹

In Lake Michigan, Category I PHCZs share a similar time trend as exemplified by that of 1368-BCZ (Figure 3). It features a relatively high and constant concentration in deeper core segments dated before 1900, followed by a rapid decrease to lower concentrations extending through to the present surface sediments. Although 1368-BCZ was proposed to result from historical industrial production of indigo dye,²³ its high flux in the 1600s is inconsistent with an anthropogenic source. Decreases in sediment PHCZ levels occurred around 1900, a time period that saw rapid urbanization and industrialization in the region. Large scale changes in land cover occurred due to agricultural development, with virgin northern mesic forests, which had dominated in presettlement era, largely replaced by nonforested land.³⁰ Certain pollen species decreased coupled with sharp rises of ragweed (*Ambrosia*) and other plant pollens in sediments of regional lakes.³¹ These changes in land cover could have altered the source and characteristics of the natural organic matter (NOM) in Lake Michigan and other Great Lakes.

Another salient observation for Category I PHCZs is the strong dependence of concentrations on water depth at sampling locations in Lakes Michigan and Huron. The dependence is best evident when both the concentration and water depth are expressed in logarithms (Figure 5A). In Lake Superior, the dominant congener, UNC-12, in Ponar grabs showed moderate dependence on water depth ($r = 0.45$ and $p = 0.04$); but most others did not, due likely to their low detection rates and concentration levels. In Ponar grabs from all three lakes ($N = 112$), the regressions are highly significant ($r = 0.67$ and $p = 10^{-21}$ for the category, and r range of 0.4–0.8 and p range of 10^{-5} – 10^{-30} for individuals). This is not the case for t-PCBs ($r = -0.017$, $p = 0.86$) and BDE209 ($r = -0.12$, $p = 0.22$), which may indicate different sources between these man-made pollutants and Category I PHCZs. The correlation of Category I PHCZ concentrations with TOC concentrations was weak for Ponar grab samples from Lake Michigan ($r = 0.35$, $p = 0.07$, $N = 29$); however, a significant negative correlation with TOC was found for the net input flux at the core surface ($r = -0.82$, $p = 6 \times 10^{-4}$, $N = 13$) of Category I PHCZs. NOM,

