

Concentrations, Trends, and Air–Water Exchange of PAHs and PBDEs Derived from Passive Samplers in Lake Superior in 2011

Zoe Ruge,[†] Derek Muir,[‡] Paul Helm,[§] and Rainer Lohmann*,[†]

[†]Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island 02882-1197, United States

[‡]Environment Canada, Aquatic Contaminants Research Division, 867 Lakeshore Road, Burlington, Ontario L7S 1A1, Canada

[§]Ontario Ministry of the Environment and Climate Change, Water Monitoring Section, 125 Resources Road, Toronto, Ontario M9P 3V6, Canada

Supporting Information

ABSTRACT: Polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenylethers (PBDEs) are both currently released into the environment from anthropogenic activity. Both are hence primarily associated with populated or industrial areas, although wildfires can be an important source of PAHs, as well. Polyethylene passive samplers (PEs) were simultaneously deployed in surface water and near surface atmosphere to determine spatial trends and air–water gaseous exchange of 21 PAHs and 11 PBDEs at 19 sites across Lake Superior in 2011. Surface water and atmospheric PAH concentrations were greatest at urban sites (up to 65 ng L^{-1} and 140 ng m^{-3} , respectively, averaged from June to October). Near populated regions, PAHs displayed net air-to-water deposition, but were near equilibrium off-shore. Retene, probably depositing following major wildfires in the region, dominated dissolved PAH concentrations at most Lake Superior sites. Atmospheric and dissolved PBDEs were greatest near urban and populated sites (up to 6.8 pg L^{-1} and 15 pg m^{-3} , respectively, averaged from June to October), dominated by BDE-47. At most coastal sites, there was net gaseous deposition of BDE-47, with less brominated congeners contributing to Sault Ste. Marie and eastern open lake fluxes. Conversely, the central open lake and Eagle Harbor sites generally displayed volatilization of PBDEs into the atmosphere, mainly BDE-47.



INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenylethers (PBDEs) are two classes of persistent organic pollutants (POPs) that have been monitored in the Great Lakes' atmosphere over the past two decades as part of the International Atmospheric Deposition Network (IADN) program.^{1–3} POPs are resistant to natural degradation, bioaccumulate, elicit adverse effects on human health and the environment, and undergo long-range transport.⁴ Another Great Lakes program has monitored the time trends of POPs in lake trout across the Great Lakes.^{5,6} The IADN program, with its single master station per Great Lake has been instrumental in understanding time trends of airborne organic contaminants across the Great Lakes region.

Yet, IADN has not been designed to understand spatial trends, nor was it designed to determine the trends and cycling of organic pollutants in the waters of the Great Lakes themselves. To be able to answer questions linked to air–water exchange and loadings of POPs to the Great Lakes, spatially resolved air and water measurements are required. The study described here is part of our effort to enhance our understanding of POPs cycling by deploying passive samplers in air and water at numerous sites around the Great Lakes, in this case Lake Superior. Samplers covered a range of sites—

urban, remote coastal and open-lake sites across Lake Superior to help discern trends and fluxes.

Passive samplers integrate contaminant concentrations over time, representing time-weighted averages over their accumulation period.^{7,8} In general, passive- and active-sampler derived concentrations agree within a factor of 2 to 3.^{8,9} When using the same passive sampler, in our case polyethylene, in air and water, the compound's air–water activity (or fugacity) gradient can be directly assessed.¹⁰

Of the known PAHs, seven are identified as probable human carcinogens.¹¹ PAHs are composed of two or more fused aromatic rings released as the result of incomplete combustion of both anthropogenic (fossil fuels) and natural (biomass) sources.^{12,13} They can also result from petrogenic releases (oil spills) and volatilization from polluted soils.^{14,15} PAHs are actively emitted to the environment through vehicle exhaust, industrial activity, residential heating, and wildfires,¹⁶ leading to

Special Issue: Ron Hites Tribute

Received: May 28, 2015

Revised: September 28, 2015

Accepted: October 5, 2015

Published: October 5, 2015

a ubiquitous presence and continued atmospheric deposition across the Great Lakes.¹³

