

Organophosphate Esters in Sediment of the Great Lakes

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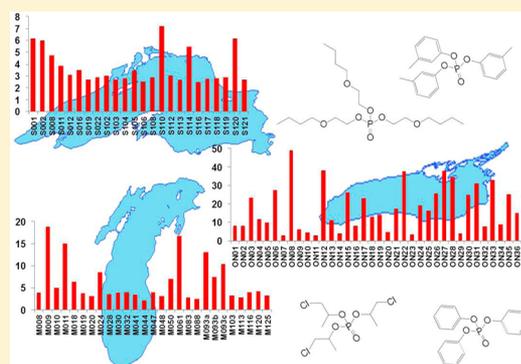
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Supporting Information

ABSTRACT: This is the first study on organophosphate ester (OPEs) flame retardants and plasticizers in the sediment of the Great Lakes. Concentrations of 14 OPEs were measured in three sediment cores and 88 Ponar surface grabs collected from Lakes Ontario, Michigan, and Superior of North America. The sum of these OPEs (Σ_{14} OPEs) in Ponar grabs averaged 2.2, 4.7, and 16.6 ng g⁻¹ dw in Lakes Superior, Michigan, and Ontario, respectively. Multiple linear regression analyses demonstrated statistically significant associations between logarithm concentrations of Σ_{14} OPEs as well as selected congeners in surface grab samples and sediment organic carbon content as well as a newly developed urban distance factor. Temporal trends observed in dated sediment cores from Lake Michigan demonstrated that the recent increase in depositional flux to sediment is dominated by chlorinated OPEs, particularly tris(2-chloroisopropyl) phosphate (TCPP), which has a doubling time of about 20 years. Downward diffusion within sediment may have caused vertical fractionation of OPEs over time. Two relatively hydrophilic OPEs including TCPP had much higher concentrations in sediment than estimated based on equilibria between water and sediment organic carbon. Approximately a quarter (17 tonnes) of the estimated total OPE burden (63 tonnes) in Lake Michigan resides in sediment, which may act as a secondary source releasing OPEs to the water column for years to come.



INTRODUCTION

Phosphorus is one of the most effective elements for retarding fire.¹ Organophosphate esters (OPEs) are widely used as flame retardants in plastics, textiles, electronic equipment, furniture, and building materials.^{2,3} Nonchlorinated alkyl phosphates have also been used as plasticizers, hydraulic fluids, lacquer, antifoam agents, glues and extractants for some metals.³ Use of OPEs began in the early 20th century, then increased rapidly during the 1940s and continued for later decades.¹ With the phasing out of polybrominated diphenyl ethers (PBDEs) during the 2000s, production and use of OPEs as alternative flame retardants have increased significantly in recent years.^{4,5}

Similar to other additive flame retardants, OPEs inevitably enter the environment during their production, use and disposal. It was estimated that approximately 80% of the annual consumption of OPE hydraulic fluids escaped to the environment through leakage from hydraulic systems in the 1960s.¹ OPEs have been detected in various environmental

compartments, including indoor air and dust, the atmosphere, wastewater and sludge, surface and drinking water, sediment, and biological samples including human blood, milk, and placenta.^{3,6–8} In the United States, there are at least four manufacturers of OPE flame retardants,⁹ although locations of their production facilities are not clear.

In the Great Lakes region, the concentration of OPEs in air was found to be ~100- to ~1200-fold greater than those of brominated flame retardants.^{10,11} Similarly, concentrations of OPEs in water collected from Lakes Erie, Michigan, and Huron were greater than concentrations of brominated flame retardants.¹² OPEs were also found in fish, herring gulls, and their eggs in the Great Lakes region.^{13–16} Sediments, which can

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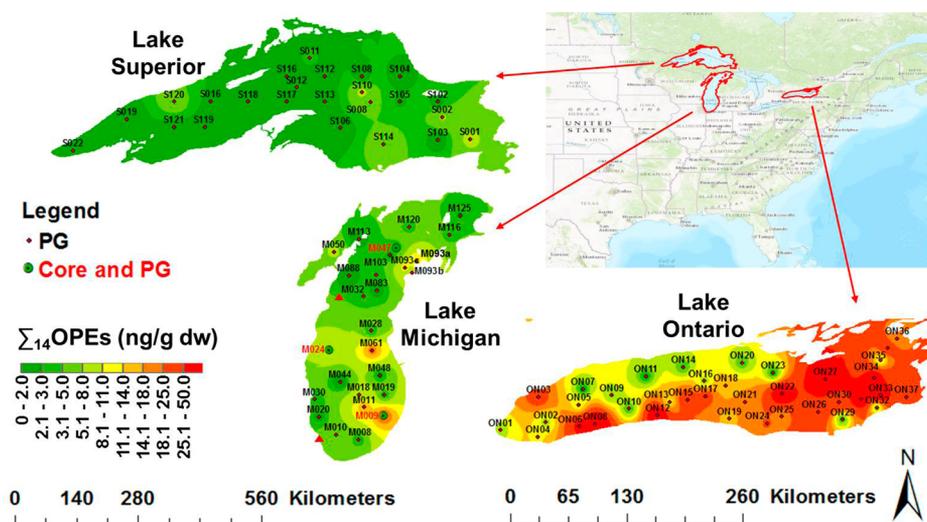


Figure 1. Sampling locations and spatial distribution of Σ_{14} OPEs in Ponar grab sediments. The red triangles in Lake Michigan are the bulk water sampling locations from ref 12. The inverse distance weight (IDW) interpretation in the geostatistical analysis tool of ArcGIS 10.3 (Redlands, CA) was used to illustrate the spatial distribution of Σ_{14} OPEs based on measured concentrations in Ponar grab samples.

serve as a sink or potential source of organic pollutants, have been found to be contaminated with OPEs in locations around the world.^{17–20} However, to our knowledge, there were no published reports on OPEs in the sediments of the Great Lakes prior to this study. This represents a major gap in our knowledge of the environmental fate of OPEs in the largest freshwater system in the world.

To date, relatively hydrophobic chemical pollutant groups have been investigated extensively in environmental monitoring efforts, especially those using sediment of natural waters. In comparison, the behavior of persistent organic pollutants with polar functional groups is less understood. Molecules of OPEs possess both polar and nonpolar moieties, and thus are considered amphiphilic. The octanol–water partition coefficient (K_{ow}) spans 10 orders of magnitude among the 14 OPE flame retardants and plasticizers listed in the Supporting Information, SI, Table S1. Once in sediment, all of these OPEs are considered persistent with estimated half-lives ranging from months to >4 years.²¹

In this work, we report measured concentrations of the 14 OPE flame retardants and plasticizers in sediment samples collected from Lakes Ontario, Michigan, and Superior. The acquired data set enabled an examination of the spatial distribution pattern and temporal trend as well as the influencing factors. The distribution between sediment particulate matter and pore water in the sediment was assessed, based on equilibrium partitioning theory; and the dependence of such phase distributions on the physicochemical property of the analytes was examined.

MATERIALS AND METHODS

Collection and Characterization of Sediments. Sediments were collected from Lakes Michigan, Superior, and Ontario during 2010 to 2013 onboard the USEPA Research Vessel R/V *Lake Guardian*. Sampling locations are shown in Figure 1, and site information is provided in Table S2. A total of 88 Ponar grab samples were collected. Sediment cores were collected at three sites in southern (M009), central (M024), and northern (M047) Lake Michigan. Detailed sampling methods are provided in the SI.

Water and solid contents, porosity, wet and dry bulk density, particle density, and sediment organic carbon (OC) were measured by use of standard methods described elsewhere.²² Segments of cores were dated by use of profiles of ^{210}Pb , ^{241}Am , ^{226}Ra , and ^{137}Cs .²³ Activities of these isotopes were quantified by use of gamma spectroscopy using well-type HPGe detectors. Mass sedimentation rate and focusing factor were derived from activities of ^{210}Pb as detailed previously.²⁴

Identification and Quantification of OPEs. Concentrations were measured for 14 OPEs, including trimethyl phosphate (TMP), triethyl phosphate (TEP), tri-*n*-propyl phosphate (TPrP), tri-*iso*-butyl phosphate (TiBP), tri-*n*-butyl phosphate (TnBP), tris(2-butoxyethyl) phosphate (TBEP), tris(2-ethylhexyl) phosphate (TEHP), triphenyl phosphate (TPhP), cresyl diphenyl phosphate (CDPP), tri-*m*-cresyl phosphate (TCrP), 2-ethylhexyl diphenyl phosphate (EHDPP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCP). Chemical structures and basic information on each of the 14 OPEs are summarized in Table S1.

Laboratory procedures included extraction by ultrasonication, cleanup using solid phase extraction cartridges, and analysis by liquid chromatography-tandem mass spectrometry (LC-MS/MS). Details of these methods are described in SI, and instrumental operational parameters are summarized in Table S3. Typical extracted ion chromatograms of a sediment extract and an OPE standard mixture are given in Figure S1.

Quality Control. A matrix blank was a sediment sample from about 50 cm depth of a core collected in 2011 from the Yellow Sea of China. Fourteen OPEs of 20 ng each were spiked into 1.0 g of the matrix blank with triplicates. The recoveries of 12 OPEs ranged from 78% to 108% (Table S3). The recoveries of EHDPP and TEHP were 47% and 27%, respectively. The relative standard deviations (RSD) of measured OPE concentrations in the matrix spike ranged from 3%–13% except for TEHP, which had an RSD of 38%. Results reported in this paper were not adjusted by the spiking recoveries.

Three field blanks (Na_2SO_4 , prepurified by baking at 500 °C overnight) from Lakes Superior, Michigan, and Ontario,

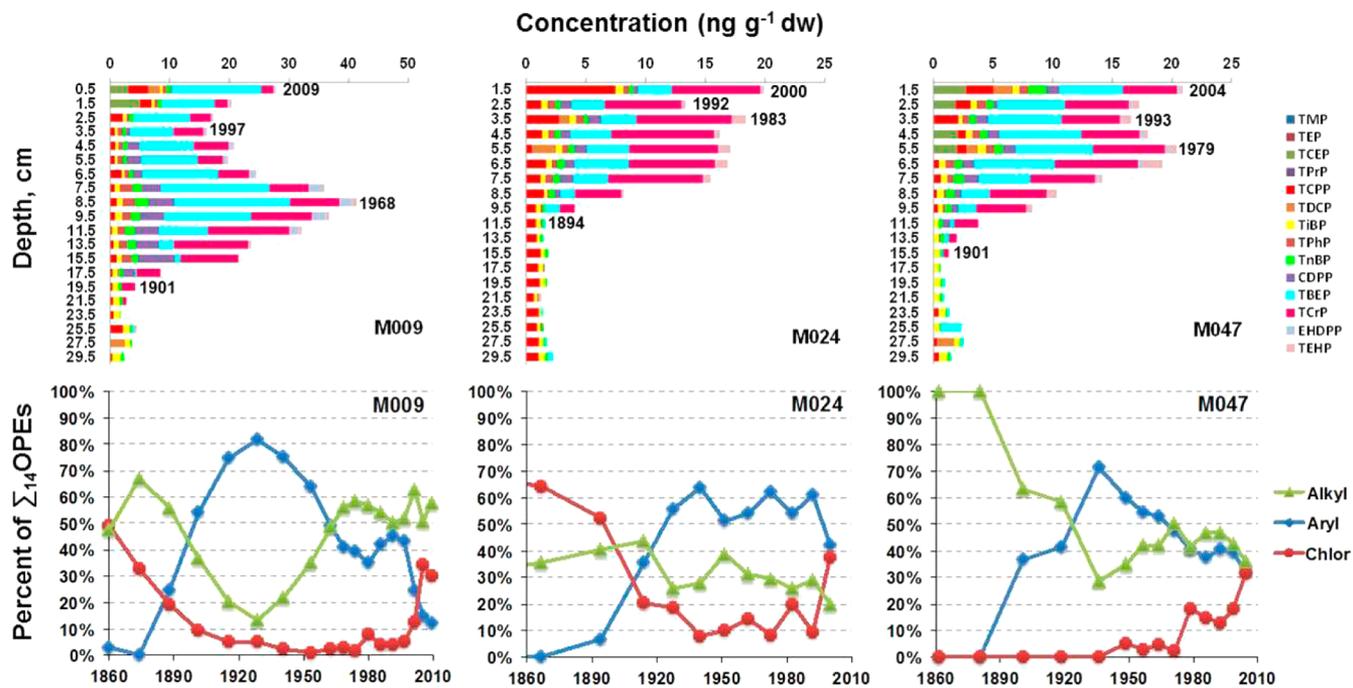


Figure 2. Concentrations of Σ_{14} OPEs against depth in sediment cores from Lake Michigan (upper), and the variations in percentages of alkyl- (sum of TMP, TEP, TPrP, TiBP, TnBP, TBEP, and TEHP), aryl- (sum of TPhP, CDPP, TCrP, and EHDPP), and chlorinated (sum of TCEP, TCPP, and TDCP) OPEs (lower).

respectively, were processed in the same manner as collected sediment samples. TCPP, TiBP, TnBP, and TBEP were detected in the field blanks in the concentration range of N.Q. – 0.44 ng g⁻¹ dw. On average, Σ_{14} OPEs in the field blank comprised 1%, 10%, and 23% of the concentration in Ponar grab sediment samples from Lakes Ontario, Michigan, and Superior, respectively. One procedural blank (consisting of only extracting solvent) was analyzed with every batch of samples, and TCPP, TiBP, TPhP, and TnBP were commonly detected at lower levels (<15%) than those in the samples. The reported concentrations of OPEs in all the sediment samples were after subtractions of the levels measured in the procedural and field blanks.

Data Analyses. In data analysis, N.D. (not detected) was defined as < three times of the signal-to-noise ratio ($S/N < 3$). N.Q. (not quantified) was defined as $S/N > 3$ but <10. In calculation of the detection rate, samples with N.Q. were included. Both N.Q. and N.D. were replaced by half of the method quantification limits (MQL) in statistical data analysis. MQL of OPEs ranged from 0.04 to 1.4 ng g⁻¹ dw (Table S3).

Statistical analyses were conducted using SPSS version 18.0 (SPSS Inc.) and Microsoft Excel (2010) with StatPlus (version 5 for Mac OS). Chemical inventories at all sites were estimated with the use of concentration data obtained from both Ponar grab and core samples. Net deposition flux was estimated for each core segment and used to illustrate the time trend. The averages of inventories and fluxes were multiplied by the water surface area of the lakes to estimate the lake-wide total mass load and annual mass loading rate, respectively. Details and equations are provided in the SI.

