

Occurrence of Atrazine and Related Compounds in Sediments of Upper Great Lakes

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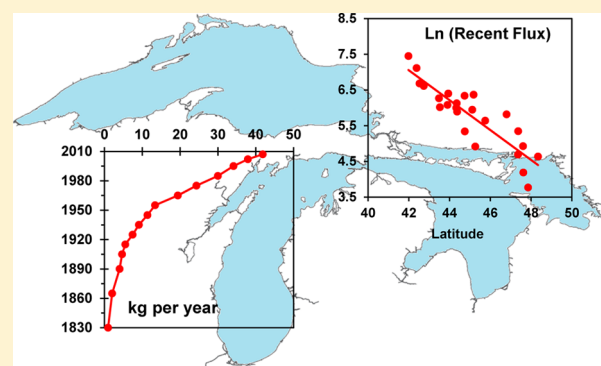
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Supporting Information

ABSTRACT: Surface grab and core sediment samples were collected from Lakes Michigan, Superior, and Huron from 2010 to 2012, and concentrations of herbicides atrazine, simazine, and alachlor, as well as desethylatrazine (DEA), were determined. Concentrations of atrazine in surface grabs ranged from 0.01 to 1.7 ng/g dry weight and are significantly higher in the southern basin of Lake Michigan (latitude <44°) than other parts of the three lakes. The highest concentration of alachlor was found in sediments of Saginaw Bay in Lake Huron. The inventory and net fluxes of these herbicides were found to decline exponentially from the south to the north. The concentration ratio of DEA to atrazine (DEA/ATZ) increased with latitude, suggesting degradation of atrazine to DEA during atmospheric transport. DEA/ATZ also increased with sediment depth in the sediment cores. Diffusion of deposited herbicides from the upper sediment into deeper sediments has occurred, on the basis of the observed patterns of concentrations in dated sediment cores. Concentrations of atrazine in pore water were estimated and were higher than those reported for the bulk waters, suggesting the occurrence of solid-phase deposition of atrazine through the water column and that contaminated sediments act as a source releasing atrazine to the overlying water.



INTRODUCTION

Current agricultural practices often involve extensive use of herbicides.¹ Atrazine [1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine], simazine [6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine], and alachlor [2-chloro-2,6-diethyl-*N*-(methoxymethyl)acetanilide] are among those used in the United States. Atrazine and simazine are both triazines and were initially registered as herbicides in 1958 and 1956, respectively.^{2,3} Alachlor, a chloroacetanilide, was first registered in 1969.⁴ From 1992 to 2011, reported annual usages on crops were 32 000–36 000 tons for atrazine, 1814–2722 tons for simazine, and 454–22 680 tons for alachlor.⁵ These herbicides are primarily used in the “Corn Belt” near the Great Lakes of North America, including the states of Iowa, Illinois, and Indiana and parts of others.^{1,5} Their use has been banned by

the European Union because of ubiquitous and unpreventable water contamination. Atrazine is classified as a Restricted Use Pesticide in the United States.⁶ According to the U.S. Environmental Protection Agency (EPA), atrazine is an endocrine disruptor,⁶ simazine may have reproductive or developmental toxicity,⁷ and alachlor was classified as a “likely” human carcinogen at high dose.⁴

Compared with organochlorine pesticides, atrazine and related compounds are more soluble in water. A major concern is their potential to leach from soils to surface and ground

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waters that are used as sources of drinking water;³ thus, most monitoring efforts to date have been conducted for water. Atrazine was found in waters of all five Laurentian Great Lakes.^{8–10} In rivers of the Midwestern U.S., elevated concentrations of atrazine, simazine, and alachlor were found during runoff events following applications.^{11–15} Atrazine is considered to be persistent in water, with a half-life of >200 days.¹⁶ In the environment, atrazine and some other triazines can degrade to desethylatrazine (DEA) and desisopropylatrazine (DIA); DIA and DEA can further degrade to desethyl-desisopropylatrazine (DDA), and all of them could also be hydroxylated.^{17,18} DEA and DIA were detected in the water of Lake Michigan.² In addition, atrazine, DEA, and DIA have been detected in air, including the vapor phase, particulate phase, and precipitation, of the Great Lakes region.^{2,19} Chemical structures and environmentally important physicochemical properties of atrazine and related compounds are summarized in Table S1.

In contrast to research on water and air, reports on the presence of atrazine and related compounds in sediment are limited. In rural ponds of Ontario, Canada, atrazine was found in sediment with concentrations as high as 6.4 mg/kg (compared with 17 $\mu\text{g/L}$ in water) after accidental spills of atrazine during 1971 to 1985.²⁰ Atrazine, DEA, DIA, simazine, or alachlor were detected in sediments of an agricultural drainage ditch in the Mississippi Delta,²¹ wetlands of Texas, New Mexico, and Oklahoma,²² a small eutrophic lake in Switzerland,²³ managed realignment sites in England,²⁴ the German Bight in the North Sea,²⁵ Ebro delta of Tarragona in Spain,²⁶ coastal lagoon of Northern Adriatic in Italy,²⁷ and Songhua River Basin in northeastern China.²⁸ However, reports on herbicides in the sediments of the Great Lakes are notably sparse or nonexistent.

The objectives of this study were to investigate the spatial distribution, total mass accumulation, and temporal trends and to examine influencing factors, of atrazine, simazine, and alachlor as well as atrazine degradation product DEA in sediments of Lakes Michigan, Superior, and Huron. Additionally, concentrations of these compounds in sediment pore water were estimated and compared with previously reported concentrations in the bulk water of the lakes. To our knowledge, this is the first report on these herbicides in sediments of the Great Lakes and among only a few such reports in North America.

EXPERIMENTAL SECTION

Sampling. Surface and core sediments were collected from the U.S. EPA Research Vessel (R/V) *Lake Guardian*. Most samples from Lake Michigan were collected in September, 2010; additional samples from Lake Michigan (4 sampling sites) and all samples from Lake Superior were collected in June, 2011. Samples from Lake Huron including Georgian Bay and the North Channel were collected in 2012. Sampling locations are shown in Figure S1, with detailed information provided in Table S2.

Grab samples of surface sediments were collected using a Ponar sampler. Each Ponar grab (PG) sample was homogenized using a paint mixer driven by an electric drill. Most sediment cores were collected by an Ocean Instrument MC400 multicorer (San Diego, California). Cores from sites M024, M032, M047, and M050 were collected by use of a box corer, and those from M008, M009, M011, and M018 were collected using an Ekman dredge corer.

At each site, four cores (10 cm in diameter) were obtained and sectioned using hydraulic extruders. All cores from Lake Michigan were sectioned into 1 cm intervals to a depth of 10 cm and then 2 cm intervals to a depth of 30 cm or the end. All cores from Lake Superior and two cores from Lake Huron (H038 and H061) were sectioned into 0.5 cm segments to a depth of 5 cm and then 1 cm segments to 15 cm depth, followed by 2 cm segments to 25 or 27 cm. The other cores from Lake Huron were sectioned into 1 cm intervals to a depth of 15 cm, followed by 2 cm intervals to a depth of 35 cm or the end of the cores. Different sectioning depths were selected on the basis of predicted sedimentation rates at different sites for best possible resolution of deposition chronology. To minimize potential “smearing”, sediment within 2 mm of the wall of the coring tube was trimmed off and discarded. After each segment was cut, all sectioning gear was thoroughly cleaned using tap water, acetone, and deionized water. At each site, the segments at corresponding depths were combined and mixed using stainless steel spoons in glass bowls.

Well-mixed samples of Ponar grab and composite core segments were distributed into precleaned 125 mL amber glass jars with Teflon-liner screw caps and immediately frozen. Samples were transported to the laboratory in coolers, where they were stored at $-20\text{ }^{\circ}\text{C}$ until further processing and analyses to determine the concentrations of targeted chemicals in this laboratory and selected radionuclides in a collaborating laboratory. Another portion was refrigerated in a 50 mL Falcon tube.

Sediment Characterization and Core Dating. From the 50 mL Falcon tube, triplicate subsamples were taken with a 3 mL syringe barrel and weighed before and after drying to constant mass, and the bulk and dry density, particle density, water and solids contents were determined by use of standard methods.^{29,30} Dried subsamples were combusted at $375\text{ }^{\circ}\text{C}$ for 24 h, and loss of mass was termed “organic matter”. Total carbon was measured using the procedures previously described.^{31–33} Samples used for determination of total organic carbon were acidified by slow addition of 10% HCl to excess (at least 10 mL of HCl per g dry mass of sediment) and shaken for 24 h to remove all forms of carbonate.³³ Residual acid was removed using at least three cycles of vortex mixing with deionized water, centrifugation, and removal of supernatant. The pH was measured to ensure all residual acid was removed. Acidified and washed samples were then dried, and total organic carbon was measured as above for total carbon.

Samples of cores in 125 mL jars were lyophilized and a ~ 3 g aliquot of each homogenized core section was used for dating. Activities of radionuclides ^{210}Pb and ^{137}Cs 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 against standard reference materials DL-1a (CANMET U-Th ore) for U- and Th-series radionuclides and NIST-4365 (ocean sediment) for ^{137}Cs in sample geometry. Peak areas were corrected for background, and errors were estimated from counting statistics. The mass sedimentation rate (MSR) and focusing factor (FF) obtained from cumulative excess ^{210}Pb inventories are presented in Table S2. The year of deposition for core segments was estimated using the MSR and dry mass of collected sediment. Cores collected at sites H037, S001, and S114 could not be dated due to low sediment accumulation (Table S2).

Identification and Quantification of Analytes. A standard mixture of herbicides and pesticides (Catalog # M-525.2-CP-ASL) was purchased from AccuStandard (New Haven, CT). Individual standards of atrazine, DEA, DIA, and DDA were also purchased from AccuStandard. Surrogate deuterated benzo[e]pyrene (BeP-d12) and tributyl phosphate (TBP-d27) and internal standards deuterated fluorene (FLU-d10) and ^{13}C labeled 2,4,2',4'-tetrachlorobiphenyl (PCB47L) were purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA). All solvents were HPLC or Optima grade and purchased from Fisher Scientific (Pittsburgh, PA). Silica gel (100–200 mesh, 75–150 μm , grade 644), alumina (neutral, Brockmann I, 50–200 μm by Acros Organics), and granular anhydrous sodium sulfate (Na_2SO_4) were also obtained from Fisher Scientific. Alumina and Na_2SO_4 were activated at 500 $^\circ\text{C}$ for 8 h, and silica gel was activated at 160 $^\circ\text{C}$ for at least 16 h or 500 $^\circ\text{C}$ for 8 h. They were stored at 160 $^\circ\text{C}$ and cooled to room temperature in desiccators before use.