Likewise, emissions of PBDEs are associated with urban areas due to their presence in consumer and industrial products from which they are continuously released, transported in the atmosphere and deposited.^{17,18} PBDEs are brominated flame retardants in widespread use since the 1970s¹⁹ and easily released to the atmosphere because they are not chemically incorporated into polymer matrices.²⁰ They can also be released from low temperature burning, such as waste fires where both PBDEs and PAHs may be emitted.²¹ While BDE-209 is easily lost from the atmosphere by wet and dry deposition, 90% of the removal of gas-phase congeners with 2–6 bromines is caused by photolysis.²² Lower brominated congeners tend to bioaccumulate more than higher brominated congeners and are more persistent in the environment.¹⁹ BDE-47, -99, and -100, the main components of technical PentaBDE, are nearly ubiquitous in the environment.²³ PentaBDE was voluntarily phased out by U.S. flame retardant manufacturers in 2004, however, DecaBDE was only scheduled for North American phase out in 2012.¹⁷ PBDEs remain in use in consumer products, industrial applications and landfills,²⁴ suggesting continued release to the environment and deposition into Lake Superior.

The objective of this study was to assess the spatial distribution and environmental cycling of PAHs and PBDEs across Lake Superior. We deployed polyethylene passive samplers (PEs) in the air and water at 19 sites across Lake Superior from April–October 2011 with the aim to (1) enhance the spatial coverage of air and water sampling stations across Lake Superior; (2) determine the concentrations and spatial trends of PAHs and PBDEs; (3) discern their air–water exchange; and (4) evaluate the efficacy of PEs as tools to monitor regional POP distributions.

MATERIALS AND METHODS

Sampling Methodology. Low density PE (2 mil) was cut into approximately 10 × 40 cm strips from commercial sheeting (Berry Plastics Corporation, Evansville, IN) yielding passive samplers ~2 g each. PEs were cleaned successively in dichloromethane and hexane for 24 h each. PEs were spiked with performance reference compounds (PRCs) to account for mass-transfer limitations during deployment. Deuterated PAHs (naphthalene-d₈, pyrene-d₁₀), brominated biphenyls (dibromobiphenyl, tetrabromobiphenyl, pentabromobiphenyl) and octachloronaphthalene (Ultra Scientific, North Kingstown, RI; Cambridge Isotopes, Andover, MA) were equilibrated with the PEs in 80:20 methanol:water on a shaker table for 4 weeks based on the procedure reported by Booij et al. (2002).²⁵ PEs were woven onto stainless steel wire and distributed to collaborators and volunteers. Air PEs were deployed in inverted bowl stations at 11 coastal and three open-lake sites (see TOC). Surface water PEs (unprotected) were deployed in tandem with the coastal air samplers, as well as at three open-lake sites (slightly offset from air deployments) and two additional coastal sites (in-cage deployments, see SI for details). Samples were collected in three deployment periods to evaluate temporal trends: April–June, June–August, and August–October 2011 (Table SI 3). Duplicate air samples and triplicate water samplers were deployed at two sites during each deployment. Field blanks were taken from 2 to 3 sites per deployment period. After retrieval, samplers were wrapped in foil, shipped to the lab and stored at 4 °C until analysis.

Analytical Methodology. PEs were wiped clean with Kimwipes and extracted for 24 h in ethyl acetate and condensed down. Extracts were spiked with 45–50 ng of labeled PAH (acenaphthalene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, perylene-d₁₂ from Ultra Scientific, North Kingstown, RI) and 50 ng PBDE (¹³C₁₂-BDE28, ¹³C₁₂-BDE47, ¹³C₁₂-BDE99, ¹³C₁₂-BDE153, ¹³C₁₂-BDE183 from Cambridge Isotope Laboratories) surrogates to determine analyte recovery during sample processing (see SI page 5). PAHs were analyzed on an Agilent 6890 Series GC-Agilent 5973 MS (mass spectrometer), PBDEs on a Waters Quattro micro GC Micromass MS–MS.