RESULTS

Concentrations of Σ_{14} OPEs in Ponar grab samples ranged from 0.44 to 47.82 ng g⁻¹ dw in the three lakes, and are illustrated in Figure 1. Relative abundance of individual OPEs in Ponar grab

samples are illustrated in Figure S2, with site- and congener-specific data given in Tables S4 and S5, respectively. Concentrations of OPEs in the cores from Lake Michigan are plotted against sediment depth in Figure 2 (upper panels), and are summarized in Table S6. In contrast to the findings in air and water,^{6,10,12} concentrations and accumulations of OPEs in sediments were less than those of polybrominated diphenyl ethers (PBDEs including decabromodiphenyl ether) and polychlorinated biphenyls (PCBs) previously reported for sediments in the Great Lakes.^{25–27} The generally smaller organic carbon–water partition coefficient (K_{oc}) of OPEs³ (Table S1) compared to those of PBDEs²⁸ and PCBs²⁹ indicate less potential for partitioning of OPEs from water to sediment. However, Σ_{14} OPEs were higher than the sum of PBDEs with 1 to 7 bromines.^{25–27} Concentrations of Σ_{14} OPEs in surface grabs in these three lakes are similar to those from Tai Lake (Ch: *Taihu*) in China¹⁷ and Danube river in Austria,¹⁸ but much lower than those reported in sediments from the Chicago Sanitary and Ship Canal,²⁰ rivers in Spain,¹⁹ a sea-based solid waste disposal site in Japan,³⁰ and the Elbe River and its major tributaries in Germany.³¹

Concentrations of Σ_{14} OPEs were significantly different among the lakes ($p < 0.02$), with decreasing rank order Lake Ontario > Lake Michigan > Lake Superior (Figure 1, Tables S4 and S5). This rank order is similar to those previously reported for PBDEs,^{25–27,32} PCBs,^{25–27} and other emerging flame retardants.^{33,34} In Lake Superior, concentrations of Σ_{14} OPEs were greater at southeastern sites (S001, S002, and S110) than at other sites (Table S4). Proximity of these sites to the cities of Sault Ste Marie and Marquette, MI, suggests inputs from local sources. In herring gull eggs collected in Agawa Rocks which is near sites S001 and S002, OPE concentrations appear to have greatly increased from 2004 to 2010.¹⁶ In Lake Michigan, higher concentrations (Σ_{14} OPEs > 10 ng g⁻¹ dw) and inventories (>60 ng cm⁻²) were found in the southeast

Table 1. Estimated Total Loads (\pm standard error) of OPEs in the Sediments of the Great Lakes (kg)^{a,b,c}

	Lake Superior	Lake Michigan	Lake Ontario	all 3 Lakes
TMP	n.a.	n.a.	n.a.	n.a.
TEP	800 \pm 190	n.a.	n.a.	800 \pm 190
TCEP	905 \pm 665	n.a.	n.a.	906 \pm 665
TPrP	n.a.	n.a.	n.a.	n.a.
TCPP	847 \pm 416	1307 \pm 338	886 \pm 147	3040 \pm 901
TDCP	849 \pm 614	387 \pm 270	n.a.	1237 \pm 884
TiBP	6064 \pm 510	586 \pm 117	707 \pm 48	7357 \pm 675
TPhP	172 \pm 171	648 \pm 190	2603 \pm 431	3424 \pm 792
TnBP	2064 \pm 572	1771 \pm 254	1611 \pm 264	5446 \pm 1091
CDPP	n.a.	1094 \pm 390	599 \pm 104	1693 \pm 494
TBEP	206 \pm 149	5919 \pm 1809	8026 \pm 1236	14150 \pm 3193
TCrP	1049 \pm 304	5180 \pm 1458	2314 \pm 311	8543 \pm 2073
EHDPP	68 \pm 39	109 \pm 63	364 \pm 84	541 \pm 187
TEHP	n.a.	19 \pm 19	1067 \pm 352	1087 \pm 371
Σ_{14} OPEs	13019 \pm 2063	17017 \pm 3648	18176 \pm 2290	48212 \pm 8001

^aLoad was estimated using eq S1 with the concentrations measured in Ponar grab samples. Standard error of the load was estimated from the standard error of the inventory. ^b"n.a." indicates the estimated total load <1 kg. ^c*Italic numbers* indicate lower than 30% detection rate thus the data should be interpreted with caution.

(M009, M011, and M061) and near Sleeping Bear Dunes (M093a). Sampling sites near Chicago and Milwaukee (M010, M020, and M030) are in nondepositional zone of Lake Michigan; sediments collected from these sites were sandy with less organic carbon (<2.5 mg/g dw). Pollutants entering the lake from these urban/industrial areas tend to transport with the water flow in the counterclockwise gyre of the southern basin, and deposit on the southeast side of the lake. In Lake Ontario, concentrations and inventories of Σ_{14} OPEs were in general higher in the eastern basin than in the central and west basins. However, inventory of Σ_{14} OPEs greater than 200 ng cm⁻² was found near Toronto (ON03) and the Niagara River (ON06 and ON08), and along the south coast (ON12). Fish collected near ON06 have been found to have higher levels of some OPEs than other sites across Canada.¹⁵

TBEP, TCrP, and TPhP were the most abundant OPEs in sediments across the three lakes (Table S5 and Figure S2). TBEP and TCrP are mainly used as additives in plastic products, rubber, floor cleaning agents, wallpaper and other consumer goods, as well as in the production of cables and electrical appliances.^{3,35} TBEP is the major OPE congener in waters of the Great Lakes.¹² These congeners have K_{oc} near or higher than 10⁴ (Table S1), thus greater association with sediments than most other OPEs measured in this work. Although concentrations of TiBP and TnBP were relatively low, their concentrations exceeded the method detection limits (MDL) in 97% of samples. TiBP and TnBP are important components of hydraulic and lubricating oils,³ and thus could be released from equipment on ships. Detection of EHDPP and TEHP occurred mostly in Lake Ontario. Together, all the three chlorinated OPEs (TCEP, TCPP, and TDCP) accounted for 10.6% of Σ_{14} OPEs, and TCPP was the most abundant among chlorinated OPEs. TCPP has been used in rigid and flexible polyurethane foams, and to replace the more toxic TCEP.³ It was reported as the most abundant chlorinated congener in the atmosphere¹⁰ and water¹² in the Great Lakes region. The highly polar congeners TMP, TEP, and TPrP were detected in <19% of the Ponar grab samples, and together accounting for less than 1.5% of Σ_{14} OPEs in the sediment.

Associations between concentrations of OPEs for which detection frequencies were greater than 85% were investigated

by use of Spearman rank correlations (nonparametric test). Correlations among the OPEs varied among lakes (Table S7). In Lake Superior, TiBP and TnBP were significantly correlated, and normalization to OC strengthened the correlation. These may suggest that TiBP and TnBP in the lake share similar sources. In Lake Michigan, TBEP and TCrP were significantly correlated. In Lake Ontario, TnBP, TPhP, TBEP, and TCrP were significantly correlated. However, in Lakes Michigan and Ontario, normalization to OC content did not strengthen the correlations between congeners, which suggests that the impact of local sources may outweigh the influence of sediment organic matter on the OPE concentrations in these two lakes.

With the measured concentrations, inventories of OPEs at each sampling sites were estimated using eq S1. The inventories of Σ_{14} OPEs estimated from using the concentrations from cores collected at sites M009, M024, and M047 were 178, 38, and 44 ng cm⁻², which were comparable with the estimates of 127, 38, and 13 obtained by the use of concentrations in Ponar grabs collected at the same sites (Table S4). With the use of eq S2, the total accumulation of Σ_{14} OPEs in the sediments of the three lakes was estimated to be in the range of 40–60 tonnes (Table 1).

DISCUSSION

Spatial Distribution and Urban Impact. Chemical pollutants, which are released predominantly from anthropogenic sources, are likely to have higher concentrations at locations near urban and industrialized areas. To assess the urban impact on the spatial distribution of pollutants in the Great Lakes region, we previously developed urban distance factor (UDF) based on the population (P) and distance between sampling site and cities (D) in the region.³² In this work, the UDF database was expanded to include more communities on lake shores and metropolitan areas in the States and Province in the Great Lakes region, with updated population data of the 2010 and 2011 censuses in the U.S. and Canada, respectively. Seven different forms of UDF were calculated for each sampling location (SI Text). UDF2, which is defined as P divided by square root of D , was found to correlate strongly with the natural logarithms of OC based concentrations ($r = 0.35$, p -value = 9×10^{-4}) or inventories ($r = 0.56$,

p -value = 2×10^{-8}) for Σ_{14} OPEs, as well as individual OPE congeners with detection frequency >60% in Ponar grab samples ($r > 0.35$ and $p < 6 \times 10^{-4}$, excluding TCPP and TiBP for which $r > 0.24$ and $p < 0.03$). The UDF2 values are included in Table S2 for all the sampling locations.

In addition to potential source locations, the concentrations of OPEs exhibited increases with increasing sediment OC content. Studies on sorption mechanisms of OPEs on soil and sediment particles are currently scarce.^{36,37} While organic matter of the sediments accommodates nonpolar organics predominantly by hydrophobic interaction, stronger specific interactions involving electron donor/acceptor or hydrogen bond could occur between numerous polar functional groups of the natural organic matter and the polar moieties of sorbates such as OPEs. With UDF2 and sediment OC content as independent variables, multiple linear regression models were developed and are presented in Figure 3 and Table S8.

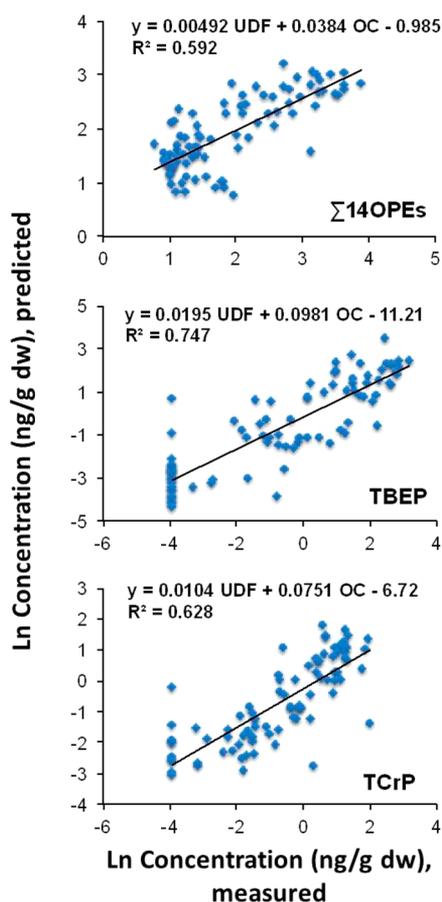


Figure 3. Comparison of predicted concentrations with measured concentrations of OPEs in Ponar grab sediments using the multivariable linear regression models ($N = 88$). The regression statistics are summarized in Table S8.

Sediment OC and impact of human activities are the main controlling factors influencing the distribution of OPEs in the sediment across the three lakes, together accounting for approximately 59% of the variance in concentration for Σ_{14} OPEs.

There is evidence that OPEs undergo long-range atmospheric transport.^{10,38} The OPEs targeted in this work vary widely in their volatility, with vapor pressure ranging from 10^{-5} to >100 Pa (Table S1). We found that the relative abundance

of OPEs differs largely among the three lakes (Figure S2). In Lake Superior, the congeners with the greatest concentrations were relatively volatile TiBP and TnBP. In comparison, heavier congeners TBEP and TCrP had greater detection rates and concentrations in Lakes Michigan and Ontario. The mean ratio (TiBP + TnBP)/(TBEP + TCrP) in Lake Superior was 10.7, which is much greater than those in Lakes Michigan (1.9) and Ontario (0.46). With higher vapor pressures, TiBP and TnBP are more likely to enter air and reach remote locations via atmospheric transport. In contrast, the heavier TBEP and TCrP have greater K_{oc} thus are more likely to bind to sediments after local inputs.

Temporal Trends and Downward Mobility. OPEs have already been used for >150 years;³ however, information for production volume during the earlier years is not available. As shown in Figure 2, in deeper sediments dated before year 1900, concentrations of Σ_{14} OPEs were low and relatively constant but still greater than the MDL. After 1900, concentrations and fluxes of Σ_{14} OPEs began to increase and peaked in the 1970s to 1980s. A decrease was observed in sediments deposited in the 1990s; however, a rebound after 2000 was observed at all three sites although the number of data points is limited. At sites M047 and M024, the highest concentrations and fluxes of Σ_{14} OPEs were in the uppermost segments of cores. At site M009, Σ_{14} OPEs in surficial segment dated 2009 was $28 \text{ ng g}^{-1} \text{ dw}$, which is almost double $16 \text{ ng g}^{-1} \text{ dw}$ observed in sediments deposited during the late 1990s, although still below the historical peak of $41 \text{ ng g}^{-1} \text{ dw}$ in core segment deposited during the 1960s (Figure 2). Net depositional fluxes of OPEs at these sites were estimated using eq S3. The recent depositional fluxes were 0.83, 0.19, and $0.25 \text{ ng m}^{-2} \text{ yr}^{-1}$ for Σ_{14} OPEs at sites M009, M024, and M047, respectively. The observations are clear evidence of the re-emergence of OPEs as environment pollutants. The recent increasing trend is consistent with observations of OPEs in other environmental matrices,^{7,39} and can be attributed to large scale replacement of PBDEs with OPE flame retardants in consumer goods.^{4,40,41} The observed increases in the environment may also reflect the tripled worldwide production volume of OPEs—from approximately 100 000 tonnes per year in 1992 to 341 000 tonnes per year in 2007.⁴²

Different time trends were observed among targeted OPEs. The above-mentioned increases in recent years appear to be dominated by the rapid increase of chlorinated congeners (Figure 2, lower panels), especially TCPP. Exponential increases were observed for TCPP at all three coring sites since the 1950s, with apparent doubling time t_2 around 20 years (Figure 4). It has been reported that the consumption of TCPP has continued to increase since the mid-1960s.⁴³ After the phase-out of the more toxic TCEP and with increasing use of polyurethane foam, production of TCPP (a replacement of TCEP) has increased markedly from the 1980s.⁴³ In 2000, worldwide production of TCPP was 36,000 t; in recent years, TCPP represents ~80% of the chlorinated OPEs produced in Europe.⁴⁴ TCPP was found to be the dominant (at 180 ng/g) among eight OPEs in the sediment of Liverpool Bay and the Rivers Mersey and Tees in the U.K.⁴⁵ It was detected in air, water, and bird eggs from the Great Lakes region.^{10–14,16} These observations highlight the need to establish benchmarks for TCPP in various environmental media to prevent adverse biological effects. In contrast to TCPP, all alkyl and aryl OPEs with the exception of TBEP decreased exponentially at site M009 after 1960, with apparent half-lives ($t_{0.5}$) ranging from 15

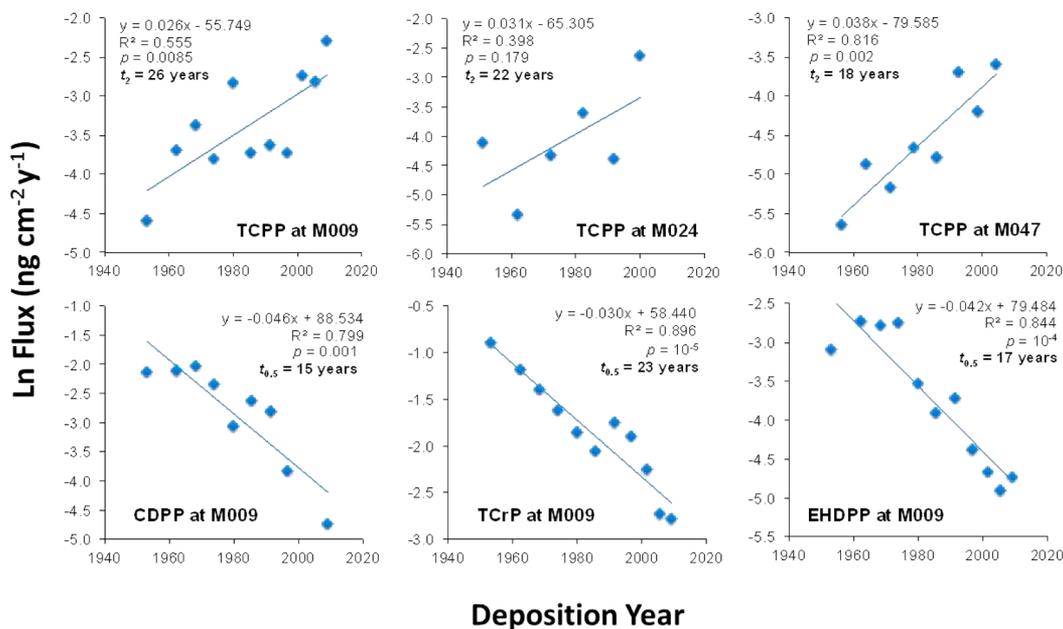


Figure 4. First-order kinetics plots of net depositional flux of selected OPEs to sediment of Lake Michigan. Only core segments dated after 1950 are included, and the apparent doubling time t_2 and half-life $t_{0.5}$ are calculated as $\ln 2$ divided by the slopes of the regressions.

to 40 years (Figure 4). The production of TCrP was predicted to decline $\sim 5\%$ each year during the period of 1978–1982.⁴⁶ TBEP displayed no trend over the core depth. Both increases and decreases in the depositional fluxes were observed at M024 and M047 depending on individual OPEs, but most trends were statistically insignificant ($p > 0.05$).