A detailed description of laboratory procedures has been published elsewhere.³⁴ In brief, approximately 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 using a hexane and acetone (1:1, v/v) mixture at 100 $^\circ\text{C}$ with heating time of 5 min and static time of 10 min in each cycle. The extract was concentrated in a rotary evaporator and solvent-exchanged into hexane. A glass column (11 mm id \times 40 cm long) was prefilled with dichloromethane (DCM). Then, the column was filled from bottom to top with 1 g of granular anhydrous Na_2SO_4 , 8 g of alumina, 4 g of silica gel, and 4 g of granular anhydrous Na_2SO_4 . 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 (v/v) mixture (F-2), 100 mL of DCM (F-3), and 100 mL of methanol (F-4). The target analytes of this work were in F-3 and F-4, which were solvent exchanged into hexane. Surrogates BeP-d12 and TBP-d27 were eluted in F-3 and F-4, respectively, along with the target analytes.³⁴ Aliquots of both fractions were placed in a 200 μL glass insert of a 2 mL vial for instrumental analysis.

An Agilent 7890 gas chromatograph (GC) coupled with an Agilent 7000 triple quadrupole mass spectrometer (QQQ-MS) was used to identify and quantify targeted analytes. The multimode injection port was operated in solvent vent mode with 60 μL (20 $\mu\text{L} \times 3$) of total injection per run. The inlet temperature started at 0 $^\circ\text{C}$, which was held for 2.1 min, and then increased to 300 $^\circ\text{C}$ at 600 $^\circ\text{C}/\text{min}$. The vent flow was 300 mL/min. The purge flow was 60 mL/min at a run time of 3 min. The carrier gas was helium, and the flow was kept constant at 1.2 mL/min. A Restek RXi-XLB capillary column (30 m \times 0.25 mm i.d. \times 0.10 μm film thickness) was used for separation. The initial oven temperature was set at 50 $^\circ\text{C}$, which was held for 3 min, then increased to 100 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$, then increased to 300 $^\circ\text{C}$ at 5 $^\circ\text{C}/\text{min}$, and kept for 5 min until the run was completed. The GC-MS interface was kept at 300 $^\circ\text{C}$. Temperature of the electron impact (EI) ion source was set at 230 $^\circ\text{C}$, and temperatures of both quadrupole 1 and quadrupole 2 were set at 150 $^\circ\text{C}$. Data were acquired in multiple reactions monitoring (MRM) mode. Transition ions of the target analytes, surrogates, and internal standards are summarized in Table S3a, and example total ion chromatograms are provided in Figure S2a. Atrazine, simazine, and

alachlor were analyzed in all the samples. DEA was analyzed in all Ponar grab samples, four cores (M011, M018, M032, and M041) of Lake Michigan, and all cores in Lakes Superior and Huron.

To ensure correct identification of analytes, the extracts of Ponar grab sediment from site M044 and core from M018 were solvent-exchanged into methanol and filtered through nylon 0.2 μm , 500 μL centrifugal filters (VWR, Radnor, PA), then analyzed by an Agilent 1260 HPLC (Agilent Technologies, Santa Clara, CA), and interfaced with a 3200 Q Trap triple quadrupole/linear ion trap mass spectrometer (AB Sciex; Toronto, Canada) for atrazine, DEA, DIA, and DDA. The ion transitions used for identification and quantification are given in Table S3b. The LC mobile phase A was 0.1% formic acid water solution, and B was 0.1% formic acid methanol solution. The flow rate was 200 $\mu\text{L}/\text{min}$. The initial mobile phase was 95% A (5% B). It was decreased to 80% in 2 min and held until 5 min, then decreased to 50% in 5 min, further decreased to 20% in another 5 min, and finally to 5% in 2 min and held for 2 min. Sample chromatograms are shown in Figure S2b. The comparison between GC and HPLC analyses revealed relatively large uncertainties in the analyses of DIA; therefore, data for DIA are not discussed further in this paper, although it was found in most samples.

Quality Control. Two laboratory procedural blanks (Na_2SO_4) were processed along with sediment samples of each core, and four blanks were prepared for Ponar grab samples in each lake. Concentrations of target compounds in the blanks ranged from below detection limit (N.D.) to 0.1 ng/g dry weight (dw). Surrogates BeP-d12 (8 ng) and TBP-d27 (8 ng) were added to each sample before extraction, and their respective average recovery \pm standard deviation (S.D.) was $103 \pm 21\%$ and $93 \pm 28\%$ ($N = 500$), respectively. A number of samples were re-extracted or the extracts were reinjected into GC/MS in order to meet the quality control criteria that the recoveries of both surrogates must be between 60% and 135%. The concentrations are reported in this paper without adjustment based on surrogate recoveries. One sample from each core and two samples of the Ponar grabs in each lake were analyzed in duplicate. The average relative percentage differences (RPDs) for atrazine, simazine, alachlor, and DEA are $17 \pm 26\%$ ($N = 35$), $10 \pm 10\%$ ($N = 10$), $26 \pm 36\%$ ($N = 35$), and $15 \pm 17\%$ ($N = 31$), respectively. In addition, duplicate blanks (Na_2SO_4) were spiked with the target analytes (8–20 ng each) and the average recoveries were $89 \pm 9\%$ for atrazine, $74 \pm 26\%$ for DEA, $123 \pm 5\%$ for simazine, and $129 \pm 18\%$ for alachlor. The detection limits based on three times of signal-to-noise ratio were 0.020 ng/g for atrazine, 0.22 ng/g for DEA, 4.32 ng/g for DDA, 0.024 ng/g for simazine, and 0.003 ng/g for alachlor, with the use of 5 g of sediment.

Estimation of Net Deposition Flux, Inventory, and Total Accumulation. Laboratory data for sediment cores were used to estimate the following:³⁵

$$\text{net deposition flux}_i (\text{ng m}^{-2} \text{y}^{-1}) = C_i \times \text{MSR}/\text{FF} \times 10^4 \quad (1)$$

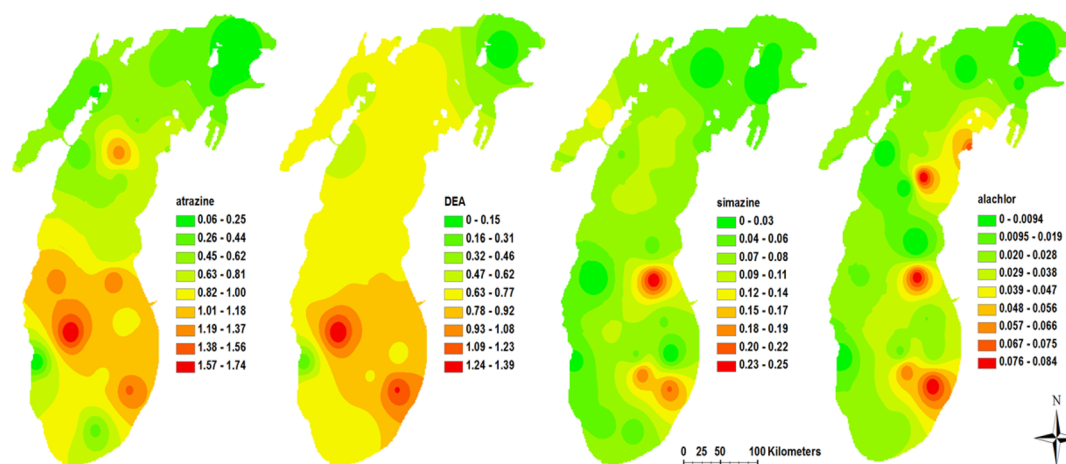
$$\text{inventory} (\text{ng cm}^{-2}) = \sum C_i \rho_{b,i} d_i \quad (2)$$

$$\begin{aligned} \text{annual loading rate} (\text{kg y}^{-1}) \\ = \text{average flux} \times \text{lake water surface area} \times 10^{-6} \end{aligned} \quad (3)$$

Table 1. Median (Range) Concentrations (ng/g dw)^a and Detection Rates (%) of Atrazine, DEA, Simazine, and Alachlor in Sediment Samples from Lakes Michigan, Superior, and Huron

| lake | N | atrazine | DEA | simazine | alachlor |
|--------------|----------------|-----------------------|-----------------------|----------------------|------------------------|
| Ponar Grab | | | | | |
| Michigan | 29 | 0.67 (0.06–1.74) 100% | 0.68 (0.11–1.39) 97% | 0.43 (0.01–1.42) 79% | 0.02 (0.001–0.085) 76% |
| Superior | 24 | 0.09 (0.01–1.73) 63% | 0.11 (0.11–0.72) 17% | 0.01 (0.01–2.67) 21% | 0.001 (0.001–0.077) 4% |
| Huron | 59 | 0.15 (0.01–0.74) 66% | 0.61 (0.11–0.96) 68% | 0% | 0.001 (0.001–0.43) 17% |
| Core Surface | | | | | |
| Michigan | 9 ^b | 4.94 (2.53–6.18) 100% | 2.46 (1.25–2.77) 100% | 1.39 (0.01–1.91) 89% | 0.18 (0.06–0.33) 100% |
| Superior | 9 | 1.15 (0.10–1.66) 100% | 0.89 (0.11–1.51) 89% | 0% | 0.05 (0.001–0.12) 78% |
| Huron | 9 | 2.67 (1.26–3.28) 100% | 1.63 (0.76–2.80) 100% | 0% | 0.14 (0.05–0.28) 100% |

^aValues below detection limit are replaced by 1/2 detection limit; dw = dry weight. ^bN = 4 for DEA.

**Figure 1.** Inverse distance weighted interpretation of spatial distribution of target herbicides in surface sediment of Lake Michigan (Unit: ng/g dw).

$$\text{total load (kg)} = \text{average inventory} \times \text{lake water surface area} \times 10^{-2} \quad (4)$$

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 g cm⁻² y⁻¹, and the FF is dimensionless (Table S2). The water surface areas of Lakes Michigan, Superior, and Huron are 57 800, 82 100, and 59 600 km², respectively. Other constants are for unit conversions. The “average” used in eqs 3 and 4 was either the mean of cores or the average inverse distance weighted interpretation results from spatial analysis of ArcGIS 10 based on cores.

RESULTS AND DISCUSSION

Spatial Variation. Table 1 summarizes the medians and ranges of measured concentrations in both Ponar grab samples and the surface segments (0–1 or 0–0.5 cm) of sediment cores. Data obtained for individual coring stations are presented in Table S4. Concentrations in the top segments of cores are in general higher than those in Ponar grabs at the same location. This was expected because the Ponar sampler penetrated to depths exceeding 10 cm, where the sediment is generally less contaminated (see below). The concentrations of atrazine are about 2–20 times higher than those predicted from water data in the 1990s for Lakes Michigan (0.072 ng/g), Superior (0.005 ng/g), and Huron (0.063 ng/g).³⁶ Consistent with the geographic pattern of agricultural uses,⁵ concentrations of atrazine in the sediment are in the rank order of Lake Michigan > Lake Huron > Lake Superior. This is in general agreement with the north to south increasing pattern of atrazine concentration in water of the Great Lakes.⁹ Table S5

summarizes the results from other sediment studies for comparison purposes.