Quality Assurance/Quality Control. PE matrix spikes were prepared in each batch of approximately 20 samples. Analyte concentrations were recovery corrected. Average surrogate recoveries for PAHs were generally >50–60% and spiked matrix recoveries of unlabeled PAHs were typically around 100% (Table SI 9). Average surrogate recoveries for PBDEs ranged from 80 to 150% and spiked matrix recoveries were typically 80–90% (Table SI 18). Method blanks were prepared with each batch of samples to monitor for laboratory contamination. Method blanks ranged from 280–3400 pg/g PE for PAHs and bd–140 pg/g PE for PBDEs (see SI for details). Samples were blank-corrected by subtracting the average of the method and field blank concentrations. Only concentrations greater than three times the standard deviation of the average blank values are reported (Table SI 8, Table SI 17). Standard checks were analyzed every 10 samples to monitor instrument performance.

Calculations/Data Analysis. At each site, 21 PAHs and 11 PBDEs were determined (for details, see SI page 6). Truly dissolved concentrations of POPs in water, C_W (pg L⁻¹), were calculated as²⁶

$$C_W = C_{PEW}/K_{PEW} \quad (1)$$

where C_{PEW} is the concentration of the POP in the PE when in equilibrium with water (pg kg_{PE}⁻¹), and K_{PEW} is the POP partitioning coefficient from water into polyethylene (L kg⁻¹). K_{PEW} values were obtained from Lohmann (2012)²⁷ and temperature-corrected according to a modified form of the Van't Hoff equation

$$K_{PEW(T)} = K_{PEW(298K)} \cdot 10^{(-(\Delta H_{vap}/R) \cdot [(1/298K) - (1/T)])} \quad (2)$$

where ΔH_{vap} is the enthalpy of vaporization (kJ mol⁻¹) (Table SI 5, Table SI 14), R is the gas constant (kJ K⁻¹ mol⁻¹) and T is the average water temperature during deployment (Kelvin) (Table SI 4). Gas-phase atmospheric POP concentration, C_A , was determined with the same calculations, substituting the air-PE partitioning coefficient, K_{PEA} , for K_{PEW} .

The extent of equilibrium achieved for each compound was determined by fitting the equilibrium of the performance reference compounds and their temperature-corrected log K_{PE} values to a model curve derived as

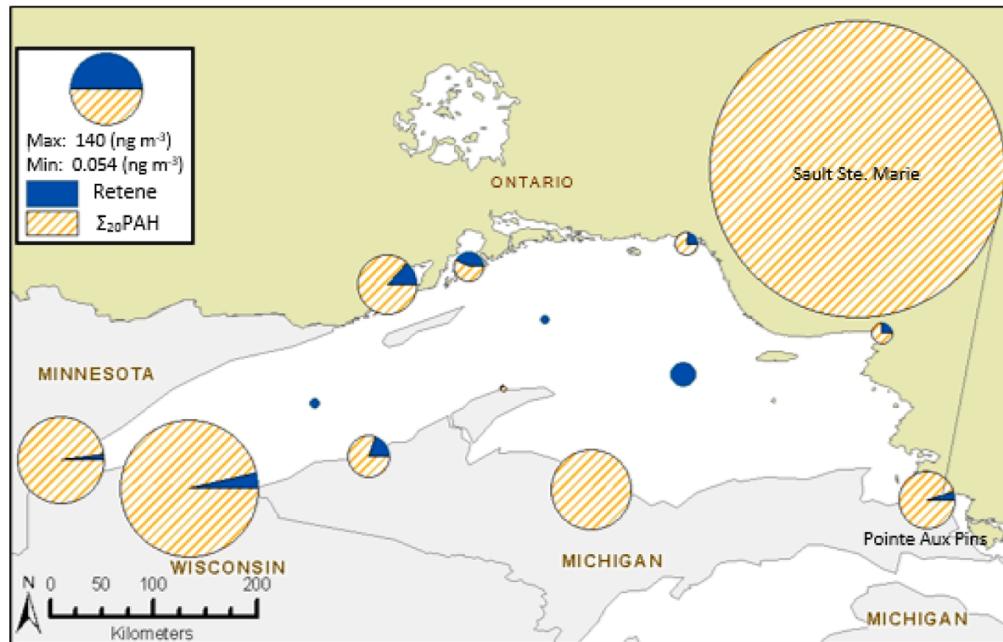
$$\% \text{ equilibrium} = 1 - e^{(-(R_s \cdot t)/(V \cdot K_{PE}))} \quad (3)$$