For compounds that are relatively water-soluble, therefore mobile in aqueous phase, the chronological profile recorded in dated sediment cores may not be in good agreement with the actual deposition history. For example, extensive downward transport of herbicide atrazine ($\log K_{oc} = 2.35$) as well as some perfluorinated compounds in sediment cores of Lake Michigan was reported.^{23,24} Assuming equilibrium conditions, the distribution between particle and pore water of sediment depends on hydrophobicity of the chemical ($\log K_{oc}$), the solid-to-water mass ratio (r_{sw}), and the organic content of the particles (f_{oc}), but is independent of chemical concentration. Thus, the fraction of the compound in pore water of the sediment can be estimated using the equation below.⁴⁷ Figure 5A illustrates the results of applying this equation to the sediment of this work.

$$f_{iw} = \frac{1}{1 + r_{sw} \cdot K_{oc} \cdot f_{oc}} \quad (1)$$

The targeted OPEs vary widely in their affinity to organic matter, with $\log K_{oc}$ ranging from 1.10 to 6.87 (Table S1). It is clear from Figure 5A, while OPEs with $\log K_{oc} > 5$ are almost completely associated with sediment particles, a significant portion of OPEs with $\log K_{oc} < 3$ can be present in pore water. This may have facilitated postdepositional transport to deeper sediment due to downward diffusion over time. We observed that, in all three cores, the summed fraction of less hydrophobic congeners ($\log K_{oc} < 3.5$) exhibits a rapid rise to near unity in deeper sediment (Figure 5B). Higher downward mobility of the more polar congeners relative to those more hydrophobic is likely to cause fractionation of a chemical mixture over the depth of sediments in a sufficiently long time period. The occurrence of natural fractionation of the OPEs in

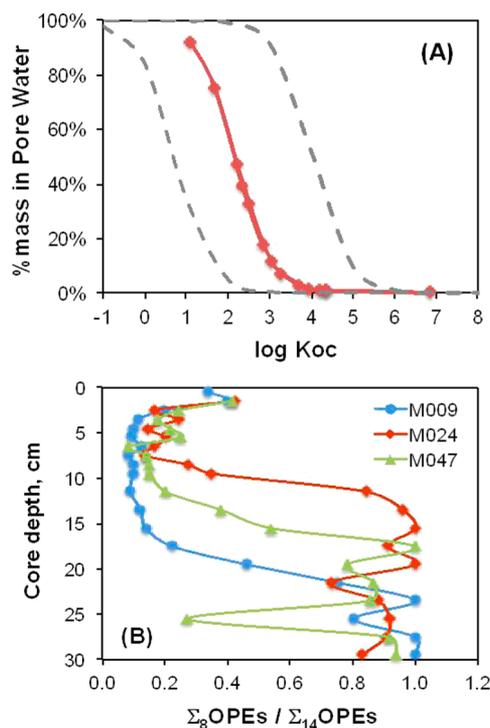


Figure 5. (A) Mass percent of OPEs that are present in pore water, calculated using eq 1. The dashed line on the right is drawn using the lowest OC content (0.55 mg/g dw) and the lowest solid–water mass ratio (0.17 kg/L), while the dashed line on the left using the highest OC content (50.6 mg/g dw) and the highest solid–water mass ratio (3.76 kg/L), measured in the Ponar grab samples of this work. The red dots are the median values of individual OPEs in all Ponar grab samples. (B) Variation with sediment depth of summed fraction of the 8 relatively polar OPEs ($\log K_{oc} < 3.5$) in three cores from Lake Michigan.

lake sediments over time is yet to be confirmed by future studies. Congener-specific information on the production and use history, especially that before 1900, is highly desired.

Transformation after burial is another process that may affect the apparent time trend observed in sediment cores. Non-chlorinated alkyl and aryl OPEs, such as TiBP, TnBP, TCrP, TPhP, and TBEP, tend to be more readily biodegradable than chlorinated OPEs such as TCPP, TCEP, and TDCP.^{7,42} However, the occurrence of degradation of OPEs cannot be confirmed based on the chronological profiles recorded in the three sediment cores of this work.

Load Estimation and Phase Distribution between Water and Sediment. Concentration data are available for 11 OPEs dissolved in bulk water samples collected in spring 2012 from Lake Michigan, at a central location (latitude 44.2, longitude -87.3) and a southern location (latitude 41.9, longitude -87.6).¹² By multiplying the volume of water in Lake Michigan (4,920 km³) with the reported Σ OPEs concentration (9.3 ng/L),¹² the total load of OPEs dissolved in the lake water is roughly 46 tonnes. Compared with the total load of 17 tonnes in the sediment (Table 1), it appears that about 27% of the OPEs in Lake Michigan resides in the sediment. This percentage is about 20% if the calculation is based on the same set of seven congeners (TCEP, TCPP, TDCP, TPhP, TnBP, TBEP, and TEHP) reported in water¹² and sediment. The sum of 63 tonnes does not include the amounts in suspended or settling particulates and living biota, for which data are not available.

TCPP, TnBP, and TBEP had >50% detection frequency in this work in the Ponar grab sediment samples collected in lower (latitude <45) Lake Michigan ($N = 9$). With their concentrations in the bulk water,¹² bulk phase distribution ratio, which is defined here as the measured concentration in the sediment organic carbon (ng kg⁻¹ OC) to that in water (ng L⁻¹), was calculated for the three congeners. Different pairs of sediment and water sampling sites were tested. For example, the ratio was calculated by the use of only one sediment site that is the nearest to each water sampling site, a number of sediment sites in proximity to each of the water sampling sites, areas divided by latitude, or lake-wide average from all sediment sites to the average at the two water sampling sites. The calculated distribution ratio ranged from 10^{4.0} to 10^{5.2} L/kg for TCPP, which is 2 to 3 orders of magnitude higher than its K_{oc} value of 10^{2.2} L/kg (Table S1). Similarly, the distribution ratio of TnBP ranged from 10^{4.7} to 10^{5.3} L/kg, much higher than its K_{oc} of 10^{3.28} L/kg. However, the distribution ratio of TBEP, ranging from 10^{3.8} to 10^{4.8} L/kg, matched well with its K_{oc} of 10^{4.38} L/kg. Such differences were found to be much greater in the southern basin than the central area of the lake. The gaps between the distribution ratio and K_{oc} were also reported to be greater for PCBs with lower log K_{ow} values; alteration of the natural organic matter composition and sorption kinetics are among plausible explanations.⁴⁸ The results of this work for OPEs suggest that the difference between the distribution ratio and K_{oc} could also be time- and location-related, as the gap tends to be more pronounced for emerging and re-emerging pollutants such as TCPP, and at near-source locations. The significance of these findings with regard to bioavailability and sediment risk assessment is yet to be fully realized.

This work provides solid evidence that sediment of the Great Lakes has been contaminated with quantifiable levels of OPE flame retardants and plasticizers, and that the deposition of some OPEs to sediment appears to be accelerating. Due to their continued uses in North America, the input of OPEs to sediment of the Great Lakes may continue for years to come. The possibility that the contaminated sediment act as a

secondary source releasing OPEs to the overlying water warrants future studies.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05484.

Detailed methods, structures, and physical and chemical properties of organophosphate esters (Table S1), sampling site information (Table S2), analytical parameters and quality control using LC-MS/MS (Table S3), concentrations and inventories of Σ_{14} OPEs in Ponar grab sediments (Table S4), concentration and detection rate of individual OPEs in the Ponar grab sediments of Lakes Ontario, Michigan, and Superior (Table S5), concentration of individual OPEs and Σ_{14} OPEs and the flux of Σ_{14} OPEs in sediment cores from Lake Michigan (Table S6), Spearman's correlation coefficient among OPEs (Table S7), multiple linear regressions statistics by SPSS (Table S8), LC-MS/MS extracted ion chromatograms of a sediment extract and OPE standard mixture (Figure S1), and relative abundance of individual OPEs in Ponar grab sediments (Figure S2) (PDF)

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Supporting Information

Organophosphate Esters in Sediment of the Great Lakes

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Text: Detailed Methods

Sediment sampling. A Ponar grab sampler was used to collect surface sediments, which were decanted on board the ship and then homogenized using a drill-driven paint mixer. A total of 88 Ponar grab samples were collected. The three sediment cores were collected by use of a box corer. Individual cores obtained from the box corer were extruded and sectioned on the ship by use of hydraulic extruders. Cores were sectioned into 1.0 cm intervals from the top (most recently deposited) for the first 10 cm, followed by 2 cm segments for the remainder of the core. In order to minimize smearing, approximately 2 mm of sediment which touched the tube wall was removed and discarded. After each slice was removed, stainless steel sectioning tools were thoroughly cleaned by use of three washes with hexane, followed by acetone, and finally deionized water prior to operations on the subsequent slice. At each site, segments of cores at corresponding depths were composited into a Pyrex® mixing bowl and homogenized. Samples were packed into pre-cleaned 125 mL amber glass jars, 50 mL Falcon® tubes, and vials for various laboratory measurements. All Ponar grab samples and core segments were stored in glass at -20 °C, and those in Falcon tubes were stored at 4 °C.

Chemicals. All unlabeled OPEs standards (>98%) were purchased from Dr. Ehrenstorfer GmbH (Germany) except TiBP (>98%) which was from Adamas-beta (Shanghai, China). Among labeled standards, tributyl-d27-phosphate (TnBP-d27) and tripropyl-d21-phosphate (TPrP-d21) from Cambridge Isotope Laboratories (Tewksbury, MA), and trimethyl-d9-phosphate (TMP-d9), triethyl-d15-phosphate (TEP-d15) and triphenyl-d15 -phosphate (TPhP-d15) from C/D/N Isotopes Inc. (Pointe-Claire, Canada) were used as surrogate standards. HPLC grade acetonitrile and dichloromethane were purchased from Fisher Scientific (Fair Lawn, NJ). Formic acid (99% purity) was purchased from Fluka (Buchs, Switzerland). Ultrapure water (18.3 MΩ) was obtained from a Milli-Q ultrapure Gradient system (Millipore, Bedford, MA).

Stock solutions of individual OPEs (1000 mg L⁻¹) were prepared by dissolving the OPEs in acetonitrile. A working stock solution containing the 14 OPEs (10 mg L⁻¹ each) was prepared by dilution of the stock solutions with ultrapure water / acetonitrile (60 / 40). All of the stock solutions were stored at 4 °C in the dark.

Extraction and Cleanup. Samples were freeze-dried and ground. Ultrasonic assisted extraction was used to extract the target OPEs from the sediments. Briefly, 1.0 g freeze dried sediment sample was weighed into 15 mL Corning tube, and then the surrogate standards (5 deuterated OPEs) were added. The mixture was then incubated overnight. After that, 5 mL acetonitrile was added and the resulting solution was vortexed and then extracted in an ultrasonic bath (KQ600DE, Kunshan, China). The extract was centrifuged at 9,500 rpm for 5 min, and the supernatant was collected. The residual sediment was extracted twice following the same procedure. The combined extract was then concentrated by nitrogen blowing, and 1 mL dichloromethane was added to wash the Corning tube. The resulting dichloromethane was transferred subjected to solid-phase extraction (SPE). The SPE cartridge (Supelclean ENVI Florisil, 6 mL, 1 g) (Supelco, Bellefonte, PA) was pre-conditioned by 12 mL acetonitrile and 12 mL dichloromethane. After sample loading, the cartridge was washed with 9 mL dichloromethane and the eluent was discarded. Then 10 mL acetonitrile was used to eluent the adsorbed OPEs. The resulting eluent was concentrated under nitrogen blowing and re-dissolved in

ultrapure water / acetonitrile (60/40, 200 μL) for liquid chromatography (LC) tandem mass spectrometry (MS/MS) analysis.

Analysis by LC-MS/MS. Separation of the OPEs was accomplished by using an ultra-performance liquid chromatography (UPLC) system (ACQUITY UPLC, Waters, USA) equipped with a BEH C18 column (2.1 mm \times 100 mm; particle size, 1.7 μm , Waters, Mildford, MA). The injection volume was 10 μL , and the column temperature was set at 45 $^{\circ}\text{C}$. In the gradient elution, a binary mobile phase of an aqueous solution of 0.1% formic acid (A) and acetonitrile (B) was utilized (0.2 mL/min). The gradient was set as follows: 0 min (40% B), 0.5 min (40% B), 3.0 min (50% B), 4.5 min (55% B), 8.5 min (70% B), 9 min (100% B), 13.8 min (100% B), 13.9 min (40% B), and 15.5 min (40% B). A TSQ Quantum Access (Thermo Scientific, USA) triple quadrupole mass spectrometer was hyphenated with LC for the determination of the 14 OPEs. The electrospray ionization was employed in the positive ion scan and multiple reaction monitoring mode, and the following conditions were set: peak width resolution 0.7 m/z, spray voltage 4000 V, collision gas pressure 1.5 mTorr, and capillary temperature 300 $^{\circ}\text{C}$. The analytical parameters for the OPEs including retention time, precursor ion, quantification ion, qualification ion, and collision energy, were given in Table S3.

Estimation of Loading Parameters. Measured concentrations were used to estimate the cumulative parameters using established equations,¹ as described below.

Chemical inventory represents the total accumulation of the chemical per unit area of the lake bottom at specified sampling site.

$$\text{Inventory (ng cm}^{-2}\text{)} = \sum C_i \times \rho_{b,i} \times d_i \quad [\text{S1}]$$

where C_i is the chemical concentration ($\text{ng g}^{-1} \text{ dw}$), $\rho_{b,i}$ is the dry mass bulk density (g cm^{-3}), and d_i is the sample thickness (cm) of core segment i or Ponar grab sample i . For Ponar grab samples, the d_i can be viewed as the averaged penetration depth of the sampler into sediment, and may differ among sites depending on the in situ bulk density of the sediment. In applying equation [S1] to the data obtained for Ponar grabs, d_i was set to be 20 cm when $\rho_{b,i} < 0.6 \text{ g cm}^{-3}$, 10 cm for samples with $0.6 < \rho_{b,i} < 1.0 \text{ g cm}^{-3}$, and 5 cm when $\rho_{b,i} \geq 1.0 \text{ g cm}^{-3}$. The total loads in each lake were calculated as follows:

$$\text{Total load (kg)} = \text{Average inventory} \times \text{Lake surface area} \times 10^{-2} \quad [\text{S2}]$$

The surface areas of Lakes Superior, Michigan, and Ontario are 82100, 57800, and 18960 km^2 , respectively.

Net deposition flux $_i$ represents the mass of a chemical entered the core segment i per unit area in a specific year:

$$\text{Net deposition flux}_i \text{ (ng cm}^{-2} \text{ y}^{-1}\text{)} = C_i \times \text{MSR} / \text{FF} \quad [\text{S3}]$$

For the three cores from Lake Michigan, mass sedimentation rates (MSR) values were previously determined to be 0.065, 0.019, and 0.031 $\text{g cm}^{-2} \text{ y}^{-1}$, and focusing factor (FF) was 2.2, 1.98, and 2.64 (dimensionless), for sites M009, M024 and M047, respectively.² Finally, the annual loading rates in each lake were calculated as follows:

$$\text{Annual loading rate (kg y}^{-1}\text{)} = \text{Average} \times \text{Lake surface area} \times 10^{-2} \quad [\text{S4}]$$

The constants in all the equations above are for unit conversions.

Urban Distance Factor (UDF). This work expands from our previous uses of UDF by defining and comparing seven different forms of UDF,³ as defined below:

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

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

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

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

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

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

Table S1. Organophosphate Esters Analyzed in This Work.

Abbr'n	Full Name	Formula	MW	Chemical Structure	Vapor pressure at 25 °C (Pa) *	log K _{ow} ⁴	log K _{oc} ⁵
TMP	Trimethyl phosphate	C ₃ H ₉ O ₄ P	140.07	$\text{O}=\text{P}(\text{O}-\text{CH}_3)_3$	1.1×10^2	-0.65	1.10
TEP	Triethyl phosphate	C ₆ H ₁₅ O ₄ P	182.15	$\text{O}=\text{P}(\text{O}-\text{CH}_2\text{CH}_3)_3$	5.2×10^1	0.80	1.68
TCEP	Tris(2-chloroethyl) phosphate	C ₆ H ₁₂ Cl ₃ O ₄ P	285.49	$\text{O}=\text{P}(\text{O}-\text{CH}_2\text{CH}_2\text{Cl})_3$	8.2	1.44	2.48
TPrP	Tri-n-propyl phosphate	C ₉ H ₂₁ O ₄ P	224.23	$\text{O}=\text{P}(\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3)_3$	3.2	1.87	2.83
TCPP	Tris(2-chloroisopropyl) phosphate	C ₉ H ₁₈ Cl ₃ O ₄ P	327.57	$\text{O}=\text{P}(\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl})_3$	7.5×10^{-3}	2.59	2.21
TDCP	Tris(1,3-dichloro-2-propyl) phosphate	C ₉ H ₁₅ Cl ₆ O ₄ P	430.90	$\text{O}=\text{P}(\text{O}-\text{CH}(\text{CH}_2\text{Cl})\text{CH}_2\text{Cl})_3$	4.0×10^{-5}	3.65	2.35
TiBP	Tri-iso-butyl phosphate	C ₁₂ H ₂₇ O ₄ P	266.31	$\text{O}=\text{P}(\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)_2)_3$	1.7	3.6	3.05
TPhP	Triphenyl phosphate	C ₁₈ H ₁₅ O ₄ P	326.28	$\text{O}=\text{P}(\text{O}-\text{C}_6\text{H}_5)_3$	1.5×10^{-3}	4.59	3.72
TnBP	Tri-n-butyl phosphate	C ₁₂ H ₂₇ O ₄ P	266.31	$\text{O}=\text{P}(\text{O}-(\text{CH}_2)_3\text{CH}_3)_3$	1.5×10^{-1}	4.00	3.28
CDPP	Cresyl diphenyl phosphate	C ₁₉ H ₁₇ O ₄ P	340.31	$\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{O}-\text{P}(=\text{O})(\text{O}-\text{C}_6\text{H}_5)_2$	2.6×10^{-3}	3.70	3.93
TBEP	Tris(2-butoxyethyl) phosphate	C ₁₈ H ₃₉ O ₇ P	398.47	$\text{O}=\text{P}(\text{O}-(\text{CH}_2)_2\text{O}-(\text{CH}_2)_3\text{CH}_3)_3$	1.6×10^{-4}	3.75	4.38
TCrP	Tri-m-cresyl phosphate	C ₂₁ H ₂₁ O ₄ P	368.36	$\text{O}=\text{P}(\text{O}-\text{C}_6\text{H}_4(\text{CH}_3))_3$	1.5×10^{-5}	5.11	4.35
EHDPP	2-Ethylhexyl diphenyl phosphate	C ₂₀ H ₂₇ O ₄ P	362.40	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2-\text{O}-\text{P}(=\text{O})(\text{O}-\text{C}_6\text{H}_5)_2$	6.7×10^{-3}	6.64	4.21
TEHP	Tris(2-ethylhexyl) phosphate	C ₂₄ H ₅₁ O ₄ P	434.63	$\text{O}=\text{P}(\text{O}-\text{CH}_2\text{CH}(\text{CH}_2)_3\text{CH}_3)_3$	1.1×10^{-5}	9.49	6.87

* calculated by Estimation Programs Interface Suite (EPI) WEB 4.1 software by U.S. EPA, 2013.