Spatial variations in concentration within individual lakes are illustrated in Figure 1 for Lake Michigan and Figure S3 for Lakes Superior and Huron, on the basis of the results of Ponar grab samples. In Figure S4 and Table S6, the data are further compared among eight geographic regions of the study area. On the basis of Fisher’s exact test, concentrations of both atrazine and simazine were significantly higher in southern Lake Michigan than in other regions including northern Lake Michigan (Table S6). From the core data (Table S4), the highest recent net flux of atrazine was observed at M008 and M009 near the mouths of the heavily contaminated Grant, St. Joseph, and Kalamazoo Rivers,² indicating significant impact of riverine inputs to southern Lake Michigan. Site M050 in Green Bay had significantly lower concentrations of atrazine than all sites in the main lake. A similar south–north comparison for Lake Michigan was reported for atrazine in the particulate phase of air.² These observations are consistent with the larger agricultural land coverage, as well as higher concentrations of atrazine in tributaries, in the southern drainage basin compared to the northern basin of Lake Michigan.² In Lake Superior, the concentration of atrazine was higher in the western than in the eastern part of the lake (Figure S4 and Table S6). In Lake Huron, the differences in atrazine and simazine concentrations among northern and southern main lakes as well as the North Channel and Georgian Bay were found to be statistically insignificant.

Concentrations of alachlor were lower than those of other herbicides investigated. Agricultural use of alachlor has decreased significantly since 1994.⁵ In the Corn Belt, alachlor

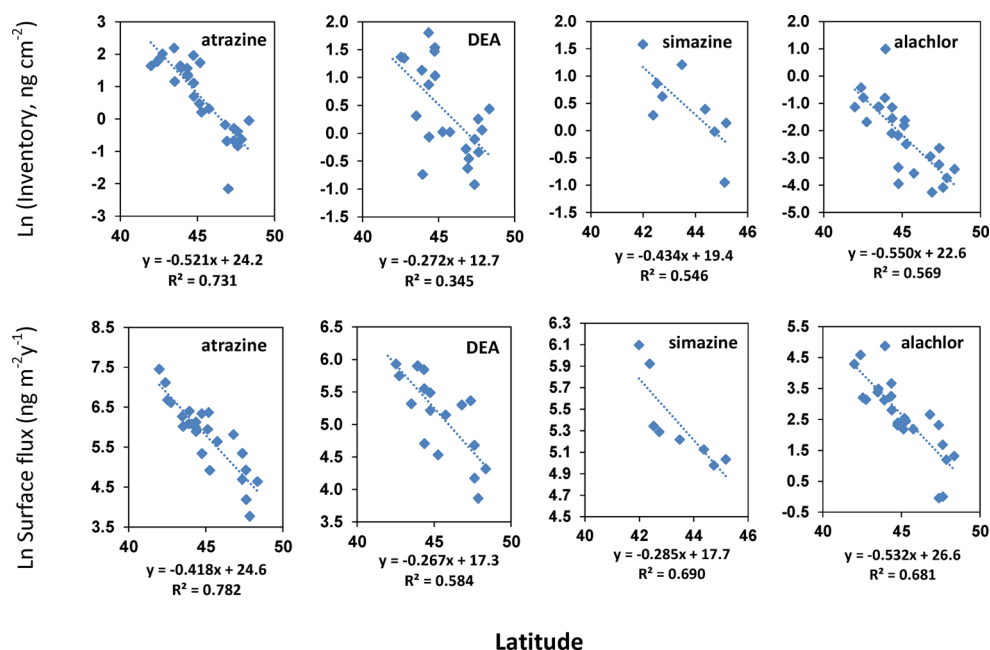


Figure 2. Dependence of inventory and surface flux on the latitude of the sampling locations for selected herbicides. The plots for simazine use data from Lake Michigan only. All regressions are significant at 95% confidence level.

in wet deposition was less than that of atrazine and tended to fall closer to the agricultural field where it was applied.¹ In addition, alachlor in water was found to be rapidly transformed to 2-[(2,6-diethylphenyl)-(methoxymethyl)amino]-2-oxoethanesulfonate (ESA).¹⁴ In contrast to the other herbicides in this study, there was no statistically significant difference in alachlor concentrations between the southern and northern basins ($p = 0.436$) of Lake Michigan, which may be due in part to the relatively high concentrations near the Sleeping Bear Dunes (sites M093a–c) in the northern basin (Figure 1). In Lake Superior, alachlor was found in only one Ponar grab sample collected at S011. In Lake Huron, alachlor was found in 17% of samples with the highest concentration (0.43 ng/g) at site H001 in Saginaw Bay, indicating local uses. The correlations between concentrations of alachlor and those of atrazine and DEA are comparatively weak (Table S7), consistent with the different use histories between alachlor and atrazine.

Over the entire study area across the three lakes, the inventory and net fluxes of these herbicides were found to decline exponentially with the increasing latitude of the sampling sites (Figure 2). Evidence of long-range transport of atrazine over at least 500 km has been reported from analyzing rainwater and air.³⁷ The observations in this work provide further evidence using sediment data. The empirical “half-distance” is the distance over which the net surface flux and inventory in the sediment is reduced by 50%. It was estimated by the use of eq 5 below, which assumes first order decline with increasing distance.

$$d_{1/2} \text{ (km)} = -\ln 2 / \text{slope} \times 111.2 \quad (5)$$

where slopes of regressions are presented in Figure 2 and 111.2 km per degree latitude was used for unit conversion. For atrazine, $d_{1/2}$ was approximately 150 ± 18 km for the inventory and 180 ± 21 km for the recent depositional flux, with the uncertainties calculated from the relative standard errors of the slopes.

DEA/Atrazine Ratio. Degradation product DEA was detected in most Ponar grab samples from Lakes Michigan and Huron, and the concentrations are similar between the two lakes (Table 1). DEA was found at only four sampling sites (S002, S108, S116, and S119) in Lake Superior. The dependence on the latitude is weaker for DEA than for the herbicides discussed above (Figure 2), and its empirical half-distance is much longer at about 280 ± 90 km for the inventory and 290 ± 60 km for the recent depositional flux. The degradation of DEA may lead to the formation of DDA,¹⁷ however, DDA was found in only a few of the samples at the relatively high detection limit.

The DEA to atrazine concentration ratio (DEA/ATZ) has often been used as an indicator of atrazine degradation.^{15,18,19,38} Low DEA/ATZ ratios, e.g., <0.1 , occur in streams during runoff shortly after application of atrazine. The ratio increases after considerable degradation of atrazine to DEA has occurred in soil.¹ A comparatively large ratio (~ 0.5) of DEA/ATZ in rainfall suggests degradation of atrazine in the atmosphere.¹ For Lake Michigan, the median DEA/ATZ was 0.68 (range of 0.43–1.04) in the open lake water and 0.77 (range of 0.08–3.7) in waters of tributaries during 1994 and 1995.² In air above Lake Michigan, DEA/ATZ in precipitation and particulates averaged 0.52 and 0.25, respectively.² In this study, the median DEA/ATZ ratio was 0.42 (range of 0.30–0.47) in surface sediment samples from Lake Michigan. Furthermore, the ratio increased with increasing latitude of the sampling sites over the entire study area (Figure 3), suggesting that transformation of atrazine to DEA occurred while transporting northwards.

In most cores in which DEA was measured, a pattern of increasing DEA/ATZ ratio with increasing sediment depth was observed (Figure 4). The ratio of 0.3–1 observed at core surfaces tends to be constant to a particular depth and then increases to as high as 6 in deeper sediments. This could be an indication of transformation of atrazine to DEA in deeper sediments; however, it may also be caused by possibly more rapid downward diffusion of DEA due to its greater water

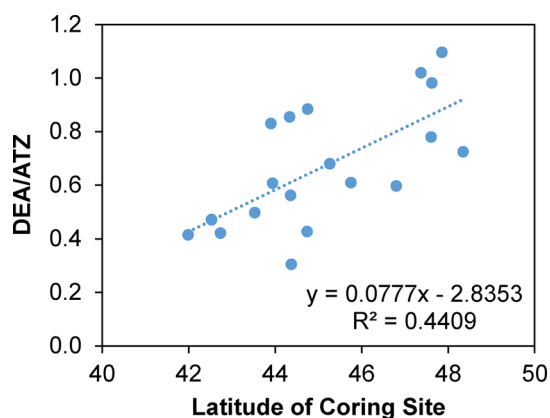


Figure 3. Variation in concentration ratio of DEA over atrazine (DEA/ATZ) with latitude in core surface sediment samples of Lakes Michigan, Superior, and Huron ($p = 0.002$).

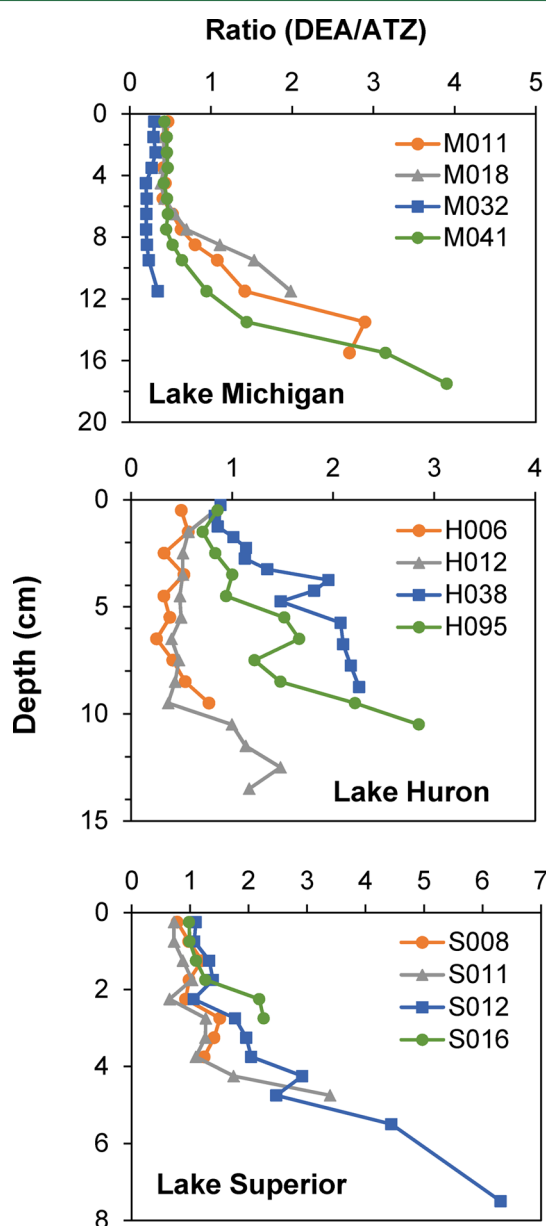


Figure 4. Variation in concentration ratio of DEA over atrazine (DEA/ATZ) with depth in selected sediment cores.