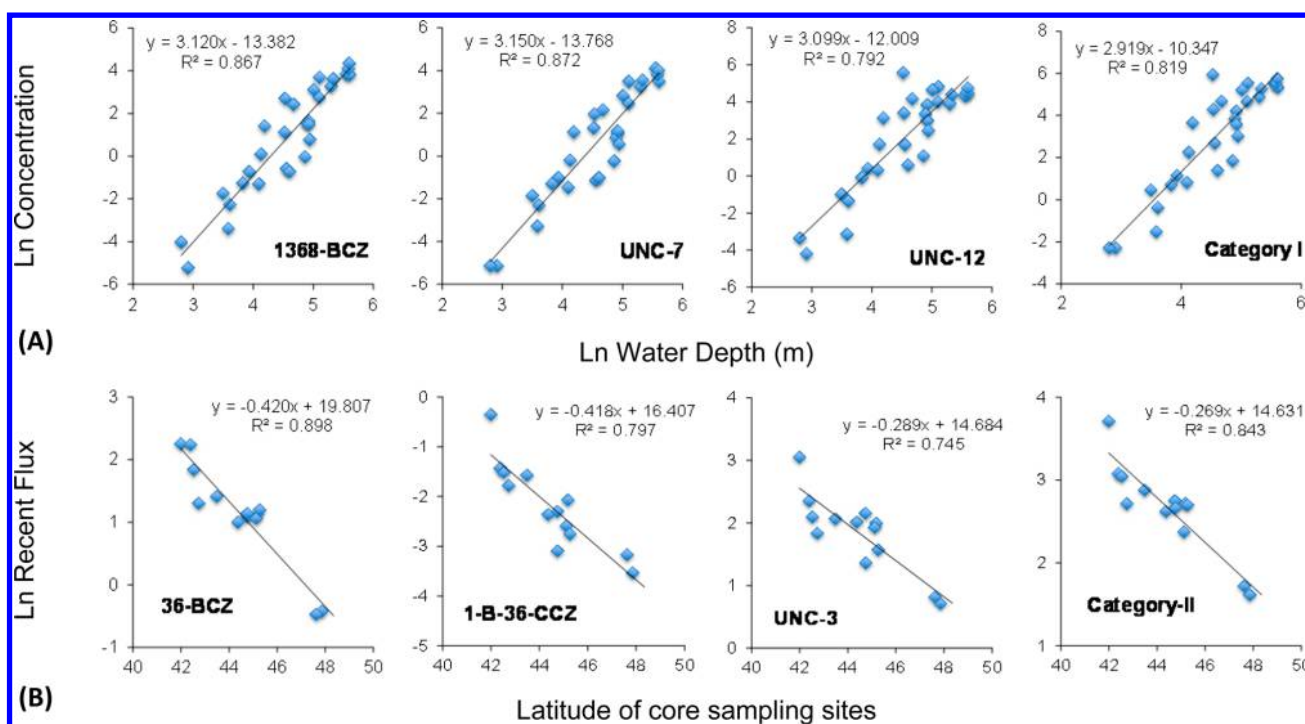


Figure 5. Regression analyses for selected PHCZs in sediment samples. (A) Dependence of concentrations (ng/g dw) on water depth of selected Category I PHCZs in Ponar grab sediment samples from Lake Michigan ($N = 29$). (B) Dependence of recent flux ($\mu\text{g}/\text{cm}^2 \text{y}^{-1}$) on latitude of sampling sites of selected Category II PHCZs in samples from Lakes Michigan, Superior, and Huron ($N = 13$). All regressions shown are statistically significant ($p < 0.01$).

either lacustrine or terrigenous in origin, is continuously altered by microbes during settling through lake water and after burial in sediments.^{32–34} In Lake Michigan, algal organic carbon largely diminishes when it settles to >100 m in water, while terrestrial NOM is more refractory.^{33,34} Changes in chemical composition of the NOM occur, and some chemicals (e.g., perylene, a polycyclic aromatic hydrocarbon) have been considered as a product of the diagenesis of NOM, while some chemical groups (e.g., fatty acids) have been used as NOM biomarkers.^{32–34} Various alkaloids, particularly carbazole alkaloids, in plant matter³⁵ could be biogenic precursors of PHCZs. Carbazole derivatives are the dominant form of nitrogen in petroleum, and have been used as tracers for petroleum migration.³⁶ With regard to halogen sources, the Michigan Basin and Illinois Basin have rich brine sources in deep rock formations, as evidenced by the numerous salt seeps and springs in the region.³⁷ Given that natural halogenation of organics favors iodine and bromine over chlorine, it is not surprising that most Category I PHCZs are brominated and iodinated. We also note here the lack of known industrial sources for most mixed halogenated carbazoles (particularly those having all three halogens). Combining these observations, we conclude that the origin of Category I PHCZs is predominantly natural.

Category II. Category II includes 36-BCZ, 136-BCZ, UNC-3, UNC-6, UNC-10, and 1-B-36-CCZ. These account for about 30% of Σ_{26} PHCZs in the total sediment load of the three lakes. These PHCZs have no more than three halogen atoms in their molecular formulas. We consider these compounds to be of emerging concern because their deposition with sediments has been increasing in recent decades, in most cases since the 1950s. Temporal trends exhibited by most Category II PHCZs, as shown for 136-BCZ in Figure 3, are similar to those of

Category I in having relatively high and consistent inputs before 1900 followed by decreases. In contrast to Category I, however, decreases of Category II compounds after the late 19th century did not last long; increases in recent decades are clearly observed in the cores of this work.

Compared with Category I, concentrations of PHCZs in Category II are more evenly distributed across the upper Great Lakes with the median concentrations in Ponar grabs differing within 1 order of magnitude among the three lakes. Exponential declines of inventories and fluxes with increasing latitude (in fewer cases, with longitude) have been found for many industrial pollutants such as PCBs, PBDEs, and emerging halogenated flame retardants in the Great Lakes basin. This trend is attributed to the human population distribution pattern in the region and the occurrence of air deposition following long-range atmospheric transport.^{10–13} The regressions of logarithm recent fluxes against latitude are strong for BDE209 ($r = -0.89$, $p < 10^{-8}$) and PCBs ($r = -0.76$, $p < 10^{-4}$) in the surface core sediment samples of this study ($N = 24$). Similarly, the recent fluxes exhibit a strong log-linear dependence on the latitude of the sampling locations over the three lakes for Category II PHCZs as a group ($r = -0.92$, $p = 10^{-5}$), as well as for individual compounds having two bromines (36-BCZ and UNC-3) and 1-B-36-CCZ (Figure 5-B).

Category III. Category III includes 3-CCZ, 3-BCZ, and 36-CCZ, together contributing about 2% of Σ_{26} PHCZs. We observed increasing concentrations with increasing sediment depth for all category III PHCZs as shown in Figure 3 for 3-CCZ, suggesting that these smaller molecular weight PHCZs could be formed as dehalogenation products of heavier PHCZs in sediment or underwent downward diffusion to deeper sediment. Dehalogenation is known to have occurred in sediment where anaerobic conditions prevail. For example,

PCBs at heavily contaminated sites show a clear sign of dechlorination, as the fractions of less chlorinated homologues increase with depth of sediments.^{11,38}