Table S2. Sampling Site Information.

Site	Latitude	Longitude	Depth (m)	UDF2	Site	Latitude	Longitude	Depth (m)	UDF2	Site	Latitude	Longitude	Depth (m)	UDF2
S001	46.9930	-85.1612	95	366	M019	42.7335	-86.5833	93	484	ON08	43.3575	-78.9396	81	558
S002	47.3603	-85.6208	154	356	M020	42.3665	-87.6672	46	512	ON09	43.5975	-78.8016	141	542
S008	47.6058	-86.8177	301	346	M024	43.4830	-87.4882	150	454	ON10	43.4856	-78.6554	159	536
S011	48.3438	-87.8250	230	329	M028	43.8003	-86.7998	137	444	ON11	43.7587	-78.5158	86	518
S012	47.8553	-88.0418	238	336	M030	42.6600	-87.7382	18	496	ON12	43.4306	-78.4144	88	525
S016	47.6212	-89.4633	180	328	M032	44.3715	-86.9333	257	424	ON13	43.5414	-78.3143	186	517
S019	47.3703	-90.8535	188	333	M041	44.7367	-86.7213	272	414	ON14	43.8342	-78.2063	84	501
S022	46.8002	-91.7508	55	332	M044	42.9528	-87.3155	92	478	ON15	43.5598	-78.1656	191	511
S102	47.6173	-85.6973	92	351	M047	45.1783	-86.3745	200	403	ON16	43.7172	-78.0267	132	501
S103	46.9838	-85.6972	164	364	M048	43.0585	-86.6630	107	473	ON17	43.5902	-78.0111	188	505
S104	48.0382	-86.3217	189	340	M050	45.1165	-87.4165	33	399	ON18	43.6819	-77.8487	150	498
S105	47.6177	-86.3217	81	348	M061	43.4742	-86.7847	137	457	ON19	43.3993	-77.8194	75	510
S106	47.1807	-87.3183	219	352	M083	44.4737	-86.7060	270	422	ON20	43.8722	-77.7130	53	487
S108	48.0392	-86.9493	227	338	M088	44.7187	-87.1740	95	412	ON21	43.5414	-77.6859	178	500
S110	46.7735	-86.9495	138	342	M093a	44.9622	-86.0552	100	411	ON22	43.6093	-77.3759	153	490
S112	48.0393	-87.5733	216	335	M093b	44.7712	-86.1168	60	416	ON23	43.7938	-77.4648	59	484
S113	47.6177	-87.5730	171	342	M093c	44.8562	-86.2430	129	413	ON24	43.3621	-77.5008	124	506
S114	46.9095	-86.5980	398	361	M103	45.0623	-86.4918	207	406	ON25	43.4180	-77.3762	206	498
S116	48.0392	-88.2007	254	332	M113	45.3267	-87.0090	37	395	ON26	43.4583	-77.0697	236	489
S117	47.6175	-88.2007	270	339	M116	45.4008	-85.4995	36	402	ON27	43.7312	-77.0169	90	478
S118	47.6175	-88.8420	189	336	M120	45.5288	-86.1708	140	395	ON28	43.5638	-76.7081	214	479
S119	47.1955	-89.5048	197	338	M125	45.7225	-85.3317	16	395	ON29	43.3952	-76.8645	75	487
S120	47.6185	-90.0712	178	329	ON01	43.3039	-79.7340	25	569	ON30	43.5429	-76.9066	226	483
S121	47.1955	-90.0727	146	335	ON02	43.3713	-79.3533	104	573	ON31	43.7474	-76.6018	82	471
M008	41.9842	-87.0142	66	521	ON03	43.5829	-79.4167	53	621	ON32	43.4921	-76.5820	63	480
M009	42.3850	-86.5915	62	494	ON04	43.2478	-79.4188	42	567	ON33	43.5982	-76.5484	160	475
M010	42.0662	-87.3792	51	548	ON05	43.5166	-79.0803	140	567	ON34	43.8958	-76.5487	58	466
M011	42.5283	-86.9220	164	493	ON06	43.3360	-79.0700	71	566	ON35	43.9926	-76.4901	50	462
M018	42.7338	-86.9995	165	485	ON07	43.6486	-79.0407	117	565	ON36	44.0780	-76.4125	27	459
										ON37	43.5832	-76.3334	47	473

Table S3. Analytical Parameters and Quality Control using LC-MS/MS.

	CAS#	Retention time (min)	Precursor (m/z)	Quantification (m/z)	Qualification (m/z)	Collision energy (ev)	Spiking recoveries (%) ^a	RSD (%) ^b	MLQ (ng g ⁻¹)
TMP	512-56-1	1.48	141.0 141.0	109.1	79.3	17 23	97	9	0.15
TEP	78-40-0	2.20	183.0 183.0	99.2	81.3	18 24	99	7	0.12
TCEP	115-96-8	3.33	284.9 286.9	99.2	99.2	30 29	85	13	1.4
TPrP	513-08-6	4.84	225.1 225.1	99.2	141.1	18 10	91	3	0.18
TCPP	13674-84-5	5.52	326.9 328.9	99.1	99.1	30 29	108	10	0.30
TDCP	13674-87-8	7.88	430.9 432.9	99.2	99.1	28 29	95	13	0.66
TiBP	126-71-6	8.51	267.1 267.1	99.1	155.0	18 6	100	5	0.10
TPhP	115-86-6	8.42	327.0 327.0	214.9	152.1	25 33	92	8	0.10
TnBP	126-73-8	8.69	267.1 267.1	99.2	155.1	18 10	94	5	0.08
CDPP	26444-49-5	9.50	341.0 341.0	229.0	152.1	27 33	88	12	0.26
TBEP	78-51-3	9.76	399.1 399.1	299.0	199.0	12 15	84	4	0.04
TCrP	563-04-2	10.70	369.1 369.1	165.1	243.0	43 27	78	8	0.04
EHDPP	1241-94-7	11.01	363.1 363.1	251.0	152.1	39 12	47	13	0.04
TEHP	78-42-2	13.78	435.2 435.2	99.1	113.2	30 12	27	38	0.10

a. Each OPE was spiked at 20 ng g⁻¹ dw

b. RSD = relative standard deviation of replicates (N = 3)

c. MLQ = method quantification limits

Table S4. Concentrations and Inventories (Inv.) of Σ_{14} OPEs in Ponar Grab Sediments.

Lake Superior				Lake Michigan				Lake Ontario			
Sample ID	ng g ⁻¹ dw	ng g ⁻¹ OC	Inv. ng cm ⁻²	Sample ID	ng g ⁻¹ dw	ng g ⁻¹ OC	Inv. ng cm ⁻²	Sample ID	ng g ⁻¹ dw	ng g ⁻¹ OC	Inv. ng cm ⁻²
S001	5.4	2394	27.4	M008	2.2	123	25.7	ON01	6.8	575	53.5
S002	5.2	756	49.0	M009	18	446	127.0	ON02	6.9	337	41.4
S008	3.4	338	28.7	M010	3.6	1530	21.7	ON03	22	841	229.5
S011	2.2	103	12.6	M011	14	392	69.0	ON04	11	876	106.6
S012	1.4	66	8.3	M018	4.9	210	25.5	ON05	8.8	345	49.8
S016	1.9	153	14.5	M019	2.2	306	14.2	ON06	26	1112	207.1
S019	1.0	60	8.0	M020	1.6	737	8.1	ON07	1.4	154	16.1
S022	1.2	71	7.0	M024	7.2	234	38.2	ON08	48	1707	318.7
S102	1.4	575	15.8	M028	2.1	519	10.7	ON09	4.7	224	27.1
S103	1.1	119	11.1	M030	2.4	1313	17.6	ON10	2.9	636	22.2
S104	1.2	79	8.6	M032	2.6	106	12.0	ON11	1.6	495	10.9
S105	1.8	771	24.5	M041	1.9	96	8.8	ON12	37	1271	250.6
S106	0.80	47	4.5	M044	0.44	47	2.8	ON13	10	359	50.0
S108	1.2	74	8.0	M047	2.4	137	13.1	ON14	2.7	3345	13.0
S110	5.8	3928	27.8	M048	1.5	58	11.1	ON15	25	703	108.8
S112	1.4	75	9.0	M050	5.5	112	17.8	ON16	6.5	268	36.9
S113	1.0	56	6.8	M061	15	487	105.9	ON17	22	633	102.5
S114	4.2	1369	27.3	M083	1.2	44	5.9	ON18	12	400	60.5
S116	0.81	35	4.4	M088	0.87	106	5.3	ON19	13	623	129.8
S117	1.1	51	6.0	M093a	12	437	84.9	ON20	3.2	2197	17.9
S118	1.1	149	11.2	M093b	6.0	273	47.9	ON21	16	775	86.0
S119	1.2	74	7.9	M093c	8.9	323	65.1	ON22	36	868	158.6
S120	4.7	479	43.5	M103	1.5	69	7.6	ON23	1.9	643	11.3
S121	1.1	90	8.2	M113	1.08	117	8.1	ON24	18	646	113.5
				M116	2.6	2595	13.3	ON25	15	465	64.7
				M120	2.7	111	13.9	ON26	24	747	106.0
				M125	1.9	3481	13.8	ON27	37	975	169.7
								ON28	33	1017	137.7
								ON29	2.8	467	24.2
								ON30	24	887	97.7
								ON31	30	683	153.5
								ON32	6.2	890	42.1
								ON33	32	940	153.1
								ON34	7.5	538	61.7
								ON35	24	530	98.6
								ON36	14	272	71.3
								ON37	22	3656	144.6

Table S5. Concentration (ng g⁻¹ dw) and Detection Rate of Individual OPEs in the Ponar Grab Sediments.

	TMP	TEP	TCEP	TPrP	TCPP	TDCP	TiBP	TPhP	TnBP	CDPP	TBEP	TCrP	EHDPP	TEHP	Σ ₁₄ OPE
Lake Superior (N = 24)															
Average	N.D.	0.12	0.15	N.D.	0.15	0.13	0.99	0.04	0.34	N.D.	0.03	0.18	0.01	N.D.	2.16
Min	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.63	N.D.	N.Q.	N.D.	N.D.	N.D.	N.D.	N.D.	0.80
Median	N.D.	0.07	N.D.	N.D.	N.Q.	N.D.	0.95	N.D.	0.15	N.D.	N.D.	0.13	N.D.	N.D.	1.30
Max	N.D.	0.39	1.90	N.Q.	1.10	1.88	1.96	1.04	1.36	N.D.	0.46	1.36	0.19	N.D.	5.80
Detection %	0	67	29	4	54	8	100	8	100	0	13	92	13	0	
Lake Michigan (N = 27)															
Average	N.D.	N.D.	N.D.	N.D.	0.39	0.12	0.16	0.17	0.52	0.30	1.52	1.45	0.03	0.01	4.65
Min	N.D.	N.D.	N.D.	N.D.	0.44										
Median	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.15	N.Q.	0.40	N.Q.	0.48	0.70	N.D.	N.D.	2.38
Max	N.D.	N.Q.	N.Q.	N.D.	1.60	1.99	0.59	0.91	1.86	1.94	9.10	7.18	0.32	0.17	17.56
Detection %	0	4	15	0	48	15	93	63	89	59	89	85	30	26	
Lake Ontario (N = 37)															
Average	N.D.	N.D.	N.D.	N.D.	0.71	N.D.	0.61	2.62	1.43	0.59	7.29	2.07	0.31	0.96	16.59
Min	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.23	N.D.	0.22	N.D.	N.D.	N.D.	N.D.	N.D.	1.38
Median	N.D.	N.D.	N.D.	N.D.	0.48	N.D.	0.62	1.38	1.17	0.44	4.66	1.92	0.24	0.24	13.78
Max	N.D.	N.D.	N.Q.	N.Q.	3.37	N.Q.	1.07	9.03	7.62	2.19	23.74	7.37	1.44	8.38	47.82
Detection %	0	0	14	3	97	14	100	92	100	62	100	97	81	65	
All Three Lakes (N = 88)															
Average	N.D.	0.03	0.04	N.D.	0.46	0.07	0.58	1.17	0.85	0.34	3.54	1.36	0.14	0.41	8.99
Min	N.D.	N.D.	N.D.	N.D.	0.44										
Median	N.D.	N.D.	N.D.	N.D.	0.33	N.D.	0.62	0.14	0.51	N.D.	0.64	0.69	N.D.	N.D.	3.88
Max	N.D.	0.39	1.90	N.Q.	3.37	1.99	1.96	9.03	7.62	2.19	23.74	7.37	1.44	8.38	47.82
Detection %	0	19	18	2	70	13	98	60	97	44	73	92	47	35	

N.D. - Not detected

N.Q. - Detected but not quantified

Table S6. Concentration of Individual OPEs and Σ_{14} OPEs and the Flux of Σ_{14} OPEs in Sediment Cores from Lake Michigan.