solubility relative to atrazine (Table S1). The latter explanation is consistent with a previous report that atrazine rapidly biodegraded in incubated surface (<10 cm depth) sediment but not under anaerobic or denitrifying conditions in sediment from 20 cm depth in a southern Lake Ontario basin.³⁸ A similar observation was reported comparing the surface versus subsurface sediments collected from an agricultural farm.³⁹ Atrazine was also found to be least persistent in top soil, and its persistence increased with increasing soil depth.⁴⁰ A study on triazines in the water of a number of ombrotrophic lakes in Isle Royale suggests faster degradation and shorter half-lives in shallower lakes.¹⁹ Removal of the ethyl and isopropyl side chains, which leads to formation of DEA and DIA, respectively, is considered to be an aerobic process.⁴¹

Vertical Trends. Net deposition fluxes are plotted against deposition year for the four Lake Michigan coring sites in Figure 5. With the exception of alachlor, the trends in the sediments are consistent with a first order pseudokinetics increase in more recent years. For atrazine, the average apparent doubling times (t_2) are 33, 48, and 62 years in the sediments of Lakes Michigan, Superior, and Huron, respectively (Table S8). However, a closer examination of data found that, in most cases, target chemicals were detected in sediments deposited before the year 1900 (Figure 5). This emergence date is much earlier than the initial production date. In addition, the annual use of atrazine has leveled off or declined since the early 1990s,⁵ but the net deposition to sediment appears to be continuously increasing. Together, these results suggest the occurrence of vertical transport of the chemicals from upper sediment layers to deeper sediment layers. With relatively high water solubilities and low solid phase partitioning constants (Table S1), it is likely that the target compounds would have been diffusing through the sediment pore water in response to the concentration gradient, causing significant downward transport within sediment over decadal time scales.

To test this possibility, we estimated analyte concentrations in pore water, C_w , assuming equilibrium with the sediment in situ using the measured solid phase concentration as follows:

$$C_w \text{ (ng/L)} = \frac{1000 \times C_s}{f_{oc} \times K_{oc} + \frac{f_w}{(1-f_w) \times \rho}} \quad (6)$$

where C_s (ng/g dw) is the measured concentration in dried sediment, f_{oc} (dimensionless) is the measured organic carbon (OC) fraction of the sediment, K_{oc} (L/kg) is the OC-water partition coefficient (Table S1), f_w (dimensionless) is the measured mass fraction of water in sediment, and ρ is water density, 1 kg/L. Estimated concentrations in pore water of Ponar grab sediments of Lake Michigan have medians of 111, 161, 90, and 5 ng/L for atrazine, DEA, simazine, and alachlor, respectively. These correspond to approximately 39%, 65%, 53%, and 46% of the measured total (pore water + particle) mass for the four chemicals, respectively. In the absence of advection (either upward or downward), such high percentages in pore water of the upper sediment layers would result in a strong concentration gradient and thus were likely to have caused downward diffusion into deeper sediment layers, consistent with what was observed (Figure 5).

Sediment as Source to the Water Column. While diffusion from upper to lower layers in the sediment has likely been occurring, the herbicides found in the upper sediment may not result from diffusion from the overlying water at most

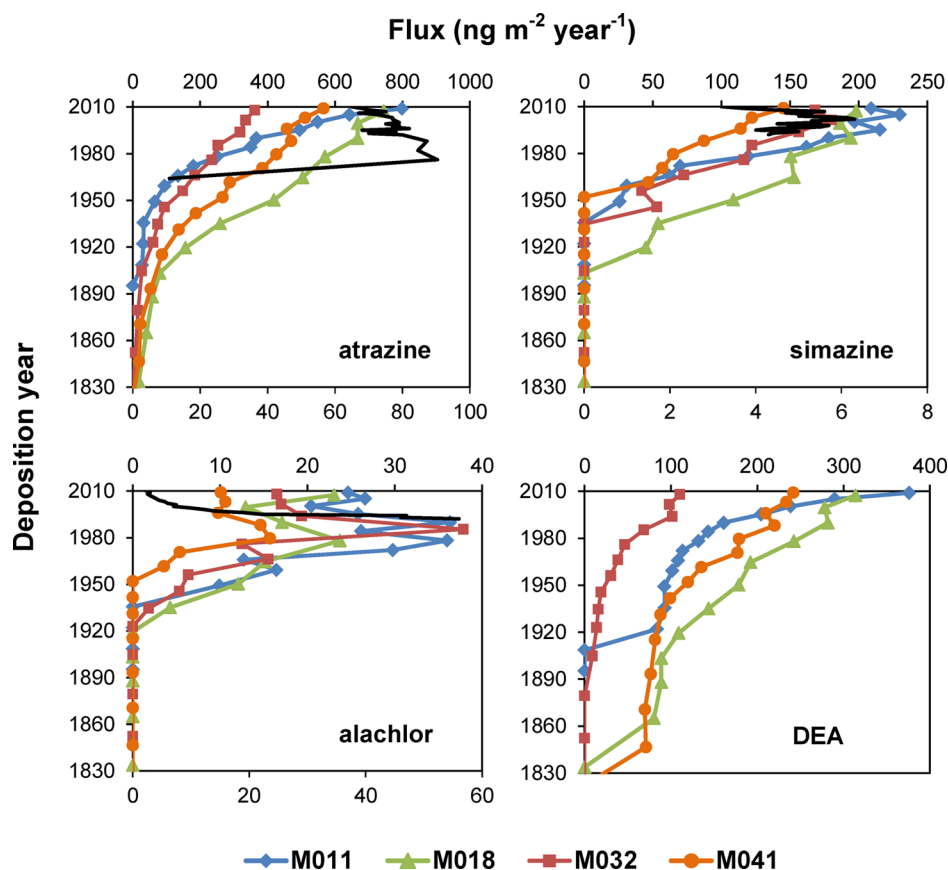


Figure 5. Apparent deposition flux of selected herbicides to the sediment at four locations of Lake Michigan, estimated using eq 1. The black lines (lower x -axis) are the annual crop uses of the three herbicides in million lbs.⁵

Table 2. Recent Annual Loading and Total Load (\pm Standard Deviation), Calculated from the Mean Concentrations in Sediment Cores Using eqs 3 and 4^a

| lake | atrazine | DEA | simazine | alachlor |
|---|-----------------|-----------------|----------------|----------------|
| Recent Annual Loading to Sediment, kg y ⁻¹ | | | | |
| Michigan | 44.4 \pm 25.6 | 11.3 \pm 14.1 | 12.1 \pm 7.5 | 1.9 \pm 1.8 |
| Superior | 11.8 \pm 7.6 | 8.3 \pm 6.0 | NA | 0.4 \pm 0.4 |
| Huron | 21.9 \pm 8.4 | 14.8 \pm 5.7 | NA | 2.1 \pm 2.2 |
| Total | 78.0 \pm 75.1 | 34.3 \pm 33.3 | 12.1 \pm 7.5 | 4.5 \pm 6.2 |
| Total Load in Sediment, kg | | | | |
| Michigan | 3329 \pm 1234 | 1184 \pm 904 | 1140 \pm 796 | 169 \pm 99 |
| Superior | 484 \pm 191 | 713 \pm 287 | NA | 23 \pm 18 |
| Huron | 1952 \pm 843 | 1514 \pm 1041 | NA | 269 \pm 480 |
| Total | 5764 \pm 5083 | 4111 \pm 3195 | 1140 \pm 796 | 461 \pm 1009 |

^aNA = not available.

sampling locations. The most recently reported concentrations of atrazine had medians (minimum to maximum) of 55 (48 to 71) ng/L, 13.2 (4.7 to 32) ng/L, and 5.4 (5.1 to 6.0) ng/L in the water of Lakes Michigan, Huron, and Superior, respectively.⁸ These are below the atrazine concentrations predicted by eq 6 for sediment pore waters, which had the medians of 111 (24 to 990) ng/L, 34 (not detected to 770) ng/L, and 14 (not detected to 260) ng/L, for Lakes Michigan, Huron, and Superior, respectively. Although the sampling dates and locations are different between the two studies, the differences suggest the occurrence of solid-phase deposition of atrazine through the water column.

Atrazine, with a $K_{oc} > 100$ (Table S1) and capable of donating and accepting hydrogen bonds,⁴² can interact with soil

and sediment organic matter by multiple mechanisms. Organic content of the sediment has been found to affect sorption, transport, and degradation of atrazine in sediments.^{43–46} Once applied to soil in crop fields or sorbed to airborne particulate matter, atrazine may not be easily desorbed from the particles. Atrazine has a reported half-life of 45 to 60 d in soils of the Midwestern U.S.³⁷ In a study of persistence of atrazine in soil using lysimeters, ring-¹⁴C-labeled atrazine was still detectable 22 years after the last application.⁴⁷ In another study, 13% to 43% of atrazine spiked into two sediments became unextractable after 2 years by the use of aqueous solutions containing methanol.⁴⁸ We therefore propose that, upon entering lakes with river inflows or via atmospheric deposition, contaminated particles may settle to the lake bed before losing much of the

sorbed atrazine, especially at near shore sites where the water is shallow. Once at the lake bottom, the herbicide can be released through desorption and can enter bulk water via diffusion and during sediment resuspension. Future work is needed to test these hypotheses.

On a lake-wide basis, the total loads of atrazine in water of lakes during the 1990s were estimated to be 176 tonnes for Lake Michigan, 75 tonnes for Lake Huron, and 36 tons for Lake Superior.⁴⁹ Compared with the sediment loads of atrazine in the three lakes (Table 2), water is the major compartment for atrazine and organic compounds with similar physicochemical properties. However, the role played by contaminated sediment cannot be ignored. Sustained release to the water from contaminated sediments of the lake and tributaries as well as the soils in the region may be at least partially responsible for the increasing atrazine concentrations observed in Lake Michigan, even though the annual use of atrazine has leveled off or declined in the Corn Belt since the early 1990s.⁵ Atrazine, simazine, DEA, and DIA are among the most frequently detected contaminants in Chicago's water supply.⁵⁰ Toxicity of these compounds on benthic diatoms and amphipods is also a serious concern.^{51,52} To this end, the findings of this work provide valuable information and insights in understanding the behavior and potential impact of these herbicides in the Great Lakes and beyond.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00706.