where R_s is the (fitted) sampling rate (L day⁻¹), t is the sampling time (days), and V is the PE volume (L).

Performance reference compound equilibrium was calculated by comparing the concentrations remaining at time t to the concentrations at time 0 (assumed to be equivalent to concentrations in the field blanks).

The direction of air–water exchange is determined by the ratio of the equilibrium concentration of the POP in air (C_{PEA} ,

A



B

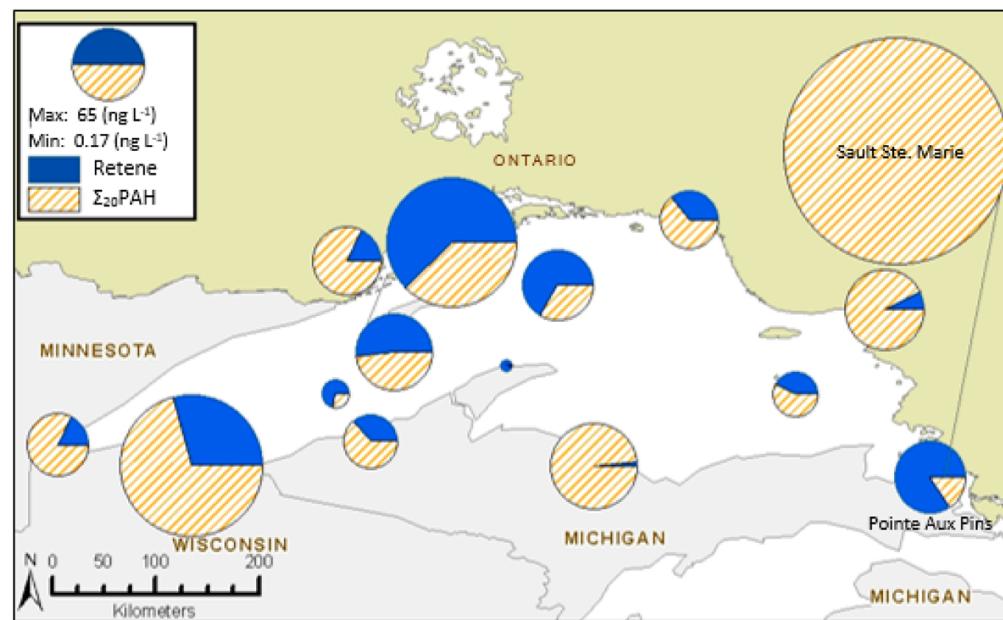


Figure 1. Average $\Sigma_{20}\text{PAH}$ (as per Table 1 minus retene) concentrations at each station. (A) Air concentrations; average from June to October 2011 for all stations except Marquette and Eagle Harbor, which only represent June–August. (B) Water concentrations; average from June to October 2011 for all stations except Marquette, which only represents June–August, and Pointe Aux Pins, which represents August–October 2011.

ng m⁻³) to the equilibrium concentrations of the POP in water (C_{PEW} , ng L⁻¹), where a ratio >1 indicates atmospheric deposition and a ratio <1 indicates volatilization from the water to the air. Net air–water fluxes (ng m⁻² day⁻¹) were calculated by modifying the equation²⁸ Flux = $k_{\text{ol}} \cdot (C_{\text{W}} - C_{\text{A}}/K_{\text{AW}})$ to

$$\text{flux} = k_{\text{ol}} \cdot [(C_{\text{PEW}} - C_{\text{PEa}}/10^3)/K_{\text{PEW}}] \quad (4)$$

where k_{ol} is mass transfer coefficient (m day⁻¹) (see SI page 7) and K_{PEW} is the POP's temperature-corrected PE-water partitioning coefficient (L kg⁻¹). Equation 4 derives air–water exchange gradients without needing to rely on Henry's