Evidence of natural origin for some PHCZs in Categories II and III has been reported. For example, 3-CCZ has been isolated from bovine urine,¹⁸ and 36-BCZ and other dihalocarbazoles from marine cyanobacteria.^{15,17} Cyanobacterium *Tolypothrix tjipana-sensis* was reported to produce chlorine-containing alkaloids with carbazole substructure.³⁹ However, anthropogenic activity cannot be excluded as a source for these PHCZs in the environment. Category II and III PHCZs cluster closely and in proximity to PCBs and BDE209 in the PCA loading plot (Figure 4), suggesting an anthropogenic impact. Literature reporting halogenation of carbazole derivatives dates back to the early 1900s or earlier;⁴⁰ halogenated carbazoles have been involved in the manufacture of various industrial products such as dyes, pharmaceuticals, organic semiconductors, and others. At present, all known Categories II and III PHCZs are commercially available except 1-B-36-CCZ.^{41,42} In sediment from the Saginaw River basin, 3-CCZ and 36-CCZ were found at much higher concentrations than highly brominated carbazoles,²² and similar compounds were found in sediment near Kavala City, Greece;¹⁶ both areas are known for diverse industrial activities. All Categories II and III PHCZs were also found in German coastal waters, with brominated congeners more frequently detected in marine than in river sediments.¹⁴ Complete homologues of CCZs (up to fully chlorinated octachlorocarbazole) have been detected near sites of chlorine production.²¹ Even for Category I PHCZs such as 1368-BCZ, industrial sources including indigo dye manufacturing, as detailed by Parette et al.,²³ cannot be excluded although they are unlikely to outweigh natural production in the upper Great Lakes.

Carbazole and Other PHCZs. Carbazole is known to have dual origins as it is naturally occurring but also has been synthesized to meet the needs of industry since the 1900s.⁴³ Carbazoles and benzcarbazoles are the dominant forms of nitrogen in petroleum and are rich in coal.⁴⁴ Since it was first discovered in coal tar in 1872,^{45,46} carbazole has been found with numerous applications primarily in the syntheses of dye and vinylcarbazole polymers.^{43,45} It is also one of the major constituents of commercial anthracene oil. Carbazole is listed as a high production volume (HPV) chemical by the Organization for Economic Co-operation and Development (OECD).⁴⁷ In addition, combustion of biomass and incineration of waste also produce carbazole.⁵

In this work, carbazole was detected in all sediment cores and almost all (97%) of the Ponar grab samples. The chronological profile (Figure 3) shows that the flux of carbazole to sediment has dramatically increased since the late 19th century, in accordance with the discovery of carbazole in the 1870s. In contrast to most PHCZs discussed above, the deposition of carbazole to sediment peaked around the 1950s, and decreased in recent decades. Spatially, carbazole had significantly higher concentrations at sites in southeastern Lake Michigan than at other sites (Figure 2). The highest level was observed in the Ponar grabs at M009 (32 ng/g dw) and M011 (25 ng/g dw), which were similar to the highest (40 ng/g dw) reported for the Saginaw River drainage basin, MI,²² but 500–1000 times lower than that in sediment from a creosote oil contaminated site in Eagle Harbor, Puget Sound, WA.⁴⁸ Across the three lakes we studied, the logarithms of carbazole concentrations at core surface, inventory, and the recent net flux are all negatively

correlated with the latitude of the sampling sites ($p < 0.05$). In the PCA loading plot (Figure 4), carbazole is located within the cluster including PHCZ Categories II and III and near PCBs and BDE209. All these observations indicate that anthropogenic sources outweigh natural origin for carbazole detected in the environment.

1368-CCZ and 2367-CCZ are not categorized in this work, as their concentrations are relatively low and the trends are not clear. They are separated from each other and other compounds in Figure 4. 1368-CCZ was found with elevated concentrations in sediment collected near a dye factory.² Also not categorized are 27-BCZ, which was not detected in any samples of this work, and 18-B-36-CCZ, which has been detected in a number of sediments from streams across southern Ontario¹⁹ but had a low median concentration (<0.03 ng/g dw) and showed no trend with depth of sediment cores in our study of the upper Great Lakes.

The large quantity and variety of PHCZs in sediments of the Great Lakes suggest potentially far-reaching implications. The dominant sources are likely to differ among individual PHCZs, and they are also location- and time- dependent. This work not only shows the complexity of the sources, but also illustrates the intertwinement of natural and human impacts. Factors including vegetation that largely determines the composition of NOM, microbes that halogenate, geologic and geographic conditions suitable for biohalogenation, and historical to present human activities, all have acted to shape the spatial and time trends of PHCZs in the Great Lakes.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b06128.

Map, coordination, and water depth of sampling sites; cutting scheme and dating data of core sediments; instrument conditions of target analytes; concentrations, fluxes, inventories, and loads of target compounds in sediment samples (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

**SPATIAL AND TEMPORAL TRENDS OF POLYHALOGENATED CARBAZOLES IN
SEDIMENTS OF UPPER GREAT LAKES — INSIGHTS INTO THEIR ORIGIN**