Tables and figures including the physicochemical properties, instrument conditions and chromatograms of target compounds, and sampling information, as well as additional results of data analyses (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

Occurrence of Atrazine and Related Compounds in the Sediments of Upper Great Lakes

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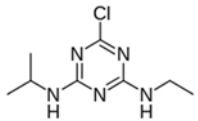
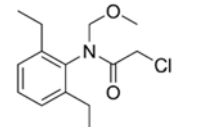
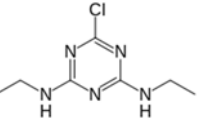
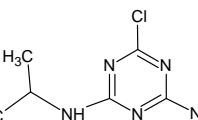
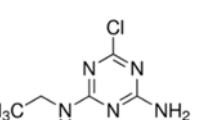
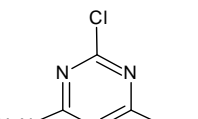
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Table S1. Physicochemical properties of target herbicides ^{1,2}

| Chemicals | MW | structure | formula | water solubility (mg/L) at 25°C | vapor pressure (Pa) at 20°C | Henry's law constant (Pa.m ³ /mol) | Log K _{ow} | Log K _{oc} |
|---|--------|---|---|---------------------------------|-----------------------------|---|---------------------|----------------------------|
| atrazine ^a | 215.68 |  | C ₈ H ₁₄ ClN ₅ | 33.8 ^[3] | 4.00E-05 | 2.88E-04 | 2.75 | 2.35 ^[2] |
| alachlor ^a | 269.77 |  | C ₁₄ H ₂₀ ClNO ₂ | 240 | 2.88E-03 | 2.20E-03 | 2.8 | 2.23 |
| simazine ^a | 201.67 |  | C ₇ H ₁₂ ClN ₅ | 5 | 8.50E-06 | 3.43E-04 | 2.18 | 2.11 |
| desethyl atrazine (DEA) ^b | 187.63 |  | C ₆ H ₁₀ ClN ₅ | 3,200 ^[3] | 1.51E-01 | 1.55E-04 | 1.51 ^[4] | 1.935, 1.9 ^[5] |
| desisopropyl atrazine (DIA) ^b | 173.6 |  | C ₅ H ₈ ClN ₅ | 670 ^[3] | 2.81E-02 | 7.83E-04 | 1.15 ^[4] | 1.746, 2.11 ^[5] |
| desethyl desisopropyl atrazine (DDA) ^b | 145.55 |  | C ₃ H ₄ ClN ₅ | 42,020 | 3.27E-02 | 1.13E-04 | 0.32 | 1.318 |

^a Unless specified, the data were obtained from Ref. [1]; ^b Unless specified, the data were obtained from U.S. EPA EPI SUITE or Ref. [2];

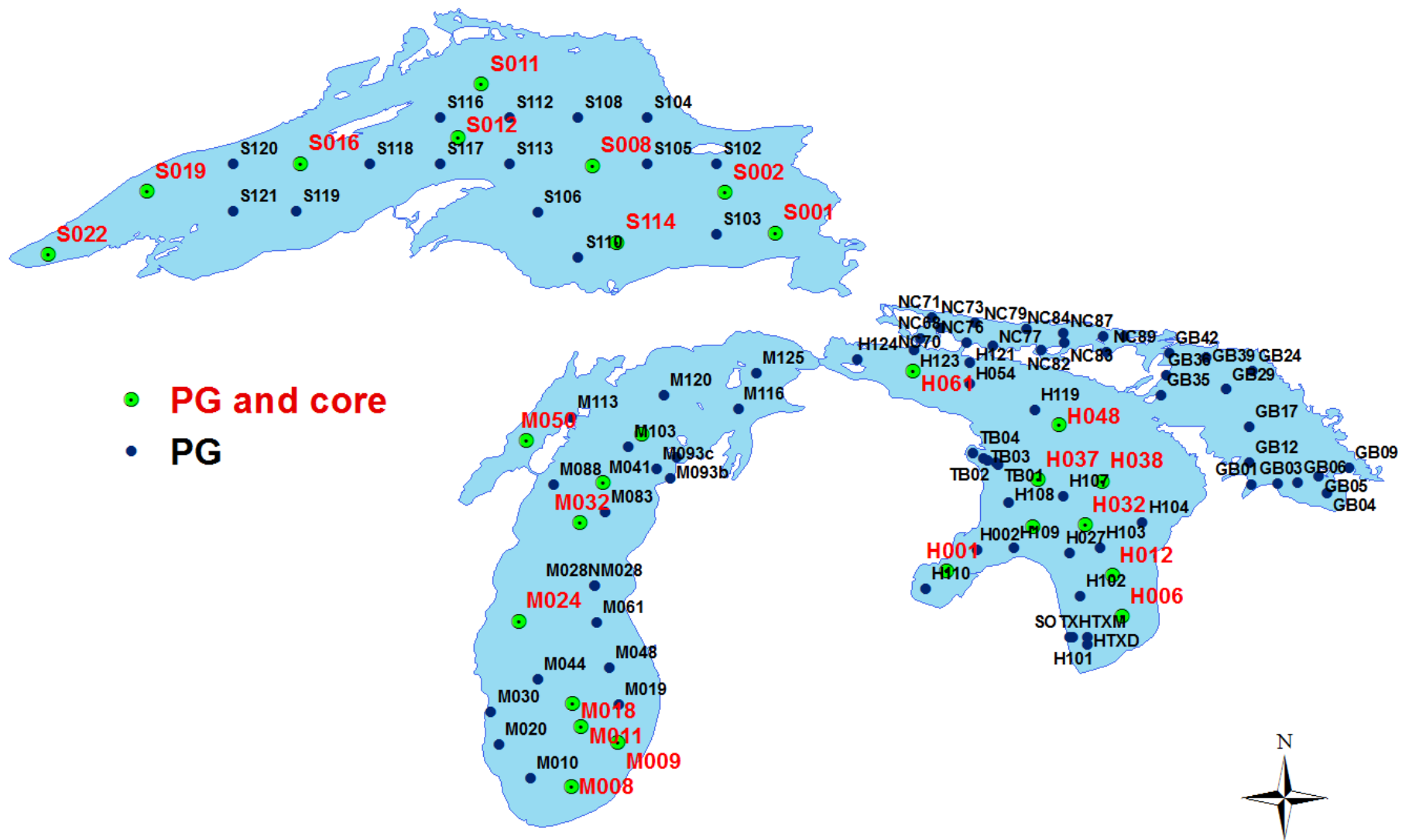


Figure S1. Sampling sites (PG: Ponar grab; labels for the sites are not all shown).

Table S2. Sampling related information

| Site ^a | Date | Latitude | Longitude | Depth (m) | MSR ^b | Focus Factor |
|--------------------------|-----------|----------|-----------|-----------|---|--------------|
| <u>Lake Michigan</u> | | | | | | |
| M008 | 9/20/2010 | 41.9842 | -87.0142 | 64 | 0.021 | 0.49 |
| M009 | 9/20/2010 | 42.3850 | -86.5915 | 60 | 0.065 | 2.2 |
| M010 | 9/17/2010 | 42.0662 | -87.3792 | 50 | | |
| M011 | 9/20/2010 | 42.5283 | -86.9220 | 160 | 0.041 | 2.99 |
| M018 | 9/20/2010 | 42.7338 | -86.9995 | 161 | 0.018 | 1.52 |
| M019 | 9/20/2010 | 42.7335 | -86.5833 | 90 | | |
| M020 | 9/17/2010 | 42.3665 | -87.6672 | 45 | | |
| M024 | 9/17/2010 | 43.4830 | -87.4882 | 146 | 0.019 | 1.98 |
| M028 | 9/19/2010 | 43.8003 | -86.7998 | 133 | | |
| M028N ^c | 5/23/2011 | 43.7998 | -86.7997 | 133 | | |
| M030 | 9/17/2010 | 42.6600 | -87.7382 | 18 | | |
| M032 | 9/18/2010 | 44.3715 | -86.9333 | 250 | 0.018 | 2.09 |
| M041 | 9/19/2010 | 44.7367 | -86.7215 | 265 | | |
| M041N^c | 5/24/2011 | 44.7375 | -86.7221 | 266 | 0.022 | 2.11 |
| M044 | 9/17/2010 | 42.9528 | -87.3155 | 90 | | |
| M047 | 9/18/2010 | 45.1783 | -86.3745 | 195 | 0.031 | 2.64 |
| M048 | 9/19/2010 | 43.0585 | -86.6630 | 104 | | |
| M050 | 9/18/2010 | 45.1165 | -87.4165 | 32 | 0.043 (1–7) ^d 0.020 (8–19) ^d | 2.85 |
| M061 | 9/19/2010 | 43.4742 | -86.7847 | 133 | | |
| M083 | 9/19/2010 | 44.4737 | -86.7060 | 263 | | |
| M088 | 9/18/2010 | 44.7187 | -87.1740 | 92 | | |
| M093a | 9/19/2010 | 44.9622 | -86.0552 | 97 | | |
| M093b | 9/19/2010 | 44.7712 | -86.1168 | 58 | | |
| M093c | 9/19/2010 | 44.8562 | -86.243 | 126 | | |
| M103 | 9/19/2010 | 45.0623 | -86.4918 | 201 | | |
| M113 | 9/18/2010 | 45.3267 | -87.009 | 36 | | |
| M116 | 5/24/2011 | 45.4014 | -85.4997 | 36 | | |
| M120 | 9/18/2010 | 45.5288 | -86.1708 | 136 | | |
| M125 | 5/24/2011 | 45.7228 | -85.3314 | 16 | | |
| <u>Lake Superior</u> | | | | | | |
| S001 | 5/25/2011 | 46.9930 | -85.1612 | 98 | N/A ^e | 0.09 |
| S002 | 5/25/2011 | 47.3603 | -85.6208 | 158 | 0.0068 | 0.82 |
| S008 | 5/25/2011 | 47.6058 | -86.8177 | 309 | 0.0067 | 0.76 |
| S011 | 5/28/2011 | 48.3438 | -87.8250 | 236 | 0.015 | 2.45 |
| S012 | 5/28/2011 | 47.8553 | -88.0418 | 245 | 0.0098 | 1.84 |
| S016 | 5/27/2011 | 47.6212 | -89.4633 | 185 | 0.0074 | 1.01 |
| S019 | 5/26/2011 | 47.3703 | -90.8535 | 193 | 0.0088 | 0.62 |

| | | | | | | |
|-------------|-----------|---------|----------|-----|---|------|
| S022 | 5/27/2011 | 46.8002 | -91.7508 | 56 | 0.018 (1–7) ^d 0.025 (8–25) ^d | 0.6 |
| S102 | 5/25/2011 | 47.6173 | -85.6973 | 95 | | |
| S103 | 5/29/2011 | 46.9838 | -85.6972 | 169 | | |
| S104 | 5/26/2011 | 48.0382 | -86.3217 | 194 | | |
| S105 | 5/25/2011 | 47.6177 | -86.3217 | 83 | | |
| S106 | 5/28/2011 | 47.1807 | -87.3183 | 225 | | |
| S108 | 5/26/2011 | 48.0392 | -86.9493 | 233 | | |
| S110 | 5/28/2011 | 46.7735 | -86.9495 | 142 | | |
| S112 | 5/28/2011 | 48.0393 | -87.5733 | 222 | | |
| S113 | 5/28/2011 | 47.6177 | -87.5730 | 176 | | |
| S114 | 5/28/2011 | 46.9095 | -86.5980 | 409 | N/A ^e | 0.63 |
| S116 | 5/28/2011 | 48.0392 | -88.2007 | 261 | | |
| S117 | 5/28/2011 | 47.6175 | -88.2007 | 277 | | |
| S118 | 5/27/2011 | 47.6175 | -88.8420 | 194 | | |
| S119 | 5/27/2011 | 47.1955 | -89.5048 | 202 | | |
| S120 | 5/26/2011 | 47.6185 | -90.0712 | 183 | | |
| S121 | 5/27/2011 | 47.1955 | -90.0727 | 150 | | |