depth	date	TMP	TEP	TCEP	TPrP	TCPP	TDCP	TiBP	TPhP	TnBP	CDPP	TBEP	TCrP	EHDPP	TEHP	Σ_{14} OPEs	Flux- Σ_{14} OPEs
cm	Year	ng g ⁻¹ dw	ng g ⁻¹ dw	ng cm ⁻² yr ⁻¹													
M009																	
0.5	2009	N.D.	N.D.	3.02	N.D.	3.37	2.02	0.39	0.67	0.58	0.29	14.98	2.07	0.29	0.13	27.82	0.83
1.5	2006	N.D.	N.D.	5.00	N.D.	2.00	N.D.	0.46	0.55	0.70	N.D.	8.75	2.21	0.25	0.45	20.37	0.60
2.5	2001	N.D.	N.D.	N.Q.	N.D.	2.17	N.D.	0.58	0.45	0.71	N.D.	9.47	3.51	0.32	0.13	17.34	0.51
3.5	1997	N.D.	N.D.	N.Q.	N.D.	0.81	N.D.	0.48	0.79	0.59	0.74	7.20	5.06	0.42	0.18	16.27	0.48
4.5	1991	N.D.	N.D.	N.Q.	N.D.	0.89	N.D.	0.47	0.80	0.74	2.03	9.12	5.79	0.81	0.18	20.83	0.62
5.5	1986	N.D.	N.D.	N.Q.	N.D.	0.81	N.D.	0.38	0.93	0.64	2.42	9.47	4.28	0.68	0.21	19.83	0.59
6.5	1980	N.D.	N.D.	N.Q.	N.D.	1.97	N.D.	0.44	0.77	0.65	1.58	12.66	5.23	0.98	0.21	24.50	0.73
7.5	1974	N.D.	N.D.	N.D.	N.D.	0.75	N.D.	0.85	2.20	1.49	3.19	18.22	6.7	2.15	0.45	35.95	1.07
8.5	1968	N.D.	N.D.	N.D.	N.D.	1.15	N.D.	0.91	2.17	2.16	4.40	19.34	8.4	2.07	0.80	41.36	1.23
9.5	1963	N.D.	N.D.	N.D.	N.D.	0.84	N.D.	1.18	1.44	1.56	4.08	14.52	10.3	2.20	0.64	36.72	1.09
11.5	1953	N.D.	N.D.	N.D.	N.D.	0.34	N.D.	0.90	1.26	1.64	4.01	8.20	13.7	1.52	0.53	32.13	0.95
13.5	1941	N.D.	N.D.	N.D.	N.D.	0.58	N.D.	0.87	1.44	1.46	3.81	2.52	12.4	0.18	0.37	23.67	0.70
15.5	1928	N.D.	N.D.	N.Q.	N.D.	1.06	N.D.	0.86	1.70	1.06	6.19	0.93	9.70	N.D.	N.Q.	21.50	0.64
17.5	1915	N.D.	N.D.	N.Q.	N.D.	0.42	N.D.	0.84	0.25	0.62	2.01	0.27	4.04	N.D.	N.Q.	8.45	0.25
19.5	1901	N.D.	N.D.	N.D.	N.D.	0.40	N.D.	1.04	N.D.	0.48	N.D.	N.D.	2.24	N.D.	N.Q.	4.16	0.12
21.5	1888	N.D.	N.D.	N.D.	N.D.	0.53	N.D.	1.04	N.D.	0.48	N.D.	N.D.	0.68	N.D.	N.Q.	2.73	0.08
23.5	1874	N.D.	N.D.	N.Q.	N.D.	0.58	N.D.	1.03	N.D.	0.14	N.D.	N.D.	N.D.	N.D.	N.D.	1.74	0.05
25.5	1860	N.D.	N.D.	N.D.	N.D.	2.19	N.D.	1.03	0.14	0.35	N.D.	0.26	N.D.	N.D.	0.47	4.44	0.13
27.5	1845	N.D.	N.D.	N.D.	N.D.	N.Q.	2.49	0.95	N.Q.	0.23	N.D.	N.D.	N.D.	N.D.	N.D.	3.67	0.11
29.5	1830	N.D.	N.D.	N.Q.	N.D.	0.37	N.D.	1.45	N.D.	0.50	N.D.	N.D.	N.D.	N.D.	N.D.	2.32	0.07
M024																	
1.5	2000	N.D.	N.D.	N.Q.	N.Q.	7.49	N.Q.	0.64	0.50	0.35	0.38	2.80	7.43	0.11	0.19	19.90	0.19
2.5	1992	N.D.	N.D.	N.D.	N.D.	1.28	N.D.	0.52	0.66	0.42	0.95	2.75	6.45	0.11	0.21	13.35	0.13
3.5	1983	N.D.	N.D.	N.D.	N.D.	2.79	0.88	0.50	0.66	0.33	1.14	2.92	8.02	0.12	1.04	18.39	0.18
4.5	1972	N.D.	N.D.	N.D.	N.Q.	1.36	N.Q.	0.49	0.54	0.49	0.81	3.41	8.63	0.11	0.36	16.22	0.16
5.5	1962	N.D.	N.D.	N.Q.	N.D.	0.49	2.01	0.52	0.56	0.47	1.05	3.51	7.46	0.15	0.87	17.10	0.17
6.5	1951	N.D.	N.D.	N.Q.	N.D.	1.70	N.D.	0.43	0.46	0.65	0.82	4.52	7.24	0.09	0.95	16.87	0.16
7.5	1940	N.D.	N.D.	N.Q.	N.Q.	1.24	N.D.	0.36	0.69	0.54	1.14	2.88	7.98	0.11	0.52	15.45	0.15

8.5	1927	N.D.	N.D.	N.Q.	N.Q.	1.51	N.D.	0.27	0.16	0.46	0.51	1.18	3.88	N.D.	0.22	8.18	0.08
9.5	1914	N.D.	N.D.	N.D.	N.D.	0.83	N.D.	0.36	0.20	0.23	N.D.	1.18	1.26	N.D.	N.D.	4.07	0.04
11.5	1894	N.D.	N.D.	N.Q.	N.Q.	0.84	N.D.	0.36	0.11	0.15	N.D.	0.13	N.Q.	N.D.	N.D.	1.60	0.02
13.5	1867	N.D.	N.D.	N.D.	N.D.	0.92	N.D.	0.28	N.Q.	0.18	N.D.	0.05	N.D.	N.D.	N.D.	1.43	0.01
15.5	1839	N.D.	N.D.	N.Q.	N.Q.	1.25	N.D.	0.36	N.D.	0.23	N.D.	N.D.	N.D.	N.D.	N.D.	1.84	0.02
17.5	1811	N.D.	N.D.	N.D.	N.Q.	1.02	N.D.	0.41	0.13	N.Q.	N.D.	N.D.	N.D.	N.D.	N.D.	1.56	0.02
19.5	1783	N.D.	N.D.	N.D.	N.D.	1.16	N.D.	0.44	N.Q.	0.15	N.D.	N.D.	N.D.	N.D.	N.D.	1.75	0.02
21.5	1755	N.D.	N.D.	N.D.	N.Q.	0.67	N.D.	0.26	0.10	N.Q.	N.D.	N.D.	N.D.	N.D.	0.24	1.27	0.01
23.5	1726	N.D.	N.D.	N.D.	N.Q.	1.08	N.D.	0.18	N.Q.	N.Q.	N.D.	0.17	N.D.	N.D.	N.D.	1.43	0.01
25.5	1696	N.D.	N.D.	N.Q.	N.Q.	0.93	N.D.	0.25	0.12	0.16	N.D.	N.D.	N.D.	N.D.	N.D.	1.46	0.01
27.5	1666	N.D.	N.D.	N.Q.	N.D.	1.08	N.D.	0.35	N.D.	0.12	N.D.	0.16	N.D.	N.D.	N.D.	1.72	0.02
29.5	1635	N.D.	N.D.	N.D.	N.D.	1.07	N.D.	0.55	N.Q.	0.23	N.D.	0.38	N.D.	N.D.	N.D.	2.23	0.02
M047																	
1.5	2004	N.D.	N.D.	2.74	N.Q.	2.33	1.62	0.52	0.78	1.50	1.10	5.30	4.58	0.18	0.29	20.93	0.25
2.5	1999	N.D.	N.D.	1.85	N.D.	1.27	N.D.	0.52	0.79	0.61	0.35	5.65	5.35	0.27	0.62	17.28	0.20
3.5	1993	N.D.	N.D.	N.Q.	N.D.	2.11	N.Q.	0.32	0.58	0.56	1.03	6.15	4.92	0.18	0.75	16.60	0.20
4.5	1986	N.D.	N.D.	2.04	N.Q.	0.70	N.D.	0.53	0.63	0.65	1.02	6.85	4.90	0.28	0.43	18.02	0.21
5.5	1979	N.D.	N.D.	1.98	N.D.	0.80	0.95	0.67	0.71	0.74	1.08	6.45	6.07	0.36	0.61	20.42	0.24
6.5	1972	N.D.	N.D.	N.Q.	N.D.	0.48	N.D.	0.53	0.78	0.63	1.03	6.74	6.99	0.31	1.75	19.23	0.23
7.5	1964	N.D.	N.D.	N.Q.	N.Q.	0.65	N.D.	0.52	0.53	0.86	1.27	4.29	5.48	0.25	0.34	14.18	0.17
8.5	1956	N.D.	N.D.	N.Q.	N.D.	0.30	N.D.	0.56	0.22	0.69	0.58	2.37	4.81	0.07	0.76	10.36	0.12
9.5	1948	N.D.	N.D.	N.D.	N.Q.	0.41	N.D.	0.36	0.22	0.51	0.58	1.50	4.19	N.Q.	0.54	8.31	0.10
11.5	1936	N.D.	N.D.	N.D.	N.Q.	N.D.	N.D.	0.46	N.D.	0.31	0.66	0.31	2.03	N.D.	N.D.	3.77	0.04
13.5	1919	N.D.	N.D.	N.Q.	N.D.	N.Q.	N.D.	0.43	0.15	0.31	N.D.	0.40	0.66	N.D.	N.D.	1.95	0.02
15.5	1901	N.D.	N.D.	N.Q.	N.Q.	N.Q.	N.D.	0.56	N.D.	0.13	N.D.	0.12	0.47	N.D.	N.D.	1.28	0.02
17.5	1881	N.D.	N.D.	N.Q.	N.D.	N.D.	N.D.	0.49	N.D.	0.11	N.D.	N.D.	N.D.	N.D.	N.D.	0.60	0.01
19.5	1861	N.D.	N.D.	N.D.	N.Q.	N.Q.	N.D.	0.60	N.D.	0.17	N.D.	0.21	N.D.	N.D.	N.D.	0.98	0.01
21.5	1842	N.D.	N.D.	N.D.	N.Q.	N.Q.	N.D.	0.55	N.Q.	0.19	N.D.	0.11	N.D.	N.D.	N.D.	0.86	0.01
23.5	1823	N.D.	N.D.	N.Q.	N.D.	0.43	N.D.	0.61	N.D.	0.10	N.D.	0.19	N.Q.	N.D.	N.D.	1.34	0.02
25.5	1803	N.D.	N.D.	N.Q.	N.Q.	N.Q.	N.D.	0.53	N.D.	0.11	N.D.	1.68	N.D.	N.D.	N.D.	2.31	0.03
27.5	1783	N.D.	N.D.	N.Q.	N.Q.	0.33	1.43	0.47	N.D.	0.09	N.D.	0.21	N.D.	N.D.	N.D.	2.52	0.03
29.5	1763	N.D.	N.D.	N.Q.	N.D.	0.46	N.D.	0.73	N.D.	0.22	N.D.	0.09	N.D.	N.D.	N.D.	1.50	0.02

N.D. - Not detected

N.Q. - Detected but not quantified

Table S7. Spearman's Correlation Coefficient (R) among OPEs with >85% detection rates.

<u>Lake Superior (N=24)</u>						
ng g⁻¹ dw	TiBP	TnBP	TCrP			
TiBP	1					
TnBP	0.789 ***	1				
TCrP	-0.261	-0.320	1			
ng g⁻¹ OC	TiBP	TnBP	TCrP			
TiBP	1					
TnBP	0.864 ***	1				
TCrP	0.391	0.265	1			
<u>Lake Michigan (N=27)</u>						
ng g⁻¹ dw	TiBP	TnBP	TBEP	TCrP		
TiBP	1					
TnBP	0.020	1				
TBEP	-0.163	0.450 *	1			
TCrP	-0.352	0.367	0.733 **	1		
ng g⁻¹ OC	TiBP	TnBP	TBEP	TCrP		
TiBP	1					
TnBP	0.480 *	1				
TBEP	0.111	0.241	1			
TCrP	-0.112	-0.200	0.401 *	1		
<u>Lake Ontario (N=37)</u>						
ng g⁻¹ dw	TCPP	TiBP	TPhP	TnBP	TBEP	TCrP
TCPP	1					
TiBP	-0.241	1				
TPhP	-0.148	0.296	1			
TnBP	0.100	-0.023	0.795 ***	1		
TBEP	0.275	-0.137	0.693 ***	0.915 ***	1	
TCrP	0.056	-0.136	0.803 ***	0.863 ***	0.832 ***	1
ng g⁻¹ OC	TCPP	TiBP	TPhP	TnBP	TBEP	TCrP
TCPP	1					
TiBP	0.435 **	1				
TPhP	-0.318	0.006	1			
TnBP	0.368 *	0.193	0.338 *	1		
TBEP	0.096	-0.302	0.369 *	0.613 **	1	
TCrP	0.127	-0.090	0.293	0.667 ***	0.766 ***	1

* $p < 0.05$; ** $p < 0.01$; *** $p < 10^{-5}$

Table S8. Multiple Linear Regressions Statistics by SPSS.

Figure 3A: $\text{Ln } \sum_{14}\text{OPEs (ng/g dw)} = - 0.985 + 0.0384 * \text{OC (mg/g)} + 0.00492 * \text{UDF}$						
	Intercept	OC	UDF2	R ²	F	p-value
model	-0.985	0.0384	0.00492	0.592	60.7	4.19E-17
p-value	6.39E-03	3.30E-11	2.33E-08			
Figure 3B: $\text{Ln TBEP (ng/g dw)} = - 11.21 + 0.0981 * \text{OC (mg/g)} + 0.0195 * \text{UDF}$						
	Intercept	OC	UDF2	R ²	F	p-value
model	-11.21	0.0981	0.0195	0.747	126.5	3.36E-26
p-value	2.75E-24	8.91E-14	5.29E-18			
Figure 3C: $\text{Ln TCrP (ng/g dw)} = - 6.72 + 0.0751 * \text{OC (mg/g)} + 0.0104 * \text{UDF}$						
	Intercept	OC	UDF2	R ²	F	p-value
model	-6.72	0.0751	0.0104	0.628	71.7	5.69E-19
p-value	2.23E-16	4.09E-12	7.63E-10			

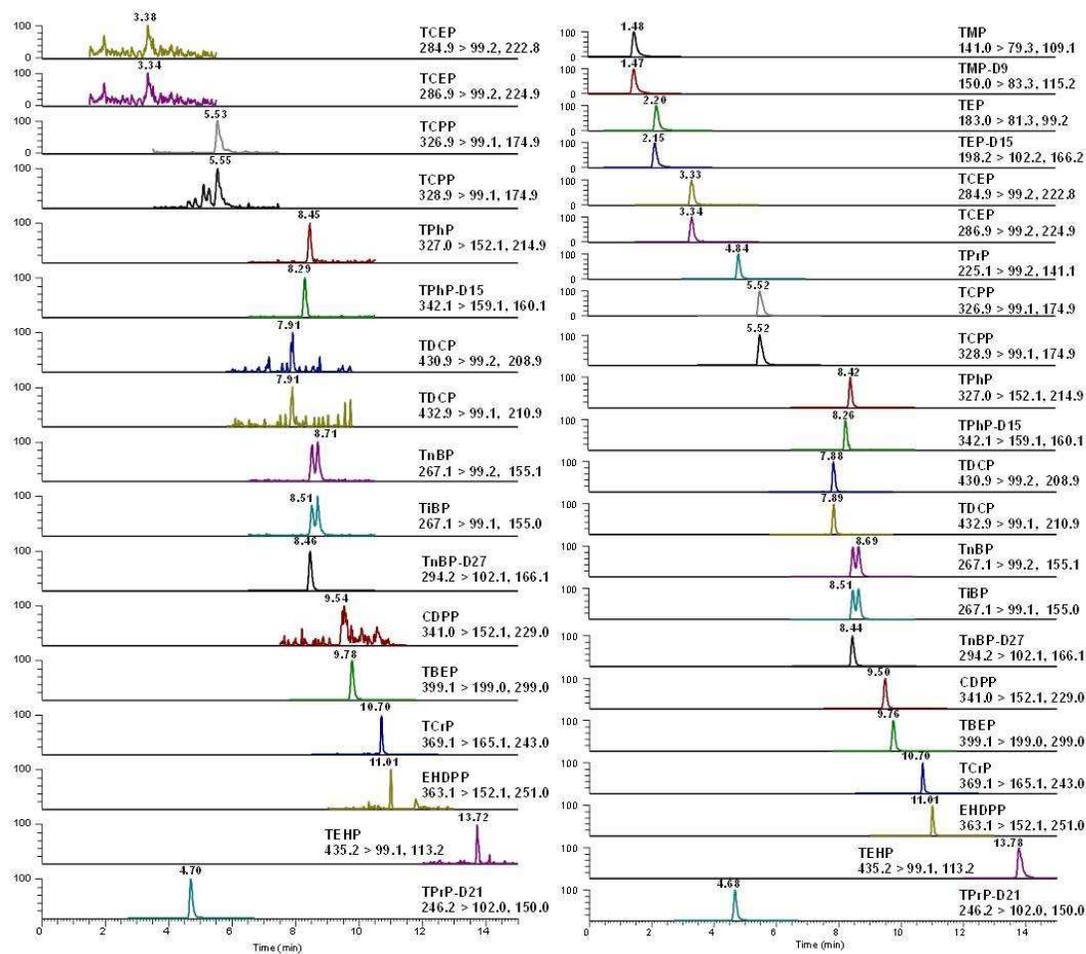


Figure S1. LC-MS / MS extracted ion chromatograms (EIC) of a sediment extract (left) and an OPE standard mixture at 100 µg L⁻¹ concentration level (right).