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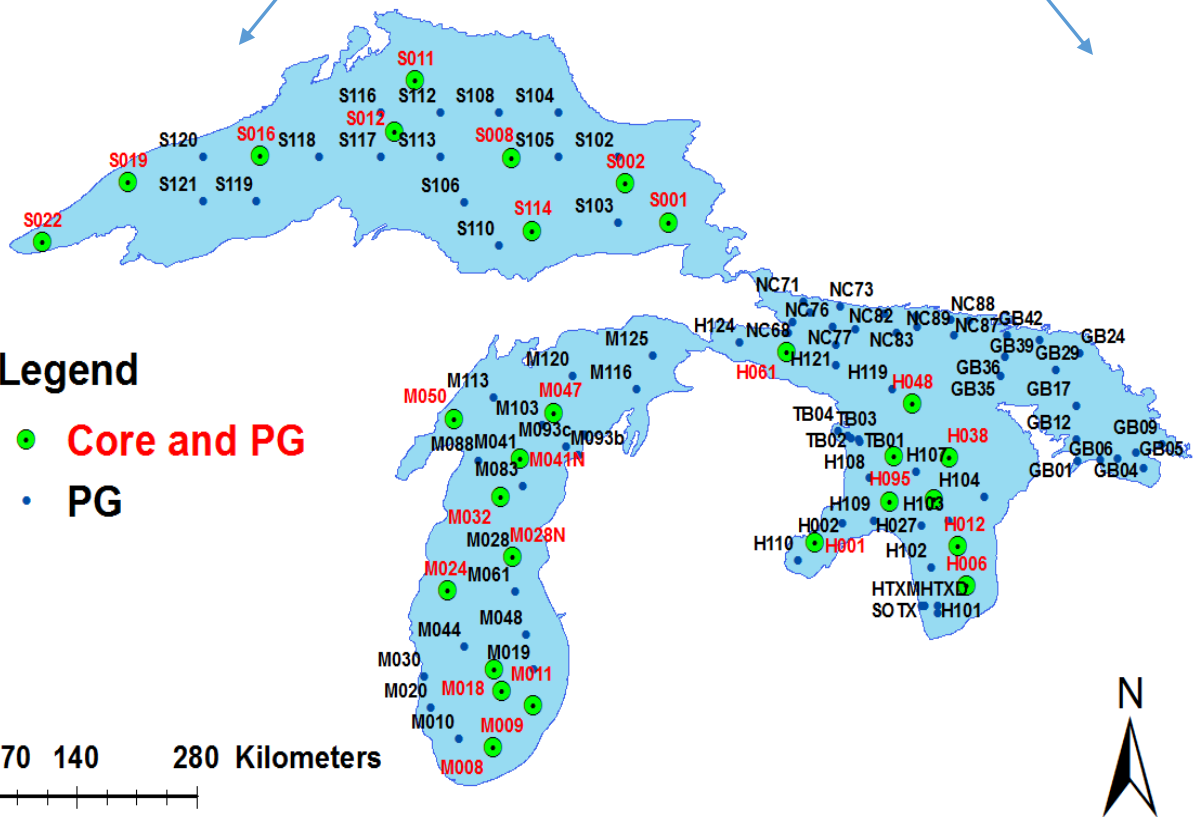


Figure S1. Sampling sites. PG = Ponar grab; labels for the Ponar grab sites are not all shown. The source of the top map is ESRI. The shape file for the upper Great Lakes (bottom) was made by extracting the Electronic Navigational Chart (ENC) data from the NOAA Office of Coast Survey.

Table S1. Sites of sediment sample collection. Location and water depth (m) 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).