Lake Huron

| | | | | | | |
|-------------|-----------|---------|----------|------|--|-------|
| GB01 | 10/6/2012 | 44.7178 | -80.8564 | 93 | | |
| GB03 | 10/6/2012 | 44.7253 | -80.6170 | 34 | | |
| GB04 | 10/6/2012 | 44.6457 | -80.1673 | 59 | | |
| GB05 | 10/6/2012 | 44.7969 | -80.2431 | 60 | | |
| GB06 | 10/6/2012 | 44.7382 | -80.4360 | 88 | | |
| GB09 | 10/6/2012 | 44.8716 | -79.9675 | 29.9 | | |
| GB12 | 10/6/2012 | 44.9202 | -80.8748 | 91 | | |
| GB17 | 10/6/2012 | 45.2449 | -80.8742 | 80 | | |
| GB24 | 10/6/2012 | 45.7457 | -80.8394 | 31 | | |
| GB29 | 10/5/2012 | 45.5836 | -81.0830 | 44 | | |
| GB35 | 10/5/2012 | 45.5257 | -81.6705 | 37 | | |
| GB36 | 10/5/2012 | 45.7082 | -81.6201 | 54 | | |
| GB39 | 10/5/2012 | 45.8729 | -81.2584 | 26.9 | | |
| GB42 | 10/5/2012 | 45.9125 | -81.5954 | 26 | | |
| H001 | 9/16/2012 | 43.9374 | -83.6142 | 12.7 | 0.16 | >3.24 |
| H002 | 9/16/2012 | 44.1249 | -83.3324 | 18.8 | | |
| H006 | 9/16/2012 | 43.5265 | -82.0185 | 62 | 0.032 (1–10) ^d 0.0083 (11–25) ^d | 2.17 |
| H012 | 9/16/2012 | 43.9007 | -82.1130 | 99 | 0.057 | 3.49 |
| H027 | 9/16/2012 | 44.0999 | -82.5025 | 65 | | |
| H032 | 9/16/2012 | 44.3542 | -82.3596 | 94 | 0.044 | 3.16 |
| H037 | 9/17/2012 | 44.7619 | -82.7836 | 76 | N/A ^e | 0.87 |
| H038 | 9/17/2012 | 44.7507 | -82.2024 | 166 | 0.0087 | 0.89 |
| H048 | 9/17/2012 | 45.2614 | -82.5912 | 183 | 0.017 | 1.6 |
| H054 | 9/18/2012 | 45.6338 | -83.4028 | 142 | | |
| H061 | 9/18/2012 | 45.7498 | -83.9164 | 122 | 0.0063 | 0.6 |

| | | | | | | |
|-------------|-----------|---------|----------|------|-------|------|
| H095 | 9/16/2012 | 44.3328 | -82.8326 | 70 | 0.014 | 1.13 |
| H101 | 9/15/2012 | 43.2690 | -82.3349 | 31 | | |
| H102 | 9/16/2012 | 43.7059 | -82.4039 | 53 | | |
| H103 | 9/16/2012 | 44.1449 | -82.2209 | 99 | | |
| H104 | 9/16/2012 | 44.3720 | -81.8380 | 132 | | |
| H107 | 9/17/2012 | 44.6154 | -82.5541 | 66 | | |
| H108 | 9/17/2012 | 44.5574 | -83.0502 | 55 | | |
| H109 | 9/16/2012 | 44.1502 | -83.0000 | 35 | | |
| H110 | 9/17/2012 | 43.7723 | -83.8037 | 6.72 | | |
| H118 | 9/17/2012 | 44.9168 | -83.1660 | 46 | | |
| H119 | 9/17/2012 | 45.3977 | -82.8107 | 135 | | |
| H121 | 10/4/2012 | 45.8189 | -83.4039 | 45 | | |
| H123 | 9/18/2012 | 45.9365 | -83.9059 | 30 | | |
| H124 | 9/18/2012 | 45.8512 | -84.4216 | 57 | | |
| NC68 | 10/4/2012 | 46.0413 | -83.8536 | 16.4 | | |
| NC70 | 10/4/2012 | 46.1365 | -83.6720 | 21.7 | | |
| NC71 | 10/4/2012 | 46.2335 | -83.7462 | 36 | | |
| NC73 | 10/5/2012 | 46.1869 | -83.3552 | 19.2 | | |
| NC76 | 10/5/2012 | 46.0003 | -83.4329 | 60 | | |
| NC77 | 10/5/2012 | 45.9704 | -83.1977 | 80 | | |
| NC79 | 10/5/2012 | 46.1230 | -82.8867 | 26.2 | | |
| NC82 | 10/5/2012 | 45.9369 | -82.7588 | 28.4 | | |
| NC83 | 10/5/2012 | 46.0000 | -82.5497 | 31 | | |
| NC84 | 10/5/2012 | 46.0917 | -82.5564 | 36 | | |
| NC87 | 10/5/2012 | 46.0611 | -82.1971 | 41 | | |
| NC88 | 10/5/2012 | 46.0553 | -81.9998 | 37 | | |
| NC89 | 10/5/2012 | 45.9165 | -82.1617 | 39 | | |
| TB01 | 10/7/2012 | 44.8996 | -83.1496 | 50 | | |
| TB02 | 10/7/2012 | 44.9387 | -83.2405 | 31 | | |
| TB03 | 10/7/2012 | 44.9552 | -83.2770 | 18.6 | | |
| TB04 | 10/7/2012 | 44.9997 | -83.3742 | 10.3 | | |
| SOTXD | 9/15/2012 | 43.3399 | -82.3335 | 37 | | |
| SOTXM | 9/15/2012 | 43.3398 | -82.4668 | 19.6 | | |
| SOTXS | 9/15/2012 | 43.3397 | -82.4991 | 12.1 | | |

^a Coring sites are in bold font

^b Mass sedimentation rate in g/cm²-y. Those in italics should be read with caution due to low Pb-210 abundance thus higher uncertainty.

^c Sampled in 2011.

^d The numbers in the parentheses are core depth in cm

^e Not available

Table S3-a. Multiple reaction mechanism transition in GC/QQQMS

| Chemicals | Precursor | Quantification | | Qualification | |
|-----------|-----------|----------------|-----------------|---------------|-----------------|
| | | Ion | CE ^a | Ion | CE ^a |
| atrazine | 214.9 | 200 | 7 | 173 | 5 |
| simazine | 200.9 | 173 | 5 | 186 | 5 |
| alachlor | 237 | 160 | 9 | 188 | 7 |
| TBP-d27 | 231.1 | 103 | 11 | 167 | 1 |
| PCB47L | 303.8 | 234 | 31 | 269 | 13 |
| Flu-d10 | 175.9 | 174 | 27 | 172 | 43 |
| DDA | 144.9 | 110 | 9 | 68 | 25 |
| DIA | 144.9 | 110 | 9 | 68 | 25 |
| DEA | 144.9 | 110 | 9 | 68 | 25 |

^a collision energy

Table S3-b. Transitions and some parameters in LC/MS/MS

| | Q1 ^a (<i>m/z</i>) | Q3 ^b (<i>m/z</i>) | DP ^c (V) | EP ^d (V) | CEP ^e (V) | CE ^f (V) | CXP ^g (V) | CUR ^h | TEM ⁱ (°C) | IS ^j (V) | GS1 ^k | GS2 ^l |
|----------|-----------------------------------|-----------------------------------|------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------|--------------------------|---------------------|------------------|------------------|
| Atrazine | 216.1 | 174.1 | 50 | 10 | 30 | 20 | 2 | 20 | 600 | 3000 | 80 | 90 |
| | 216.1 | 104.1 | 50 | 10 | 30 | 50 | 2 | | | | | |
| DEA | 188.1 | 146.2 | 50 | 10 | 30 | 40 | 2 | | | | | |
| | 188.1 | 104.1 | 50 | 10 | 30 | 40 | 2 | | | | | |
| DIA | 174.1 | 104.1 | 45 | 10 | 25 | 40 | 2 | | | | | |
| | 174.1 | 68.1 | 45 | 8 | 25 | 50 | 8 | | | | | |
| DDA | 146.1 | 79.1 | 55 | 10 | 25 | 40 | 2 | | | | | |
| | 146.1 | 68.0 | 55 | 10 | 30 | 50 | 2 | | | | | |

^a Precursor Ion; ^b Product Ion; ^c Declustering Potential; ^d Entrance Potential; ^e Collision Cell Entrance Potential; ^f Collision Energy; ^g Collision Cell Exit Potential; ^h Curtain Gas; ⁱ Temperature; ^j Ion Spray Voltage; ^k Ion Source Gas 1; ^l Ion Source Gas 2.