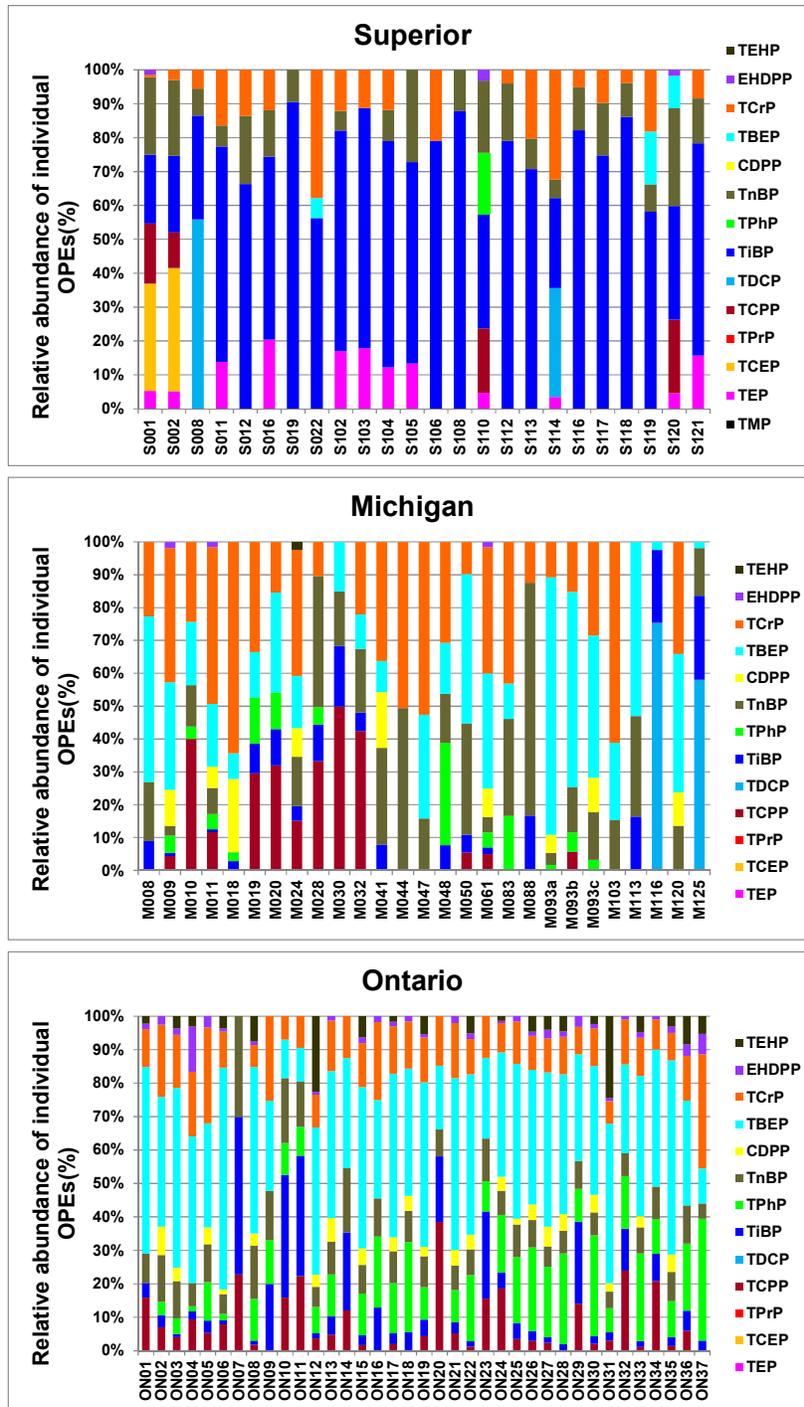


Figure S2. Relative abundance of individual OPEs in Ponar grab sediments.

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Supporting Information

Organophosphate Esters in Sediment of the Great Lakes

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Text: Detailed Methods

Sediment sampling. A Ponar grab sampler was used to collect surface sediments, which were decanted on board the ship and then homogenized using a drill-driven paint mixer. A total of 88 Ponar grab samples were collected. The three sediment cores were collected by use of a box corer. Individual cores obtained from the box corer were extruded and sectioned on the ship by use of hydraulic extruders. Cores were sectioned into 1.0 cm intervals from the top (most recently deposited) for the first 10 cm, followed by 2 cm segments for the remainder of the core. In order to minimize smearing, approximately 2 mm of sediment which touched the tube wall was removed and discarded. After each slice was removed, stainless steel sectioning tools were thoroughly cleaned by use of three washes with hexane, followed by acetone, and finally deionized water prior to operations on the subsequent slice. At each site, segments of cores at corresponding depths were composited into a Pyrex® mixing bowl and homogenized. Samples were packed into pre-cleaned 125 mL amber glass jars, 50 mL Falcon® tubes, and vials for various laboratory measurements. All Ponar grab samples and core segments were stored in glass at -20 °C, and those in Falcon tubes were stored at 4 °C.

Chemicals. All unlabeled OPEs standards (>98%) were purchased from Dr. Ehrenstorfer GmbH (Germany) except TiBP (>98%) which was from Adamas-beta (Shanghai, China). Among labeled standards, tributyl-d27-phosphate (TnBP-d27) and tripropyl-d21-phosphate (TPrP-d21) from Cambridge Isotope Laboratories (Tewksbury, MA), and trimethyl-d9-phosphate (TMP-d9), triethyl-d15-phosphate (TEP-d15) and triphenyl-d15 -phosphate (TPhP-d15) from C/D/N Isotopes Inc. (Pointe-Claire, Canada) were used as surrogate standards. HPLC grade acetonitrile and dichloromethane were purchased from Fisher Scientific (Fair Lawn, NJ). Formic acid (99% purity) was purchased from Fluka (Buchs, Switzerland). Ultrapure water (18.3 MΩ) was obtained from a Milli-Q ultrapure Gradient system (Millipore, Bedford, MA).

Stock solutions of individual OPEs (1000 mg L⁻¹) were prepared by dissolving the OPEs in acetonitrile. A working stock solution containing the 14 OPEs (10 mg L⁻¹ each) was prepared by dilution of the stock solutions with ultrapure water / acetonitrile (60 / 40). All of the stock solutions were stored at 4 °C in the dark.

Extraction and Cleanup. Samples were freeze-dried and ground. Ultrasonic assisted extraction was used to extract the target OPEs from the sediments. Briefly, 1.0 g freeze dried sediment sample was weighed into 15 mL Corning tube, and then the surrogate standards (5 deuterated OPEs) were added. The mixture was then incubated overnight. After that, 5 mL acetonitrile was added and the resulting solution was vortexed and then extracted in an ultrasonic bath (KQ600DE, Kunshan, China). The extract was centrifuged at 9,500 rpm for 5 min, and the supernatant was collected. The residual sediment was extracted twice following the same procedure. The combined extract was then concentrated by nitrogen blowing, and 1 mL dichloromethane was added to wash the Corning tube. The resulting dichloromethane was transferred subjected to solid-phase extraction (SPE). The SPE cartridge (Supelclean ENVI Florisil, 6 mL, 1 g) (Supelco, Bellefonte, PA) was pre-conditioned by 12 mL acetonitrile and 12 mL dichloromethane. After sample loading, the cartridge was washed with 9 mL dichloromethane and the eluent was discarded. Then 10 mL acetonitrile was used to eluent the adsorbed OPEs. The resulting eluent was concentrated under nitrogen blowing and re-dissolved in

ultrapure water / acetonitrile (60/40, 200 μ L) for liquid chromatography (LC) tandem mass spectrometry (MS/MS) analysis.

Analysis by LC-MS/MS. Separation of the OPEs was accomplished by using an ultra-performance liquid chromatography (UPLC) system (ACQUITY UPLC, Waters, USA) equipped with a BEH C18 column (2.1 mm \times 100 mm; particle size, 1.7 μ m, Waters, Mildford, MA). The injection volume was 10 μ L, and the column temperature was set at 45 $^{\circ}$ C. In the gradient elution, a binary mobile phase of an aqueous solution of 0.1% formic acid (A) and acetonitrile (B) was utilized (0.2 mL/min). The gradient was set as follows: 0 min (40% B), 0.5 min (40% B), 3.0 min (50% B), 4.5 min (55% B), 8.5 min (70% B), 9 min (100% B), 13.8 min (100% B), 13.9 min (40% B), and 15.5 min (40% B). A TSQ Quantum Access (Thermo Scientific, USA) triple quadrupole mass spectrometer was hyphenated with LC for the determination of the 14 OPEs. The electrospray ionization was employed in the positive ion scan and multiple reaction monitoring mode, and the following conditions were set: peak width resolution 0.7 m/z, spray voltage 4000 V, collision gas pressure 1.5 mTorr, and capillary temperature 300 $^{\circ}$ C. The analytical parameters for the OPEs including retention time, precursor ion, quantification ion, qualification ion, and collision energy, were given in Table S3.

Estimation of Loading Parameters. Measured concentrations were used to estimate the cumulative parameters using established equations,¹ as described below.

Chemical inventory represents the total accumulation of the chemical per unit area of the lake bottom at specified sampling site.

$$\text{Inventory (ng cm}^{-2}\text{)} = \sum C_i \times \rho_{b,i} \times d_i \quad [\text{S1}]$$

where C_i is the chemical concentration ($\text{ng g}^{-1} \text{ dw}$), $\rho_{b,i}$ is the dry mass bulk density (g cm^{-3}), and d_i is the sample thickness (cm) of core segment i or Ponar grab sample i . For Ponar grab samples, the d_i can be viewed as the averaged penetration depth of the sampler into sediment, and may differ among sites depending on the in situ bulk density of the sediment. In applying equation [S1] to the data obtained for Ponar grabs, d_i was set to be 20 cm when $\rho_{b,i} < 0.6 \text{ g cm}^{-3}$, 10 cm for samples with $0.6 < \rho_{b,i} < 1.0 \text{ g cm}^{-3}$, and 5 cm when $\rho_{b,i} \geq 1.0 \text{ g cm}^{-3}$. The total loads in each lake were calculated as follows:

$$\text{Total load (kg)} = \text{Average inventory} \times \text{Lake surface area} \times 10^{-2} \quad [\text{S2}]$$

The surface areas of Lakes Superior, Michigan, and Ontario are 82100, 57800, and 18960 km^2 , respectively.

Net deposition flux $_i$ represents the mass of a chemical entered the core segment i per unit area in a specific year:

$$\text{Net deposition flux}_i \text{ (ng cm}^{-2} \text{ y}^{-1}\text{)} = C_i \times \text{MSR} / \text{FF} \quad [\text{S3}]$$

For the three cores from Lake Michigan, mass sedimentation rates (MSR) values were previously determined to be 0.065, 0.019, and 0.031 $\text{g cm}^{-2} \text{ y}^{-1}$, and focusing factor (FF) was 2.2, 1.98, and 2.64 (dimensionless), for sites M009, M024 and M047, respectively.² Finally, the annual loading rates in each lake were calculated as follows:

$$\text{Annual loading rate (kg y}^{-1}\text{)} = \text{Average} \times \text{Lake surface area} \times 10^{-2} \quad [\text{S4}]$$

The constants in all the equations above are for unit conversions.

Urban Distance Factor (UDF). This work expands from our previous uses of UDF by defining and comparing seven different forms of UDF,³ as defined below:

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

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

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

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

$$D = 6378.7 \times \arccos [\sin(\text{lat1}/57.2958) \times \sin(\text{lat2}/57.2958) + \cos(\text{lat1}/57.2958) \times \cos(\text{lat2}/57.2958) \times \cos(\text{lon1}/57.2958 - \text{lon2}/57.2958)]$$

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

Table S1. Organophosphate Esters Analyzed in This Work.

Abbr'n	Full Name	Formula	MW	Chemical Structure	Vapor pressure at 25 °C (Pa) *	log K _{ow} ⁴	log K _{oc} ⁵
TMP	Trimethyl phosphate	C ₃ H ₉ O ₄ P	140.07	$\text{O}=\text{P}(\text{O}-\text{CH}_3)_3$	1.1×10^2	-0.65	1.10
TEP	Triethyl phosphate	C ₆ H ₁₅ O ₄ P	182.15	$\text{O}=\text{P}(\text{O}-\text{CH}_2\text{CH}_3)_3$	5.2×10^1	0.80	1.68
TCEP	Tris(2-chloroethyl) phosphate	C ₆ H ₁₂ Cl ₃ O ₄ P	285.49	$\text{O}=\text{P}(\text{O}-\text{CH}_2\text{CH}_2\text{Cl})_3$	8.2	1.44	2.48
TPrP	Tri-n-propyl phosphate	C ₉ H ₂₁ O ₄ P	224.23	$\text{O}=\text{P}(\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3)_3$	3.2	1.87	2.83
TCPP	Tris(2-chloroisopropyl) phosphate	C ₉ H ₁₈ Cl ₃ O ₄ P	327.57	$\text{O}=\text{P}(\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl})_3$	7.5×10^{-3}	2.59	2.21
TDCP	Tris(1,3-dichloro-2-propyl) phosphate	C ₉ H ₁₅ Cl ₆ O ₄ P	430.90	$\text{O}=\text{P}(\text{O}-\text{CH}(\text{CH}_2\text{Cl})\text{CH}_2\text{Cl})_3$	4.0×10^{-5}	3.65	2.35
TiBP	Tri-iso-butyl phosphate	C ₁₂ H ₂₇ O ₄ P	266.31	$\text{O}=\text{P}(\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)_2)_3$	1.7	3.6	3.05
TPhP	Triphenyl phosphate	C ₁₈ H ₁₅ O ₄ P	326.28	$\text{O}=\text{P}(\text{O}-\text{C}_6\text{H}_5)_3$	1.5×10^{-3}	4.59	3.72
TnBP	Tri-n-butyl phosphate	C ₁₂ H ₂₇ O ₄ P	266.31	$\text{O}=\text{P}(\text{O}-(\text{CH}_2)_3\text{CH}_3)_3$	1.5×10^{-1}	4.00	3.28
CDPP	Cresyl diphenyl phosphate	C ₁₉ H ₁₇ O ₄ P	340.31	$\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{O}-\text{P}(\text{O})(\text{O}-\text{C}_6\text{H}_5)_2$	2.6×10^{-3}	3.70	3.93
TBEP	Tris(2-butoxyethyl) phosphate	C ₁₈ H ₃₉ O ₇ P	398.47	$\text{O}=\text{P}(\text{O}-(\text{CH}_2)_2\text{O}-(\text{CH}_2)_3\text{CH}_3)_3$	1.6×10^{-4}	3.75	4.38
TCrP	Tri-m-cresyl phosphate	C ₂₁ H ₂₁ O ₄ P	368.36	$\text{O}=\text{P}(\text{O}-\text{C}_6\text{H}_4(\text{CH}_3))_3$	1.5×10^{-5}	5.11	4.35
EHDPP	2-Ethylhexyl diphenyl phosphate	C ₂₀ H ₂₇ O ₄ P	362.40	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2-\text{O}-\text{P}(\text{O})(\text{O}-\text{C}_6\text{H}_5)_2$	6.7×10^{-3}	6.64	4.21
TEHP	Tris(2-ethylhexyl) phosphate	C ₂₄ H ₅₁ O ₄ P	434.63	$\text{O}=\text{P}(\text{O}-\text{CH}_2\text{CH}(\text{CH}_2)_3\text{CH}_3)_3$	1.1×10^{-5}	9.49	6.87

* calculated by Estimation Programs Interface Suite (EPI) WEB 4.1 software by U.S. EPA, 2013.

Table S2. Sampling Site Information.