Site	Latitude	Longitude	Depth	Site	Latitude	Longitude	Depth	Site	Latitude	Longitude	Depth	Site	Latitude	Longitude	Depth
M008	41.9842	-87.0142	64	S001	46.9930	-85.1612	98	H001	43.9374	-83.6142	12.7	GB09	44.8716	-79.9675	30
M009	42.3850	-86.5915	60	S002	47.3603	-85.6208	158	H002	44.1249	-83.3324	18.8	GB12	44.9202	-80.8748	91
M010	42.0662	-87.3792	50	S008	47.6058	-86.8177	309	H006	43.5265	-82.0185	62	GB17	45.2449	-80.8742	80
M011	42.5283	-86.9220	160	S011	48.3438	-87.8250	236	H012	43.9007	-82.1130	99	GB24	45.7457	-80.8394	31
M018	42.7338	-86.9995	161	S012	47.8553	-88.0418	245	H027	44.0999	-82.5025	65	GB29	45.5836	-81.0830	44
M019	42.7335	-86.5833	90	S016	47.6212	-89.4633	185	H032	44.3542	-82.3596	94	GB35	45.5257	-81.6705	37
M020	42.3665	-87.6672	45	S019	47.3703	-90.8535	193	H037	44.7619	-82.7836	76	GB36	45.7082	-81.6201	54
M024	43.4830	-87.4882	146	S022	46.8002	-91.7508	56	H038	44.7507	-82.2024	166	GB39	45.8729	-81.2584	27
M028	43.8003	-86.7998	133	S102	47.6173	-85.6973	95	H048	45.2614	-82.5912	183	GB42	45.9125	-81.5954	26
M028N	43.7998	-86.7997	133	S103	46.9838	-85.6972	169	H054	45.6338	-83.4028	142	NC68	46.0413	-83.8536	16
M030	42.6600	-87.7382	18	S104	48.0382	-86.3217	194	H061	45.7498	-83.9164	122	NC70	46.1365	-83.6720	22
M032	44.3715	-86.9333	250	S105	47.6177	-86.3217	83	H095	44.3328	-82.8326	70	NC71	46.2335	-83.7462	36
M041	44.7367	-86.7215	265	S106	47.1807	-87.3183	225	H101	43.2690	-82.3349	31	NC73	46.1869	-83.3552	19
M041N	44.7375	-86.7221	266	S108	48.0392	-86.9493	233	H102	43.7059	-82.4039	53	NC76	46.0003	-83.4329	60
M044	42.9528	-87.3155	90	S110	46.7735	-86.9495	142	H103	44.1449	-82.2209	99	NC77	45.9704	-83.1977	80
M047	45.1783	-86.3745	195	S112	48.0393	-87.5733	222	H104	44.3720	-81.8380	132	NC79	46.1230	-82.8867	26
M048	43.0585	-86.6630	104	S113	47.6177	-87.5730	176	H107	44.6154	-82.5541	66	NC82	45.9369	-82.7588	28
M050	45.1165	-87.4165	32	S114	46.9095	-86.5980	409	H108	44.5574	-83.0502	55	NC83	46.0000	-82.5497	31
M061	43.4742	-86.7847	133	S116	48.0392	-88.2007	261	H109	44.1502	-83.0000	35	NC84	46.0917	-82.5564	36
M083	44.4737	-86.7060	263	S117	47.6175	-88.2007	277	H110	43.7723	-83.8037	7	NC87	46.0611	-82.1971	41
M088	44.7187	-87.1740	92	S118	47.6175	-88.8420	194	H118	44.9168	-83.1660	46	NC88	46.0553	-81.9998	37
M093a	44.9622	-86.0552	97	S119	47.1955	-89.5048	202	H119	45.3977	-82.8107	135	NC89	45.9165	-82.1617	39
M093b	44.7712	-86.1168	58	S120	47.6185	-90.0712	183	H121	45.8189	-83.4039	45	TB01	44.8996	-83.1496	50
M093c	44.8562	-86.2430	126	S121	47.1955	-90.0727	150	H123	45.9365	-83.9059	30	TB02	44.9387	-83.2405	31
M103	45.0623	-86.4918	201					H124	45.8512	-84.4216	57	TB03	44.9552	-83.2770	19
M113	45.3267	-87.0090	36					GB01	44.7178	-80.8564	93	TB04	44.9997	-83.3742	10
M116	45.4014	-85.4997	36					GB03	44.7253	-80.6170	34	SOTXD	43.3399	-82.3335	37
M120	45.5288	-86.1708	136					GB04	44.6457	-80.1673	59	SOTXM	43.3398	-82.4668	20
M125	45.7228	-85.3314	16					GB05	44.7969	-80.2431	60	SOTXS	43.3397	-82.4991	12
								GB06	44.7382	-80.4360	88				

a. The data in this table was previously published.¹

Table S2. Sediment core sectioning scheme and the sedimentation rates and focus factors at core collection sites

Site ID	Core Sectioning Scheme	Selected Dating Model ^a	Sedimentation Rate (g/cm ² /yr)	Focus Factor
M008	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.	CRS 1-slope	0.021	0.49
M009		CRS 1-slope	0.065	2.2
M011		CRS 1-slope	0.041	3.0
M018		CRS 1-slope	0.018	1.5
M024		CRS 1-slope	0.019	2.0
M028		Not datable	---	0.30
M032		CRS 1-slope	0.018	2.1
M041		CRS 1-slope	0.022	2.1
M047		CRS 1-slope	0.031	2.6
M050		CRS and CIC 2-slope	0.043 (0-7 cm) 0.020 (7-25 cm)	2.9
S001		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.	Not datable	---
S002	CRS 1-slope		0.0068	0.82
S008	CRS 1-slope		0.0067	0.76
S011	CRS 1-slope		0.015	2.5
S012	CRS 1-slope		0.0098	1.8
S016	CRS 1-slope		0.0074	1.0
S019	CRS 1-slope		0.0088	0.62
S022	CRS 2-slope		0.017 (0-4 cm) 0.025 (4-25 cm)	0.61
S114	Not datable		---	0.63
H001	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.	CIC 1-slope	0.16	3.2
H006		CRS 2-slope	0.032 (0-10 cm) 0.0083 (10-30 cm)	2.2
H012		CIC 1-slope	0.057	3.5
H032		CRS 1-slope	0.044	3.2
H037		Not datable	---	0.87
H038		CRS 1-slope	0.0087	0.89
H048		CRS 1-slope	0.017	1.6
H061		CRS 1-slope	0.0063	0.61
H095		CRS 1-slope	0.014	1.1