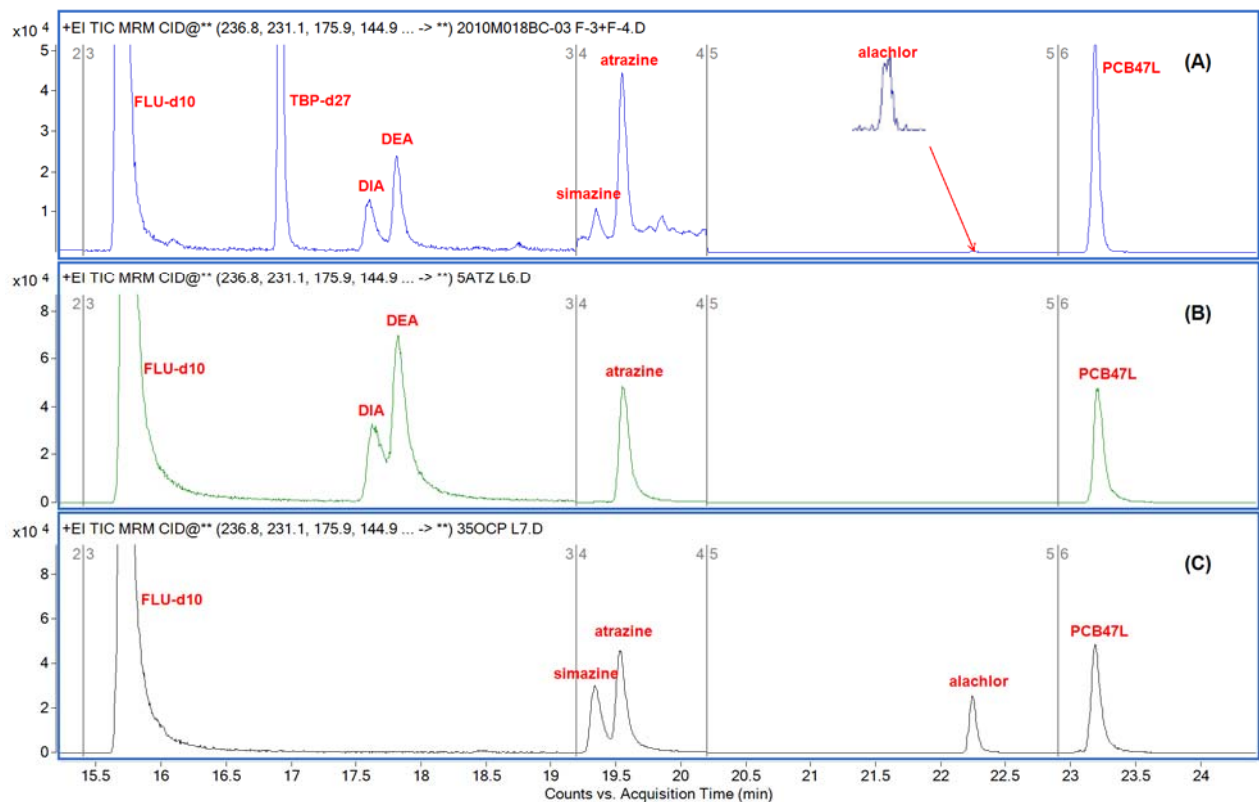


Figure S2-a. Partial GC/EIQQQ-MS chromatograms of (A) sample extracts for sediment core M018 segment (2-3 cm), and (B) standard mixture of targeted atrazine, DIA, and DEA, and (C) standard mixture of simazine, atrazine and alachlor.

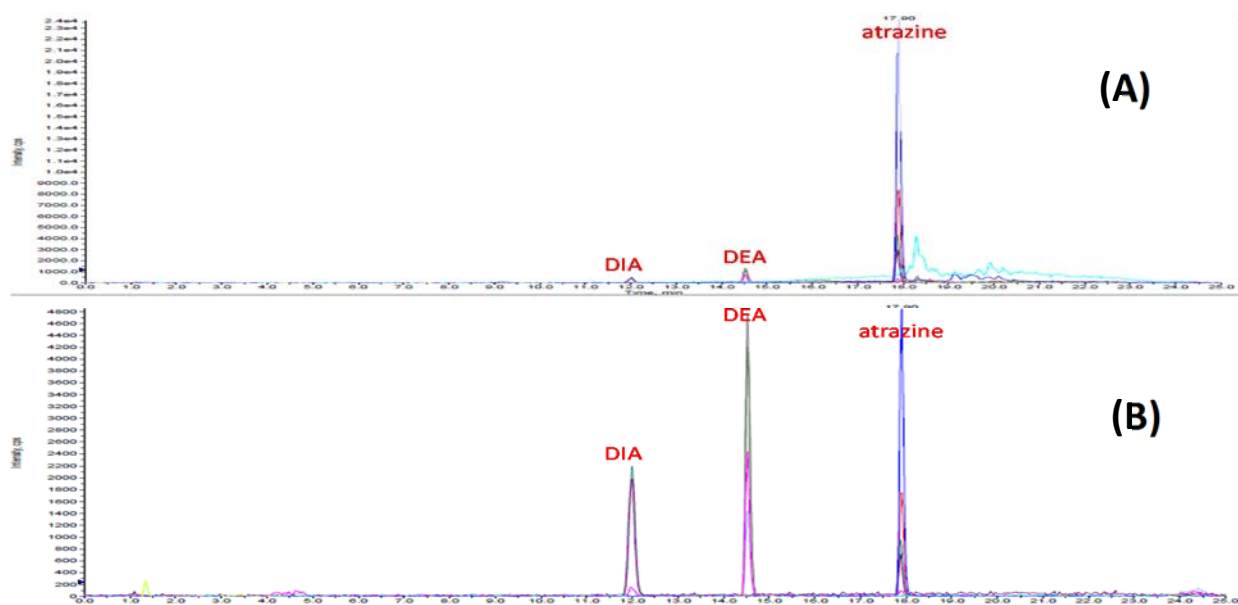


Figure S2-b. LC/MS/MS chromatograms of (A) sample extracts for sediment core M018 segment (2-3 cm), and (B) standard mixture of atrazine, DIA and DEA

Table S4. Summary of measured core surface concentrations, estimated inventory and recent flux of atrazine and related compounds in the sediments of Lakes Michigan, Superior and Huron

| Core | <u>Surface (0-1 cm) Concentration</u> (ng/g dw ^a) | | | | <u>Inventory (ng/cm²)</u> | | | | <u>Recent net deposition flux (ng/m²-yr)</u> | | | |
|------|--|------|----------|----------|--------------------------------------|------|----------|----------|---|-----|----------|----------|
| | atrazine | DEA | simazine | alachlor | atrazine | DEA | simazine | alachlor | atrazine | DEA | simazine | alachlor |
| M008 | 4.02 | | 1.04 | 0.17 | 5.15 | | 4.85 | 0.32 | 1718 | | 444 | 73 |
| M009 | 4.14 | | 1.26 | 0.33 | 5.85 | | 1.32 | 0.66 | 1228 | | 373 | 98 |
| M011 | 5.87 | 2.77 | 1.54 | 0.18 | 6.36 | 3.92 | 2.37 | 0.45 | 798 | 376 | 209 | 25 |
| M018 | 6.18 | 2.60 | 1.64 | 0.19 | 7.46 | 3.84 | 1.87 | 0.19 | 744 | 314 | 198 | 23 |
| M024 | 5.43 | | 1.90 | 0.30 | 8.90 | | 3.35 | 0.32 | 527 | | 184 | 29 |
| M032 | 4.10 | 1.25 | 1.91 | 0.19 | 3.76 | 0.94 | 1.48 | 0.21 | 362 | 110 | 168 | 17 |
| M041 | 5.40 | 2.31 | 1.39 | 0.10 | 7.07 | 4.34 | 0.98 | 0.11 | 566 | 242 | 145 | 10 |
| M047 | 4.94 | | 1.30 | 0.11 | 5.67 | | 1.15 | 0.20 | 582 | | 154 | 13 |
| M050 | 2.53 | | | 0.06 | 1.61 | | 0.39 | 0.16 | 382 | | | 9 |
| S001 | 0.10 | 0.57 | | | 0.12 | 0.63 | | | | | | |
| S002 | 1.31 | | | 0.12 | 0.51 | 0.40 | | 0.04 | 109 | | | 10 |
| S008 | 1.55 | 1.21 | | 0.06 | 0.68 | 1.29 | | 0.02 | 138 | 107 | | 5 |
| S011 | 1.66 | 1.20 | | 0.06 | 0.95 | 1.54 | | 0.03 | 103 | 75 | | 4 |
| S012 | 0.82 | 0.90 | | 0.06 | 0.53 | 1.06 | | 0.02 | 43 | 48 | | 3 |
| S016 | 0.90 | 0.89 | | | 0.43 | 0.71 | | | 66 | 65 | | |
| S019 | 1.48 | 1.51 | | 0.01 | 0.75 | 0.90 | | 0.07 | 210 | 214 | | 1 |
| S022 | 1.15 | 0.69 | | 0.05 | 0.83 | 0.75 | | 0.05 | 336 | 200 | | 14 |
| S114 | 0.70 | 0.62 | | 0.04 | 0.50 | 0.53 | | 0.01 | | | | |
| H001 | 1.26 | 0.76 | | 0.27 | 4.79 | 0.48 | | 2.69 | 602 | 365 | | 131 |
| H006 | 2.76 | 1.37 | | 0.22 | 3.18 | 1.36 | | 0.32 | 410 | 204 | | 33 |
| H012 | 2.69 | 2.23 | | 0.14 | 5.14 | 3.09 | | 0.45 | 438 | 364 | | 23 |
| H032 | 3.27 | 1.84 | | 0.28 | 3.95 | 2.38 | | 0.32 | 457 | 257 | | 39 |
| H037 | 1.34 | 1.63 | | 0.05 | 2.00 | 2.80 | | 0.02 | | | | |
| H038 | 2.13 | 1.88 | | 0.11 | 3.02 | 4.65 | | 0.04 | 208 | 184 | | 11 |
| H048 | 1.32 | 0.90 | | 0.11 | 1.23 | 1.02 | | 0.08 | 137 | 93 | | 12 |
| H061 | 2.67 | 1.63 | | 0.08 | 1.37 | 1.02 | | 0.03 | 281 | 171 | | 9 |
| H095 | 3.28 | 2.80 | | 0.21 | 4.79 | 6.06 | | 0.12 | 403 | 344 | | 26 |