Site	Latitude	Longitude	Depth (m)	UDF2	Site	Latitude	Longitude	Depth (m)	UDF2	Site	Latitude	Longitude	Depth (m)	UDF2
S001	46.9930	-85.1612	95	366	M019	42.7335	-86.5833	93	484	ON08	43.3575	-78.9396	81	558
S002	47.3603	-85.6208	154	356	M020	42.3665	-87.6672	46	512	ON09	43.5975	-78.8016	141	542
S008	47.6058	-86.8177	301	346	M024	43.4830	-87.4882	150	454	ON10	43.4856	-78.6554	159	536
S011	48.3438	-87.8250	230	329	M028	43.8003	-86.7998	137	444	ON11	43.7587	-78.5158	86	518
S012	47.8553	-88.0418	238	336	M030	42.6600	-87.7382	18	496	ON12	43.4306	-78.4144	88	525
S016	47.6212	-89.4633	180	328	M032	44.3715	-86.9333	257	424	ON13	43.5414	-78.3143	186	517
S019	47.3703	-90.8535	188	333	M041	44.7367	-86.7213	272	414	ON14	43.8342	-78.2063	84	501
S022	46.8002	-91.7508	55	332	M044	42.9528	-87.3155	92	478	ON15	43.5598	-78.1656	191	511
S102	47.6173	-85.6973	92	351	M047	45.1783	-86.3745	200	403	ON16	43.7172	-78.0267	132	501
S103	46.9838	-85.6972	164	364	M048	43.0585	-86.6630	107	473	ON17	43.5902	-78.0111	188	505
S104	48.0382	-86.3217	189	340	M050	45.1165	-87.4165	33	399	ON18	43.6819	-77.8487	150	498
S105	47.6177	-86.3217	81	348	M061	43.4742	-86.7847	137	457	ON19	43.3993	-77.8194	75	510
S106	47.1807	-87.3183	219	352	M083	44.4737	-86.7060	270	422	ON20	43.8722	-77.7130	53	487
S108	48.0392	-86.9493	227	338	M088	44.7187	-87.1740	95	412	ON21	43.5414	-77.6859	178	500
S110	46.7735	-86.9495	138	342	M093a	44.9622	-86.0552	100	411	ON22	43.6093	-77.3759	153	490
S112	48.0393	-87.5733	216	335	M093b	44.7712	-86.1168	60	416	ON23	43.7938	-77.4648	59	484
S113	47.6177	-87.5730	171	342	M093c	44.8562	-86.2430	129	413	ON24	43.3621	-77.5008	124	506
S114	46.9095	-86.5980	398	361	M103	45.0623	-86.4918	207	406	ON25	43.4180	-77.3762	206	498
S116	48.0392	-88.2007	254	332	M113	45.3267	-87.0090	37	395	ON26	43.4583	-77.0697	236	489
S117	47.6175	-88.2007	270	339	M116	45.4008	-85.4995	36	402	ON27	43.7312	-77.0169	90	478
S118	47.6175	-88.8420	189	336	M120	45.5288	-86.1708	140	395	ON28	43.5638	-76.7081	214	479
S119	47.1955	-89.5048	197	338	M125	45.7225	-85.3317	16	395	ON29	43.3952	-76.8645	75	487
S120	47.6185	-90.0712	178	329	ON01	43.3039	-79.7340	25	569	ON30	43.5429	-76.9066	226	483
S121	47.1955	-90.0727	146	335	ON02	43.3713	-79.3533	104	573	ON31	43.7474	-76.6018	82	471
M008	41.9842	-87.0142	66	521	ON03	43.5829	-79.4167	53	621	ON32	43.4921	-76.5820	63	480
M009	42.3850	-86.5915	62	494	ON04	43.2478	-79.4188	42	567	ON33	43.5982	-76.5484	160	475
M010	42.0662	-87.3792	51	548	ON05	43.5166	-79.0803	140	567	ON34	43.8958	-76.5487	58	466
M011	42.5283	-86.9220	164	493	ON06	43.3360	-79.0700	71	566	ON35	43.9926	-76.4901	50	462
M018	42.7338	-86.9995	165	485	ON07	43.6486	-79.0407	117	565	ON36	44.0780	-76.4125	27	459
										ON37	43.5832	-76.3334	47	473

Table S3. Analytical Parameters and Quality Control using LC-MS/MS.

	CAS#	Retention time (min)	Precursor (m/z)	Quantification (m/z)	Qualification (m/z)	Collision energy (ev)	Spiking recoveries (%) ^a	RSD (%) ^b	MLQ (ng g ⁻¹)
TMP	512-56-1	1.48	141.0 141.0	109.1	79.3	17 23	97	9	0.15
TEP	78-40-0	2.20	183.0 183.0	99.2	81.3	18 24	99	7	0.12
TCEP	115-96-8	3.33	284.9 286.9	99.2	99.2	30 29	85	13	1.4
TPrP	513-08-6	4.84	225.1 225.1	99.2	141.1	18 10	91	3	0.18
TCPP	13674-84-5	5.52	326.9 328.9	99.1	99.1	30 29	108	10	0.30
TDCP	13674-87-8	7.88	430.9 432.9	99.2	99.1	28 29	95	13	0.66
TiBP	126-71-6	8.51	267.1 267.1	99.1	155.0	18 6	100	5	0.10
TPhP	115-86-6	8.42	327.0 327.0	214.9	152.1	25 33	92	8	0.10
TnBP	126-73-8	8.69	267.1 267.1	99.2	155.1	18 10	94	5	0.08
CDPP	26444-49-5	9.50	341.0 341.0	229.0	152.1	27 33	88	12	0.26
TBEP	78-51-3	9.76	399.1 399.1	299.0	199.0	12 15	84	4	0.04
TCrP	563-04-2	10.70	369.1 369.1	165.1	243.0	43 27	78	8	0.04
EHDPP	1241-94-7	11.01	363.1 363.1	251.0	152.1	39 12	47	13	0.04
TEHP	78-42-2	13.78	435.2 435.2	99.1	113.2	30 12	27	38	0.10

a. Each OPE was spiked at 20 ng g⁻¹ dw

b. RSD = relative standard deviation of replicates (N = 3)

c. MLQ = method quantification limits

Table S4. Concentrations and Inventories (Inv.) of Σ_{14} OPEs in Ponar Grab Sediments.

Lake Superior				Lake Michigan				Lake Ontario			
Sample ID	ng g ⁻¹ dw	ng g ⁻¹ OC	Inv. ng cm ⁻²	Sample ID	ng g ⁻¹ dw	ng g ⁻¹ OC	Inv. ng cm ⁻²	Sample ID	ng g ⁻¹ dw	ng g ⁻¹ OC	Inv. ng cm ⁻²
S001	5.4	2394	27.4	M008	2.2	123	25.7	ON01	6.8	575	53.5
S002	5.2	756	49.0	M009	18	446	127.0	ON02	6.9	337	41.4
S008	3.4	338	28.7	M010	3.6	1530	21.7	ON03	22	841	229.5
S011	2.2	103	12.6	M011	14	392	69.0	ON04	11	876	106.6
S012	1.4	66	8.3	M018	4.9	210	25.5	ON05	8.8	345	49.8
S016	1.9	153	14.5	M019	2.2	306	14.2	ON06	26	1112	207.1
S019	1.0	60	8.0	M020	1.6	737	8.1	ON07	1.4	154	16.1
S022	1.2	71	7.0	M024	7.2	234	38.2	ON08	48	1707	318.7
S102	1.4	575	15.8	M028	2.1	519	10.7	ON09	4.7	224	27.1
S103	1.1	119	11.1	M030	2.4	1313	17.6	ON10	2.9	636	22.2
S104	1.2	79	8.6	M032	2.6	106	12.0	ON11	1.6	495	10.9
S105	1.8	771	24.5	M041	1.9	96	8.8	ON12	37	1271	250.6
S106	0.80	47	4.5	M044	0.44	47	2.8	ON13	10	359	50.0
S108	1.2	74	8.0	M047	2.4	137	13.1	ON14	2.7	3345	13.0
S110	5.8	3928	27.8	M048	1.5	58	11.1	ON15	25	703	108.8
S112	1.4	75	9.0	M050	5.5	112	17.8	ON16	6.5	268	36.9
S113	1.0	56	6.8	M061	15	487	105.9	ON17	22	633	102.5
S114	4.2	1369	27.3	M083	1.2	44	5.9	ON18	12	400	60.5
S116	0.81	35	4.4	M088	0.87	106	5.3	ON19	13	623	129.8
S117	1.1	51	6.0	M093a	12	437	84.9	ON20	3.2	2197	17.9
S118	1.1	149	11.2	M093b	6.0	273	47.9	ON21	16	775	86.0
S119	1.2	74	7.9	M093c	8.9	323	65.1	ON22	36	868	158.6
S120	4.7	479	43.5	M103	1.5	69	7.6	ON23	1.9	643	11.3
S121	1.1	90	8.2	M113	1.08	117	8.1	ON24	18	646	113.5
				M116	2.6	2595	13.3	ON25	15	465	64.7
				M120	2.7	111	13.9	ON26	24	747	106.0
				M125	1.9	3481	13.8	ON27	37	975	169.7
								ON28	33	1017	137.7
								ON29	2.8	467	24.2
								ON30	24	887	97.7
								ON31	30	683	153.5
								ON32	6.2	890	42.1
								ON33	32	940	153.1
								ON34	7.5	538	61.7
								ON35	24	530	98.6
								ON36	14	272	71.3
								ON37	22	3656	144.6

Table S5. Concentration (ng g⁻¹ dw) and Detection Rate of Individual OPEs in the Ponar Grab Sediments.

	TMP	TEP	TCEP	TPrP	TCPP	TDCP	TiBP	TPhP	TnBP	CDPP	TBEP	TCrP	EHDPP	TEHP	Σ ₁₄ OPE
Lake Superior (N = 24)															
Average	N.D.	0.12	0.15	N.D.	0.15	0.13	0.99	0.04	0.34	N.D.	0.03	0.18	0.01	N.D.	2.16
Min	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.63	N.D.	N.Q.	N.D.	N.D.	N.D.	N.D.	N.D.	0.80
Median	N.D.	0.07	N.D.	N.D.	N.Q.	N.D.	0.95	N.D.	0.15	N.D.	N.D.	0.13	N.D.	N.D.	1.30
Max	N.D.	0.39	1.90	N.Q.	1.10	1.88	1.96	1.04	1.36	N.D.	0.46	1.36	0.19	N.D.	5.80
Detection %	0	67	29	4	54	8	100	8	100	0	13	92	13	0	
Lake Michigan (N = 27)															
Average	N.D.	N.D.	N.D.	N.D.	0.39	0.12	0.16	0.17	0.52	0.30	1.52	1.45	0.03	0.01	4.65
Min	N.D.	N.D.	N.D.	N.D.	0.44										
Median	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.15	N.Q.	0.40	N.Q.	0.48	0.70	N.D.	N.D.	2.38
Max	N.D.	N.Q.	N.Q.	N.D.	1.60	1.99	0.59	0.91	1.86	1.94	9.10	7.18	0.32	0.17	17.56
Detection %	0	4	15	0	48	15	93	63	89	59	89	85	30	26	
Lake Ontario (N = 37)															
Average	N.D.	N.D.	N.D.	N.D.	0.71	N.D.	0.61	2.62	1.43	0.59	7.29	2.07	0.31	0.96	16.59
Min	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.23	N.D.	0.22	N.D.	N.D.	N.D.	N.D.	N.D.	1.38
Median	N.D.	N.D.	N.D.	N.D.	0.48	N.D.	0.62	1.38	1.17	0.44	4.66	1.92	0.24	0.24	13.78
Max	N.D.	N.D.	N.Q.	N.Q.	3.37	N.Q.	1.07	9.03	7.62	2.19	23.74	7.37	1.44	8.38	47.82
Detection %	0	0	14	3	97	14	100	92	100	62	100	97	81	65	
All Three Lakes (N = 88)															
Average	N.D.	0.03	0.04	N.D.	0.46	0.07	0.58	1.17	0.85	0.34	3.54	1.36	0.14	0.41	8.99
Min	N.D.	N.D.	N.D.	N.D.	0.44										
Median	N.D.	N.D.	N.D.	N.D.	0.33	N.D.	0.62	0.14	0.51	N.D.	0.64	0.69	N.D.	N.D.	3.88
Max	N.D.	0.39	1.90	N.Q.	3.37	1.99	1.96	9.03	7.62	2.19	23.74	7.37	1.44	8.38	47.82
Detection %	0	19	18	2	70	13	98	60	97	44	73	92	47	35	

N.D. - Not detected

N.Q. - Detected but not quantified

Table S6. Concentration of Individual OPEs and Σ_{14} OPEs and the Flux of Σ_{14} OPEs in Sediment Cores from Lake Michigan.

depth	date	TMP	TEP	TCEP	TPrP	TCPP	TDCP	TiBP	TPhP	TnBP	CDPP	TBEP	TCrP	EHDPP	TEHP	Σ_{14} OPEs	Flux- Σ_{14} OPEs
cm	Year	ng g ⁻¹ dw	ng g ⁻¹ dw	ng cm ⁻² yr ⁻¹													
M009																	
0.5	2009	N.D.	N.D.	3.02	N.D.	3.37	2.02	0.39	0.67	0.58	0.29	14.98	2.07	0.29	0.13	27.82	0.83
1.5	2006	N.D.	N.D.	5.00	N.D.	2.00	N.D.	0.46	0.55	0.70	N.D.	8.75	2.21	0.25	0.45	20.37	0.60
2.5	2001	N.D.	N.D.	N.Q.	N.D.	2.17	N.D.	0.58	0.45	0.71	N.D.	9.47	3.51	0.32	0.13	17.34	0.51
3.5	1997	N.D.	N.D.	N.Q.	N.D.	0.81	N.D.	0.48	0.79	0.59	0.74	7.20	5.06	0.42	0.18	16.27	0.48
4.5	1991	N.D.	N.D.	N.Q.	N.D.	0.89	N.D.	0.47	0.80	0.74	2.03	9.12	5.79	0.81	0.18	20.83	0.62
5.5	1986	N.D.	N.D.	N.Q.	N.D.	0.81	N.D.	0.38	0.93	0.64	2.42	9.47	4.28	0.68	0.21	19.83	0.59
6.5	1980	N.D.	N.D.	N.Q.	N.D.	1.97	N.D.	0.44	0.77	0.65	1.58	12.66	5.23	0.98	0.21	24.50	0.73
7.5	1974	N.D.	N.D.	N.D.	N.D.	0.75	N.D.	0.85	2.20	1.49	3.19	18.22	6.7	2.15	0.45	35.95	1.07
8.5	1968	N.D.	N.D.	N.D.	N.D.	1.15	N.D.	0.91	2.17	2.16	4.40	19.34	8.4	2.07	0.80	41.36	1.23
9.5	1963	N.D.	N.D.	N.D.	N.D.	0.84	N.D.	1.18	1.44	1.56	4.08	14.52	10.3	2.20	0.64	36.72	1.09
11.5	1953	N.D.	N.D.	N.D.	N.D.	0.34	N.D.	0.90	1.26	1.64	4.01	8.20	13.7	1.52	0.53	32.13	0.95
13.5	1941	N.D.	N.D.	N.D.	N.D.	0.58	N.D.	0.87	1.44	1.46	3.81	2.52	12.4	0.18	0.37	23.67	0.70
15.5	1928	N.D.	N.D.	N.Q.	N.D.	1.06	N.D.	0.86	1.70	1.06	6.19	0.93	9.70	N.D.	N.Q.	21.50	0.64
17.5	1915	N.D.	N.D.	N.Q.	N.D.	0.42	N.D.	0.84	0.25	0.62	2.01	0.27	4.04	N.D.	N.Q.	8.45	0.25
19.5	1901	N.D.	N.D.	N.D.	N.D.	0.40	N.D.	1.04	N.D.	0.48	N.D.	N.D.	2.24	N.D.	N.Q.	4.16	0.12
21.5	1888	N.D.	N.D.	N.D.	N.D.	0.53	N.D.	1.04	N.D.	0.48	N.D.	N.D.	0.68	N.D.	N.Q.	2.73	0.08
23.5	1874	N.D.	N.D.	N.Q.	N.D.	0.58	N.D.	1.03	N.D.	0.14	N.D.	N.D.	N.D.	N.D.	N.D.	1.74	0.05
25.5	1860	N.D.	N.D.	N.D.	N.D.	2.19	N.D.	1.03	0.14	0.35	N.D.	0.26	N.D.	N.D.	0.47	4.44	0.13
27.5	1845	N.D.	N.D.	N.D.	N.D.	N.Q.	2.49	0.95	N.Q.	0.23	N.D.	N.D.	N.D.	N.D.	N.D.	3.67	0.11
29.5	1830	N.D.	N.D.	N.Q.	N.D.	0.37	N.D.	1.45	N.D.	0.50	N.D.	N.D.	N.D.	N.D.	N.D.	2.32	0.07
M024																	
1.5	2000	N.D.	N.D.	N.Q.	N.Q.	7.49	N.Q.	0.64	0.50	0.35	0.38	2.80	7.43	0.11	0.19	19.90	0.19
2.5	1992	N.D.	N.D.	N.D.	N.D.	1.28	N.D.	0.52	0.66	0.42	0.95	2.75	6.45	0.11	0.21	13.35	0.13
3.5	1983	N.D.	N.D.	N.D.	N.D.	2.79	0.88	0.50	0.66	0.33	1.14	2.92	8.02	0.12	1.04	18.39	0.18
4.5	1972	N.D.	N.D.	N.D.	N.Q.	1.36	N.Q.	0.49	0.54	0.49	0.81	3.41	8.63	0.11	0.36	16.22	0.16
5.5	1962	N.D.	N.D.	N.Q.	N.D.	0.49	2.01	0.52	0.56	0.47	1.05	3.51	7.46	0.15	0.87	17.10	0.17
6.5	1951	N.D.	N.D.	N.Q.	N.D.	1.70	N.D.	0.43	0.46	0.65	0.82	4.52	7.24	0.09	0.95	16.87	0.16
7.5	1940	N.D.	N.D.	N.Q.	N.Q.	1.24	N.D.	0.36	0.69	0.54	1.14	2.88	7.98	0.11	0.52	15.45	0.15