a. CRS = constant rate of sedimentation. CIC = constant initial concentration.²

Table S3. Carbazole and halogenated carbazoles analyzed in this work

Abbrev.	Full name	Formula	Quant. ion or transition	Qual. ion or transition	Other ion	IDL (ng/g) ^a
Carbazole	Carbazole	C ₁₂ H ₉ N	166.8→139 (33) ^b	166.8→115 (37) ^b	-	0.0741
3-CCZ	3-monochloro carbazole	C ₁₂ H ₈ NCI	200.8→166 (21) ^b	200.8→140 (39) ^b	-	0.0043
36-CCZ	3,6-dichloro carbazole	C ₁₂ H ₇ NCI ₂	234.7→164 (41) ^b	234.7→200 (23) ^b	-	0.0346
1368-CCZ	1,3,6,8-tetrachloro carbazole	C ₁₂ H ₅ NCI ₄	269	267	-	0.0027
2367-CCZ	2,3,6,7-tetrachloro carbazole	C ₁₂ H ₅ NCI ₄	305	303	-	0.0080
3-BCZ	3-monobromo carbazole	C ₁₂ H ₈ NBr	244.7→166 (23) ^b	244.7→139 (41) ^b	-	0.0080
27-BCZ	2,7-dibromo carbazole	C ₁₂ H ₇ NBr ₂	325	79	-	0.0160
36-BCZ	3,6-dibromo carbazole	C ₁₂ H ₇ NBr ₂	325	79	-	0.0316
136-BCZ	1,3,6-tribromo carbazole	C ₁₂ H ₆ NBr ₃	405	79	325	0.0400
1368-BCZ	1,3,6,8-tetrabromo carbazole	C ₁₂ H ₅ NBr ₄	481	79	403	0.0107
1-B-36-CCZ	1-bromo-3,6-dichlorocarbazole	C ₁₂ H ₆ NCI ₂ Br	315	79	-	0.0118
18-B-36-CCZ	1,8-dibromo-3,6-dichlorocarbazole	C ₁₂ H ₄ NCI ₂ Br ₂	393	315	79	0.0017
UNC-1	unknown-1	C ₁₂ H ₆ NCIBr ₂	79	359	-	0.0118
UNC-2	unknown-2	C ₁₂ H ₆ NBr ₃	405	79	325	0.0400
UNC-3	unknown-3	C ₁₂ H ₇ NBr ₂	325	79	-	0.0160
UNC-4	unknown-4	C ₁₂ H ₆ NBr ₃	405	79	325	0.0400
UNC-5	unknown-5	C ₁₂ H ₅ NCIBr ₃	79	439		0.0118
UNC-6	unknown-6	C ₁₂ H ₆ NBr ₃	405	79	325	0.0400
UNC-7	unknown-7	C ₁₂ H ₅ NCIBr ₃	79	439		0.0118
UNC-9	unknown-9	C ₁₂ H ₅ NBr ₄	481	79	403	0.0107
UNC-10	unknown-10	C ₁₂ H ₆ NBr ₃	405	79	325	0.0400
UNC-11	unknown-11	C ₁₂ H ₄ NCIBr ₄	79	439	517	0.0107
UNC-12	unknown-12	C ₁₂ H ₄ NBr ₅	481	79	560	0.0107
UNC-13	unknown-13	C ₁₂ H ₄ NCIBr ₃ I	79	127	439	0.0107
UNC-14	unknown-14	C ₁₂ H ₄ NBr ₄ I	481	127	608	0.0107
UNC-15	unknown-15	C ₁₂ H ₄ NBr ₃ I ₂	79	127	528	0.0107
UNC-16	unknown-16	C ₁₂ H ₄ NCIBrI	79	127	405	0.0107

a. Instrument detection limit (IDL) with the use of 5 g sediment and 60 µL GC injection.

b. Measured by gas chromatography triple quadruple mass spectrometry with electron impact ion source, quantification and qualification ions: precursor ion→ product (collision energy).

Table S4. Medians of measured concentrations (ng/g dry weight)