Law Constants, which are arguably the least constrained physicochemical constants.^{10,29}

RESULTS AND DISCUSSION

Polycyclic Aromatic Hydrocarbons (PAHs). Spatial Distributions in Air. Averaged $\Sigma_{21}\text{PAH}$ gas-phase concentrations (June–October) ranged from <1 to >100 ng m⁻³ (Figure 1A, Table SI 10). Concentrations were always greatest at Sault Ste. Marie, (June–October mean 140 ng m⁻³), and lowest at Eagle Harbor, MI (June–August 0.054 ng m⁻³) and the open lake sites (mean 0.13–0.95 ng m⁻³) (Table 1). An urban–rural gradient, as observed in this study, can occur due

Table 1. Σ_{21} PAH Concentrations in Air (ng m^{-3}) and Water (ng L^{-1}) by Deployment Period^a

site	air (ng m^{-3})				water (ng L^{-1})			
	April–June	June–August	August–October	June–October average	April–June	June–August	August–October	June–October average
Sault Ste. Marie	70	180	95	140	110	67	62	65
Pointe Aux Pins		6.3	3.7	5.0		N/A	6.6	N/A
Ashland	5.4	12	48	30	35	16	35	26
Thunder Bay/Welcome Isle		4.5	6.4	5.4		6.0	5.9	6.0
Station 139						4.0	11	7.6
Duluth/Station 221	2.3	11	13	12		8.7	0.95	4.8
Marquette	3.5	10	N/A	N/A	10	9.4	N/A	N/A
Ontonagon		0.71	4.7	2.7		3.4	4.1	3.7
Michipicoten Bay		0.15	1.2	0.69		3.2	13	8.0
Sturgeon Bay		0.61	2.2	1.4		3.8	39	22
Foster Island		0.99	0.79	0.89		2.4	6.0	4.2
Eagle Harbor	bd	0.054	N/A	N/A		0.0041	0.34	0.17
Eastern Open Lake	bd		1.9	0.95		0.93	4.2	2.6
Central Open Lake	bd		0.26	0.13		1.6	11	6.3
Western Open Lake		0.0014	0.35	0.17		0.52	1.5	1.0

^a Σ_{21} PAH = sum of biphenyl, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, methyl phenanthrenes, fluoranthene, pyrene, retene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, perylene, benzo(j)fluoranthene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene. bd = below detection limit of GC/MS. N/A = not available due to lost polyethylene samplers or extracts.

to particle scavenging near urban sources, precipitation scrubbing, and OH radical degradation.^{30,31} PAHs tend to have a strong urban signature from vehicle emissions, power generation plants, and industrial activity.^{31–33} At some locations, atmospheric concentrations increased with increasing temperature; yet mostly the changes were within the overall uncertainty of the passive sampling (factor of 2; see Table SI 4 and Table SI 10). Atmospheric concentrations of semivolatile compounds generally have a seasonal component due to the effect of ambient temperature on the direction of pollutant transfer across the air–water interface.³⁴ It has been suggested, however, that atmospheric PAH concentrations are a function of emissions source rather than temperature,³⁵ in-line with the results presented here.

A previous sediment study measured the greatest PAH concentrations near Lake Superior's second largest city, Duluth, MN,¹² however, the study did not include Sault Ste. Marie. Although not the largest city along the Lake Superior shoreline, Sault Ste. Marie is located on the Soo Locks, which sees >70 000 000 net tons of cargo annually.³⁶ Shipping traffic may significantly contribute to local PAH concentrations, though there is also a steel mill burning coal in Sault Ste. Marie, Canada, 3 km northwest of our sampling site. Atmospheric PAH concentrations at Sault Ste. Marie were dominated by the more volatile two- and three-ring compounds, including phenanthrene (57 ng m^{-3}), acenaphthene (24 ng m^{-3}), fluorene (21 ng m^{-3}), fluoranthene (17 ng m^{-3}), methyl phenanthrenes (8.3 ng m^{-3}), plus the four-ringed pyrene (7.1 ng m^{-3}). These compounds are emitted from gasoline engines, coal combustion, and coke ovens.³¹ At the nearby Pointe Aux Pins sites, atmospheric concentrations were much smaller (see Table SI 10), pointing toward urban and industrial activities as major sources of PAHs.