^a dw = dry weight

Table S5. Concentrations of atrazine and related compounds in natural sediments

| Location | Waterbody | Sampling Year | Concentration Range | Reference |
|---|---------------------------------|---------------|-----------------------------|-------------------------|
| <u>Atrazine</u> | | | | |
| United States | Lake Michigan | 2010-2011 | N.D. to 6.18 ng/g | This study ^a |
| United States | Lake Superior | 2011 | N.D. to 1.85 ng/g | This study ^a |
| United States | Lake Huron | 2012 | N.D. to 3.28 ng/g | This study ^a |
| northeast China | Songhua River Basin | 2010 | N.D. to 40 ng/g | ⁶ |
| Beasley Lake Watershed, Sunflower County, Mississippi | agricultural drainage ditch | Before 2000 | 0.23 µg/g to 11 µg/g | ⁷ |
| Tarragona, Spain | Ebre Delta estuarine, top 10 cm | 1990-1991 | 19.2 to 39.2 ng/g | ⁸ |
| Texas, New Mexico, and Oklahoma in U.S. | wetlands | 2008-2009 | < 2 ng/g to 37 ng/g | ⁹ |
| Northern Adriatic, Italy | Coastal lagoon | 2004-2005 | 0.03-0.98 ng/g | ¹⁰ |
| German Bight | North Sea | 1993 | N.D.-0.50 ng/g ^b | ¹¹ |
| Shelton, Nebraska | unknown | Before 1994 | 0.14 to 30.9 ng/g | ¹² |
| <u>DEA</u> | | | | |
| United States | Lake Michigan | 2010-2011 | N.D. to 2.77 ng/g | This study ^a |
| United States | Lake Superior | 2011 | N.D. to 1.51 ng/g | This study ^a |
| United States | Lake Huron | 2012 | N.D. to 2.80 ng/g | This study ^a |
| Tarragona, Spain | Ebre Delta estuarine, top 10 cm | 1990-1991 | 6.5 to 19.5 ng/g | ⁸ |
| German Bight | North Sea | 1993 | N.D. - 16 ng/g ^b | ¹¹ |
| <u>Simazine</u> | | | | |
| United States | Lake Michigan | 2010-2011 | N.D. to 2.04 ng/g | This study ^a |
| Northern Adriatic, Italy | Coastal lagoon | 2004-2005 | N.D.-1.31 ng/g | ¹⁰ |
| German Bight | North Sea | 1993 | 0.11 - 4 ng/g ^b | ¹¹ |
| <u>Alachlor</u> | | | | |
| United States | Lake Michigan | 2010-2011 | N.D. to 0.61 ng/g | This study ^a |
| United States | Lake Superior | 2011 | N.D. to 0.13 ng/g | This study ^a |
| United States | Lake Huron | 2012 | N.D. to 0.77 ng/g | This study ^a |
| Northern Adriatic, Italy | Coastal lagoon | 2004-2005 | N.D.-1.75 ng/g | ¹⁰ |

^a Both Ponar and core surface (0-1 cm) segments are included.

^b The wet weight based concentration is transformed to dry weight based concentration by assuming 90% water content.

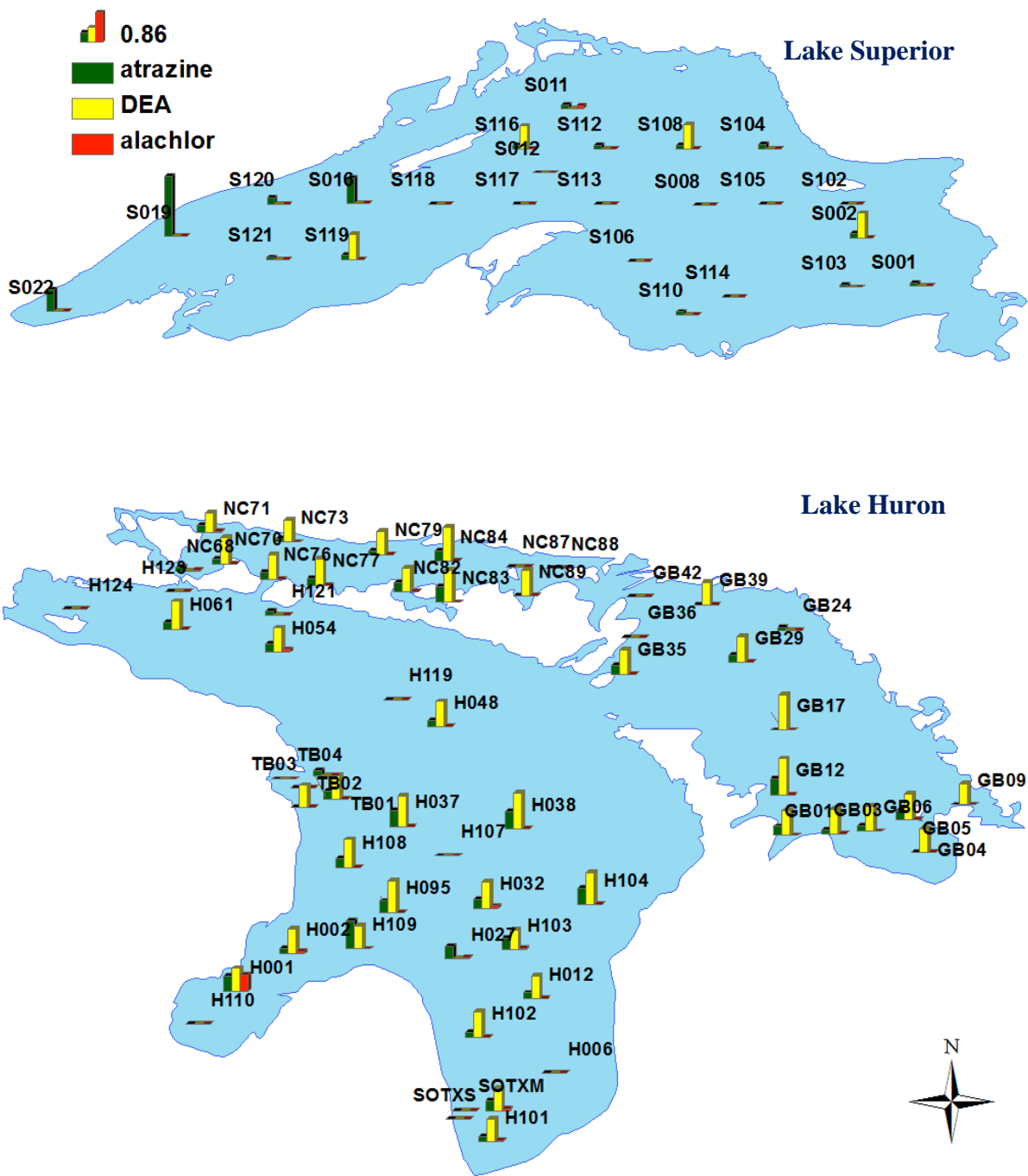


Figure S3. Spatial distribution of atrazine, DEA and alachlor concentrations (ng/g dw) in Ponar grab samples from Lake Superior and Lake Huron

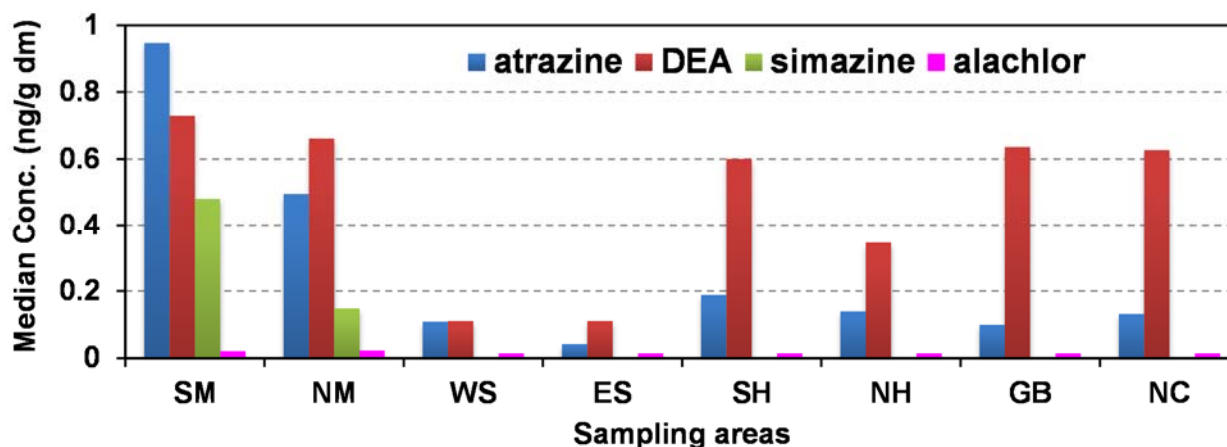


Figure S4. Comparison of median concentrations in Ponar grab samples among eight arbitrarily divided areas. See the Table below for abbreviations of the areas.

Table S6. Fisher's exact test for area comparison of chemical concentrations in Ponar grab samples. For each chemical, areas that do not share a letter are significantly different at 95% confidence level.

| Area | Abbr. | N | atrazine | DEA | simazine | alachlor |
|-----------------------------------|-------|----|----------|-----|----------|----------|
| southern Lake Michigan (<44°N) | SM | 14 | A | A | A | AB |
| northern Lake Michigan (>44°N) | NM | 15 | B | AB | B | AB |
| western Lake Superior (<87.573°W) | WS | 12 | C | C | BC | B |
| eastern Lake Superior (>87.573°W) | ES | 12 | D | C | B | B |
| southern Lake Huron (<44.4°N) | SH | 16 | CD | B | C | A |
| northern Lake Huron (>44.4°N) | NH | 16 | CD | B | C | B |
| Georgian Bay | GB | 14 | CD | B | C | B |
| The North Channel | NC | 13 | CD | B | C | B |

Table S7. Pearson correlations among concentrations of target chemicals (natural log transformed) measured in PG sediments of Lakes Michigan, Superior and Huron for the concentrations above detection limits (N = 32)

| | | atrazine | DEA | alachlor | simazine |
|-----------------|---|----------|-------|----------|----------|
| atrazine | r | 1 | | | |
| | p | | | | |
| DEA | r | 0.430 | 1 | | |
| | p | <.001 | | | |
| alachlor | r | -0.045 | 0.197 | 1 | |
| | p | 0.805 | 0.296 | | |
| Simazine | r | 0.760 | 0.631 | 0.181 | 1 |
| | p | <.001 | <.001 | 0.432 | |

Table S8. Averages (\pm S.D.) of net accumulation rate constant (k , y^{-1}), apparent doubling time (t_2 , y), and the first order regression statistics (r and p) at coring sites of Lakes Michigan, Superior and Huron, obtained from fitting pseudo first order kinetics equation.

| | | atrazine | DEA | simazine |
|---------------|-------|-------------------|-------------------|-------------------|
| Lake Michigan | N | 9 | 4 | 8 |
| | k | 0.027 \pm 0.014 | 0.018 \pm 0.008 | 0.027 \pm 0.018 |
| | t_2 | 33 \pm 19 | 44 \pm 20 | 42 \pm 36 |
| | r | 0.979 \pm 0.015 | 0.974 \pm 0.015 | 0.953 \pm 0.027 |
| | p | <0.001 | <0.001 | 0.001 \pm 0.003 |
| Lake Superior | N | 8 | 5 | |
| | k | 0.016 \pm 0.006 | 0.012 \pm 0.006 | |
| | t_2 | 48 \pm 15 | 74 \pm 44 | |
| | r | 0.943 \pm 0.051 | 0.918 \pm 0.057 | |
| | p | 0.026 \pm 0.053 | 0.002 \pm 0.002 | |
| Lake Huron | N | 7 | 6 | |
| | k | 0.018 \pm 0.01 | 0.012 \pm 0.007 | |
| | t_2 | 62 \pm 55 | 87 \pm 78 | |
| | r | 0.954 \pm 0.032 | 0.789 \pm 0.112 | |
| | p | <0.001 | 0.079 \pm 0.153 | |

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