Abbrev.	Cat. ^a	Ponar surface grab				Core top segment			
		Michigan (N = 29)	Superior (N = 24) ^b	Huron (N = 59)	All Lakes (N = 112) ^c	Michigan (N = 10)	Superior (N = 2) ^d	Huron (N = 3) ^d	All Lakes (N = 15)
Carbazole	-	3.48	0.89	0.74	1.15	16.3	2.54	2.86	2.90
3-CCZ	III	0.39	0.40	0.07	0.17	0.34	0.54	0.19	0.28
36-CCZ	III	2.03	2.22	0.67	1.02	3.26	1.40	1.10	1.59
1368-CCZ	n.a.	0.03	0.02	<0.003	0.01	0.03	0.02	0.02	0.03
2367-CCZ	n.a.	<0.01	0.07	<0.01	<0.01	<0.01	0.31	<0.01	<0.01
3-BCZ	III	0.81	0.13	0.08	0.17	0.80	0.36	0.49	0.51
27-BCZ	n.a.	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
36-BCZ	II	7.74	2.07	2.74	3.47	29.5	10.4	31.9	28.6
136-BCZ	II	0.92	0.43	0.61	0.54	5.87	2.00	22.0	6.07
1368-BCZ	I	4.06	0.53	0.04	0.12	4.72	0.55	1.37	1.80
1-B-36-CCZ	II	0.72	0.15	0.11	0.16	1.07	0.56	0.46	0.81
18-B-36-CCZ	n.a.	0.03	0.01	0.01	0.01	0.03	0.01	0.02	0.02
UNC-1	I	0.34	<0.01	<0.01	<0.01	0.30	0.10	0.19	0.19
UNC-2	I	0.05	<0.04	<0.04	<0.04	0.07	<0.04	<0.04	0.04
UNC-3	II	33.4	10.1	7.18	12.6	55.9	34.7	39.9	46.3
UNC-4	I	0.27	0.24	<0.04	0.09	0.23	0.16	<0.04	0.20
UNC-5	I	3.42	0.11	<0.01	0.04	3.12	0.07	0.78	1.49
UNC-6	II	1.05	2.93	0.30	0.67	3.80	6.44	6.79	5.85
UNC-7	I	2.91	<0.01	<0.01	<0.01	4.08	<0.01	1.11	1.73
UNC-9	I	2.38	4.64	0.04	0.12	2.02	3.56	0.40	1.73
UNC-10	II	15.2	12.7	2.10	5.99	24.2	31.3	32.3	27.2
UNC-11	I	1.43	0.10	<0.01	0.04	1.55	0.19	0.57	0.86
UNC-12	I	22.8	79.4	0.09	0.65	19.5	64.1	8.16	13.7
UNC-13	I	0.09	<0.01	<0.01	<0.01	0.20	<0.01	0.05	0.09
UNC-14	I	0.50	<0.01	<0.01	<0.01	1.26	0.09	0.45	0.71
UNC-15	I	<0.01	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01
UNC-16	I	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Category I		38.6	61.0	0.32	1.55	39.5	68.8	14.1	24.8
Category II		55.1	30.8	18.7	27.1	127	85.5	143	125
Category III		3.29	3.45	0.81	1.70	4.28	2.21	2.26	2.61
Σ ₂₆ PHCZs		112	122	22.6	38.0	176	2.21	3.24	59.2
BDE209		6.51	0.79	2.68	2.67	57.4	11.6	34.9	29.8
tPCBs		11.9	1.16	2.90	2.80	56.5	6.84	16.9	15.2

a. Category (see text), "n.a." means not able to categorize due to low concentrations and/or detection rate; b. N=21 for Cat I compounds; c. N=109 for Cat I compounds; d. The minimum number of cores analyzed for Lakes Superior and Huron for all PHCZs, all cores (N = 9 in each of the two lakes) were analyzed for carbazole, 3-CCZ, 36-CCZ and 3-BCZ.

Table S5. Medians of estimated recent depositional fluxes and inventories at coring sites^a

Abbrev.	Cat.	Recent depositional flux ($\mu\text{g}/\text{cm}^2\text{-y}$)				Inventories (ng/cm^2)			
		Michigan	Superior	Huron	All Lakes	Michigan	Superior	Huron	All Lakes
Carbazole	-	1.81	0.20	0.32	0.36	57.6	6.89	24.6	24.3
3-CCZ	III	0.04	0.05	0.03	0.04	8.51	2.43	3.38	4.61
36-CCZ	III	0.42	0.19	0.18	0.20	28.1	11.3	20.4	20.4
1368-CCZ	n.a.	<0.01	<0.01	0.03	<0.01	0.24	0.37	2.18	0.30
2367-CCZ	n.a.	<0.01	0.02	<0.01	<0.01	0.03	6.65	1.75	0.05
3-BCZ	III	0.09	0.04	0.06	0.05	14.4	0.66	5.99	6.67
27-BCZ	n.a.	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
36-BCZ	II	3.68	0.64	3.21	3.12	121	33.9	33.2	96.9
136-BCZ	II	0.67	0.13	2.82	0.67	46.0	5.71	25.2	31.3
1368-BCZ	I	0.89	0.03	0.14	0.42	184	5.84	43.5	82.6
1-B-36-CCZ	II	0.17	0.04	0.05	0.10	9.38	2.16	2.23	7.47
18-B-36-CCZ	n.a.	<0.01	<0.01	<0.01	<0.01	0.30	0.11	0.21	0.28
UNC-1	I	0.04	0.01	0.02	0.04	21.7	0.52	6.31	7.60
UNC-2	I	0.01	<0.01	<0.01	0.01	1.83	0.31	1.24	1.24
UNC-3	II	7.89	2.15	4.35	7.36	397	153	147	249
UNC-4	I	0.02	0.01	0.04	0.02	12.5	13.5	9.13	10.6
UNC-5	I	0.46	<0.01	0.11	0.24	91.1	3.63	49.6	56.0
UNC-6	II	0.53	0.40	0.72	0.53	41.6	44.9	40.3	41.9
UNC-7	I	0.86	<0.01	0.12	0.38	170	0.38	61.3	61.3
UNC-9	I	0.25	0.22	0.06	0.21	44.4	77.4	22.5	48.4
UNC-10	II	3.21	1.95	3.42	3.16	184	183	138	177
UNC-11	I	0.22	0.01	0.10	0.14	63.4	0.81	23.0	43.7
UNC-12	I	2.65	3.98	0.89	2.65	731	967	300	718
UNC-13	I	0.04	<0.01	0.01	0.02	10.3	0.06	4.88	5.82
UNC-14	I	0.22	0.01	0.08	0.13	56.8	1.07	29.8	37.4
UNC-15	I	<0.01	<0.01	<0.01	<0.01	0.70	0.06	0.22	0.56
UNC-16	I	<0.01	<0.01	<0.01	<0.01	0.81	0.06	0.07	0.39
Cat-I		5.65	4.28	1.57	4.56	1532	1071	556	1240
Cat-II		15.7	5.30	14.6	15.1	854	423	377	601
Cat-III		0.55	0.30	0.32	0.35	47.8	14.3	28.9	32.7
$\Sigma_{26}\text{PHCs}$		22.9	9.88	16.5	20.2	2396	1598	972	1954
BDE209		8.49	1.33	4.89	4.41	69.4	4.15	28.2	24.2
tPCBs		9.65	0.66	2.23	2.79	169	4.75	44.1	34.0