8.5	1927	N.D.	N.D.	N.Q.	N.Q.	1.51	N.D.	0.27	0.16	0.46	0.51	1.18	3.88	N.D.	0.22	8.18	0.08
9.5	1914	N.D.	N.D.	N.D.	N.D.	0.83	N.D.	0.36	0.20	0.23	N.D.	1.18	1.26	N.D.	N.D.	4.07	0.04
11.5	1894	N.D.	N.D.	N.Q.	N.Q.	0.84	N.D.	0.36	0.11	0.15	N.D.	0.13	N.Q.	N.D.	N.D.	1.60	0.02
13.5	1867	N.D.	N.D.	N.D.	N.D.	0.92	N.D.	0.28	N.Q.	0.18	N.D.	0.05	N.D.	N.D.	N.D.	1.43	0.01
15.5	1839	N.D.	N.D.	N.Q.	N.Q.	1.25	N.D.	0.36	N.D.	0.23	N.D.	N.D.	N.D.	N.D.	N.D.	1.84	0.02
17.5	1811	N.D.	N.D.	N.D.	N.Q.	1.02	N.D.	0.41	0.13	N.Q.	N.D.	N.D.	N.D.	N.D.	N.D.	1.56	0.02
19.5	1783	N.D.	N.D.	N.D.	N.D.	1.16	N.D.	0.44	N.Q.	0.15	N.D.	N.D.	N.D.	N.D.	N.D.	1.75	0.02
21.5	1755	N.D.	N.D.	N.D.	N.Q.	0.67	N.D.	0.26	0.10	N.Q.	N.D.	N.D.	N.D.	N.D.	0.24	1.27	0.01
23.5	1726	N.D.	N.D.	N.D.	N.Q.	1.08	N.D.	0.18	N.Q.	N.Q.	N.D.	0.17	N.D.	N.D.	N.D.	1.43	0.01
25.5	1696	N.D.	N.D.	N.Q.	N.Q.	0.93	N.D.	0.25	0.12	0.16	N.D.	N.D.	N.D.	N.D.	N.D.	1.46	0.01
27.5	1666	N.D.	N.D.	N.Q.	N.D.	1.08	N.D.	0.35	N.D.	0.12	N.D.	0.16	N.D.	N.D.	N.D.	1.72	0.02
29.5	1635	N.D.	N.D.	N.D.	N.D.	1.07	N.D.	0.55	N.Q.	0.23	N.D.	0.38	N.D.	N.D.	N.D.	2.23	0.02
M047																	
1.5	2004	N.D.	N.D.	2.74	N.Q.	2.33	1.62	0.52	0.78	1.50	1.10	5.30	4.58	0.18	0.29	20.93	0.25
2.5	1999	N.D.	N.D.	1.85	N.D.	1.27	N.D.	0.52	0.79	0.61	0.35	5.65	5.35	0.27	0.62	17.28	0.20
3.5	1993	N.D.	N.D.	N.Q.	N.D.	2.11	N.Q.	0.32	0.58	0.56	1.03	6.15	4.92	0.18	0.75	16.60	0.20
4.5	1986	N.D.	N.D.	2.04	N.Q.	0.70	N.D.	0.53	0.63	0.65	1.02	6.85	4.90	0.28	0.43	18.02	0.21
5.5	1979	N.D.	N.D.	1.98	N.D.	0.80	0.95	0.67	0.71	0.74	1.08	6.45	6.07	0.36	0.61	20.42	0.24
6.5	1972	N.D.	N.D.	N.Q.	N.D.	0.48	N.D.	0.53	0.78	0.63	1.03	6.74	6.99	0.31	1.75	19.23	0.23
7.5	1964	N.D.	N.D.	N.Q.	N.Q.	0.65	N.D.	0.52	0.53	0.86	1.27	4.29	5.48	0.25	0.34	14.18	0.17
8.5	1956	N.D.	N.D.	N.Q.	N.D.	0.30	N.D.	0.56	0.22	0.69	0.58	2.37	4.81	0.07	0.76	10.36	0.12
9.5	1948	N.D.	N.D.	N.D.	N.Q.	0.41	N.D.	0.36	0.22	0.51	0.58	1.50	4.19	N.Q.	0.54	8.31	0.10
11.5	1936	N.D.	N.D.	N.D.	N.Q.	N.D.	N.D.	0.46	N.D.	0.31	0.66	0.31	2.03	N.D.	N.D.	3.77	0.04
13.5	1919	N.D.	N.D.	N.Q.	N.D.	N.Q.	N.D.	0.43	0.15	0.31	N.D.	0.40	0.66	N.D.	N.D.	1.95	0.02
15.5	1901	N.D.	N.D.	N.Q.	N.Q.	N.Q.	N.D.	0.56	N.D.	0.13	N.D.	0.12	0.47	N.D.	N.D.	1.28	0.02
17.5	1881	N.D.	N.D.	N.Q.	N.D.	N.D.	N.D.	0.49	N.D.	0.11	N.D.	N.D.	N.D.	N.D.	N.D.	0.60	0.01
19.5	1861	N.D.	N.D.	N.D.	N.Q.	N.Q.	N.D.	0.60	N.D.	0.17	N.D.	0.21	N.D.	N.D.	N.D.	0.98	0.01
21.5	1842	N.D.	N.D.	N.D.	N.Q.	N.Q.	N.D.	0.55	N.Q.	0.19	N.D.	0.11	N.D.	N.D.	N.D.	0.86	0.01
23.5	1823	N.D.	N.D.	N.Q.	N.D.	0.43	N.D.	0.61	N.D.	0.10	N.D.	0.19	N.Q.	N.D.	N.D.	1.34	0.02
25.5	1803	N.D.	N.D.	N.Q.	N.Q.	N.Q.	N.D.	0.53	N.D.	0.11	N.D.	1.68	N.D.	N.D.	N.D.	2.31	0.03
27.5	1783	N.D.	N.D.	N.Q.	N.Q.	0.33	1.43	0.47	N.D.	0.09	N.D.	0.21	N.D.	N.D.	N.D.	2.52	0.03
29.5	1763	N.D.	N.D.	N.Q.	N.D.	0.46	N.D.	0.73	N.D.	0.22	N.D.	0.09	N.D.	N.D.	N.D.	1.50	0.02

N.D. - Not detected

N.Q. - Detected but not quantified

Table S7. Spearman's Correlation Coefficient (R) among OPEs with >85% detection rates.

<u>Lake Superior (N=24)</u>						
ng g⁻¹ dw	TiBP	TnBP	TCrP			
TiBP	1					
TnBP	0.789 ***	1				
TCrP	-0.261	-0.320	1			
ng g⁻¹ OC	TiBP	TnBP	TCrP			
TiBP	1					
TnBP	0.864 ***	1				
TCrP	0.391	0.265	1			
<u>Lake Michigan (N=27)</u>						
ng g⁻¹ dw	TiBP	TnBP	TBEP	TCrP		
TiBP	1					
TnBP	0.020	1				
TBEP	-0.163	0.450 *	1			
TCrP	-0.352	0.367	0.733 **	1		
ng g⁻¹ OC	TiBP	TnBP	TBEP	TCrP		
TiBP	1					
TnBP	0.480 *	1				
TBEP	0.111	0.241	1			
TCrP	-0.112	-0.200	0.401 *	1		
<u>Lake Ontario (N=37)</u>						
ng g⁻¹ dw	TCPP	TiBP	TPhP	TnBP	TBEP	TCrP
TCPP	1					
TiBP	-0.241	1				
TPhP	-0.148	0.296	1			
TnBP	0.100	-0.023	0.795 ***	1		
TBEP	0.275	-0.137	0.693 ***	0.915 ***	1	
TCrP	0.056	-0.136	0.803 ***	0.863 ***	0.832 ***	1
ng g⁻¹ OC	TCPP	TiBP	TPhP	TnBP	TBEP	TCrP
TCPP	1					
TiBP	0.435 **	1				
TPhP	-0.318	0.006	1			
TnBP	0.368 *	0.193	0.338 *	1		
TBEP	0.096	-0.302	0.369 *	0.613 **	1	
TCrP	0.127	-0.090	0.293	0.667 ***	0.766 ***	1

* p < 0.05; ** p < 0.01; *** p < 10⁻⁵

Table S8. Multiple Linear Regressions Statistics by SPSS.

Figure 3A: $\text{Ln } \sum_{14}\text{OPEs (ng/g dw)} = - 0.985 + 0.0384 * \text{OC (mg/g)} + 0.00492 * \text{UDF}$						
	Intercept	OC	UDF2	R ²	F	p-value
model	-0.985	0.0384	0.00492	0.592	60.7	4.19E-17
p-value	6.39E-03	3.30E-11	2.33E-08			
Figure 3B: $\text{Ln TBEP (ng/g dw)} = - 11.21 + 0.0981 * \text{OC (mg/g)} + 0.0195 * \text{UDF}$						
	Intercept	OC	UDF2	R ²	F	p-value
model	-11.21	0.0981	0.0195	0.747	126.5	3.36E-26
p-value	2.75E-24	8.91E-14	5.29E-18			
Figure 3C: $\text{Ln TCrP (ng/g dw)} = - 6.72 + 0.0751 * \text{OC (mg/g)} + 0.0104 * \text{UDF}$						
	Intercept	OC	UDF2	R ²	F	p-value
model	-6.72	0.0751	0.0104	0.628	71.7	5.69E-19
p-value	2.23E-16	4.09E-12	7.63E-10			

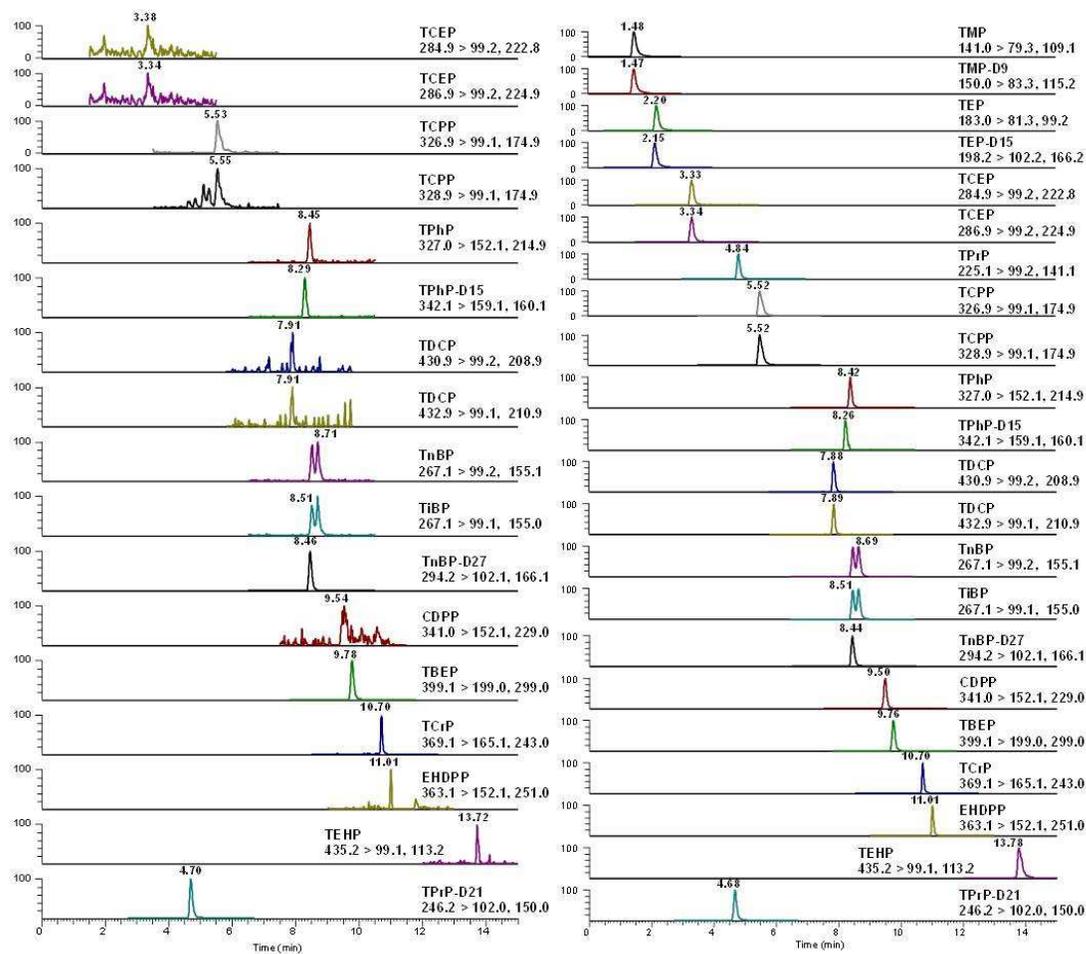


Figure S1. LC-MS / MS extracted ion chromatograms (EIC) of a sediment extract (left) and an OPE standard mixture at $100 \mu\text{g L}^{-1}$ concentration level (right).

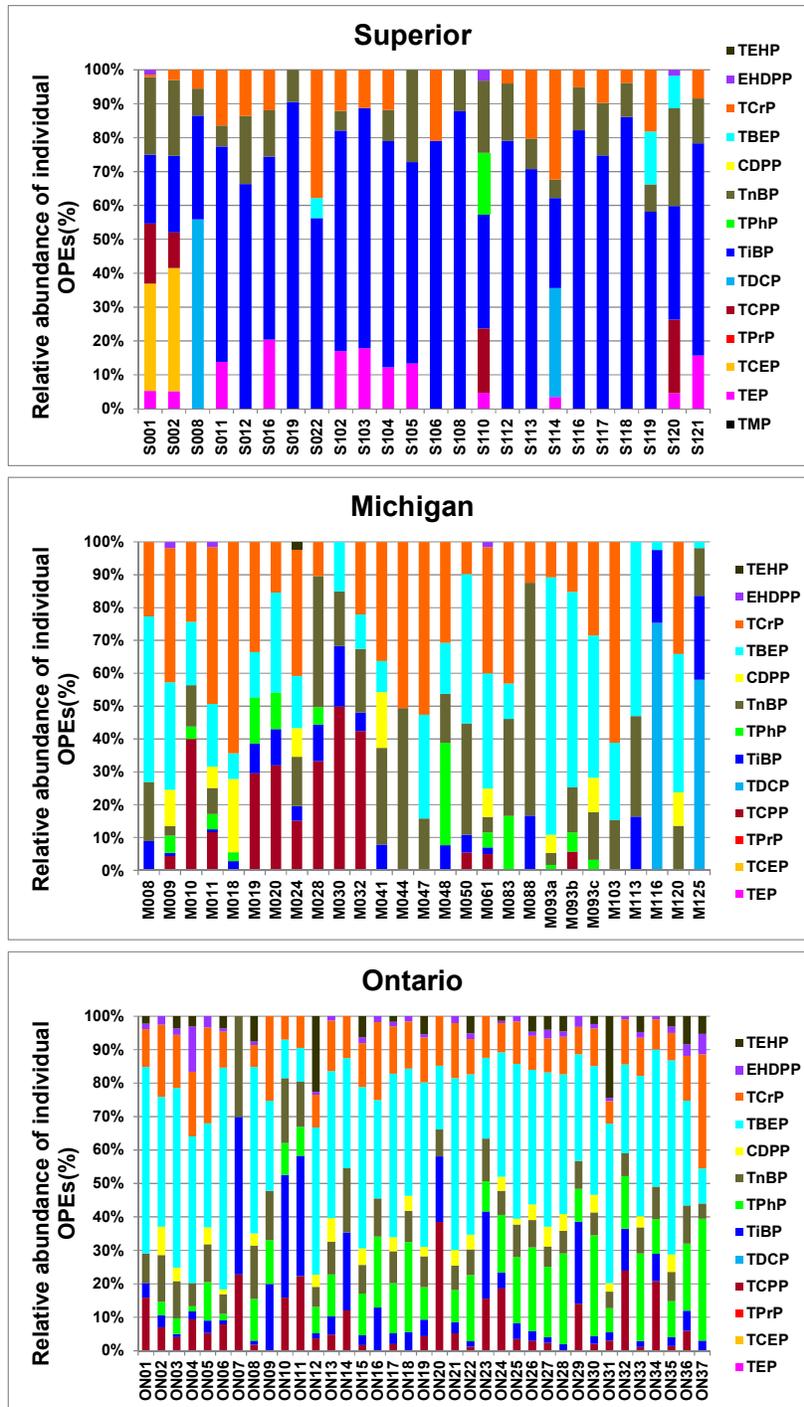


Figure S2. Relative abundance of individual OPEs in Ponar grab sediments.

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