a. The estimates should be interpreted with caution, especially for Lakes Huron and Superior due to the limited number of cores analyzed, and for all UNCs that were only semi-quantified due to the lack of chemical standards.

Table S6. Estimated total loads and recent annual loading

Abbrev.	Cat.	Total load (tonne) ^a				Recent annual loading (kg/yr) ^a			
		Michigan	Superior	Huron	All Lakes	Michigan	Superior	Huron	All Lakes
Carbazole	-	33.3	5.66	14.7	53.6	105	16.4	19.3	140
3-CCZ	III	4.92	2.00	2.02	8.93	2.49	4.24	1.60	8.33
36-CCZ	III	16.3	9.27	12.2	37.7	24.0	15.6	10.8	50.4
1368-CCZ	n.a.	0.14	0.31	1.30	1.74	0.27	0.12	1.95	2.33
2367-CCZ	n.a.	0.02	5.46	1.04	6.52	0.03	1.59	0.02	1.65
3-BCZ	III	8.35	0.54	3.57	12.5	5.22	3.08	3.46	11.8
27-BCZ	n.a.	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
36-BCZ	II	70.1	27.8	19.8	118	213	52.5	191	457
136-BCZ	II	26.6	4.69	15.0	46.3	38.6	10.5	168	217
1368-BCZ	I	106	4.80	25.9	137	51.3	2.84	8.46	62.6
1-B-36-CCZ	II	5.42	1.77	1.33	8.52	9.73	2.92	3.25	15.9
18-B-36-CCZ	n.a.	0.17	0.09	0.12	0.39	0.20	0.06	0.11	0.36
UNC-1	I	12.6	0.43	3.76	16.8	2.41	0.57	1.12	4.11
UNC-2	I	1.06	0.26	0.74	2.06	0.54	0.17	0.12	0.83
UNC-3	II	230	126	87.3	442	456	177	259	892
UNC-4	I	7.22	11.1	5.44	23.8	1.26	0.71	2.15	4.12
UNC-5	I	52.6	2.98	29.5	85.2	26.6	0.35	6.75	33.7
UNC-6	II	24.1	36.9	24.0	85.0	30.5	32.8	42.8	106
UNC-7	I	98.5	0.31	36.5	135	49.7	0.03	7.03	56.7
UNC-9	I	25.7	63.6	13.4	103	14.4	17.8	3.6	35.9
UNC-10	II	106	151	82.3	339	185	160	204	549
UNC-11	I	36.6	0.67	13.7	51.0	12.8	1.06	6.05	19.9
UNC-12	I	422	794	179	1395	153	327	53.1	534
UNC-13	I	5.94	0.05	2.91	8.89	2.29	0.03	0.34	2.65
UNC-14	I	32.8	0.88	17.8	51.5	12.6	0.41	4.78	17.8
UNC-15	I	0.40	0.05	0.13	0.58	0.20	0.03	0.03	0.26
UNC-16	I	0.47	0.05	0.04	0.56	0.09	0.03	0.03	0.15
Category I		886	879	331	2096	327	351	93.5	771
Category II		494	347	225	1065	905	435	869	2209
Category III		27.6	11.8	17.2	56.6	31.6	24.8	19.2	75.6
Σ ₂₆ PHCZs		1385	1312	579	3275	1325	811	984	3120
BDE209		40.1	3.41	16.8	60.3	491	109	292	892
tPCBs		97.4	3.90	26.3	128	558	54.2	133	745

a. These estimates should be interpreted with caution, especially for Lakes Huron and Superior due to the limited number of cores analyzed, and for all UNCs that were only semi-quantified due to the lack of chemical standards.

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