The second greatest atmospheric PAH concentrations were at Ashland, WI (June–October average 29 ng m^{-3}), a major industrial port with a history of iron ore processing, manufactured natural gas from coal, and lumber mills. It is now designated as a U.S. EPA Superfund site polluted with

benz(a)anthracene and benzo(a)pyrene (Figure SI 1, Table SI 2).³⁷ Our samplers were deployed near the Soo Line Ore dock, a now unused jetty originally serving ships and trains with iron ore. Acenaphthene (13 ng m^{-3}), phenanthrene (6.0 ng m^{-3}), fluorene (5.2 ng m^{-3}), and fluoranthene (1.6 ng m^{-3}) contributed to Ashland PAH concentrations. Retene, a PAH resulting from biomass burning and the decomposition of conifer trees, was also significantly present (ca. 4% of Σ_{21} PAHs, 1.1 ng m^{-3}). Retene is associated with wood varnish and lumber treatment,³² therefore, the lumber industry in Ashland could be contributing to the retene signal in that region.

Atmospheric PAH concentrations at other urban locations were at most a tenth to a third of those at Sault Ste. Marie and Ashland. They were still ca. 2- to 10-times greater than rural coastal sites, and several times the open-water air concentrations. Duluth had lower atmospheric PAH concentrations (June–October average 12 ng m^{-3}) than Sault Ste. Marie and Ashland despite being an urban center and possible emissions linked to shipping traffic in the Duluth/Superior harbor, the busiest port in the Great Lakes system.³⁸ This may be because the PE was deployed at the regional EPA office northeast (upwind) of the city center. Following Duluth at slightly lower PAH concentrations were Marquette (June–August average 10 ng m^{-3}) and Thunder Bay/Welcome Isle (June–October average 5.4 ng m^{-3}). The sampler at Thunder Bay was also several km removed from the city center. Concentrations were characterized by many of the same petroleum- and biomass-derived PAHs measured at shipping sites: phenanthrene, methyl phenanthrenes, fluoranthene, and pyrene. Thunder Bay and Duluth have relatively modest populations (108 000 and 86 000 people in 2011, respectively), and these samples demonstrate the effect even small cities have on local atmospheric PAH concentrations.

Eagle Harbor, MI atmospheric PAH concentrations were below the detection limit for April–June and <0.1 ng m^{-3} for June–August; August–October data were not available, however, temporal trends for other sites suggest atmospheric

concentrations may have been greater during the late summer. The IADN master station for Lake Superior is located at Eagle Harbor and has been collecting high volume air samples of PAHs since 1990.³² The site is used as the background site for Lake Superior and the entire Great Lakes region.³⁵ Typical annual IADN gas+particle PAH concentrations are ca. 1 ng m^{-3} (monthly averages were not available for comparison).^{35,16} Gas-phase PAHs concentrations measured in this study may be lower than IADN values due to differences in sampling procedure and the sampling period. PEs were deployed from April to October, when PAH emissions are lowest. IADN samplers collect air samples throughout the entire year and results are reported as annual means, including the winter months when residential heating causes a spike in PAH emissions.^{32,39} IADN relies on active sampling using a glass fiber filter coupled with XAD/PUF for sampling gas-phase compounds, whereas PEs only sample the truly gas phase fraction of atmospheric PAHs. A recent comparison between PUF- and passive sampler-collected gas-phase PAHs implied good agreement between both methods.¹⁵

Northern, rural coastal sites (Sturgeon Bay: 1.4 ng m^{-3} ; Foster Island: 0.89 ng m^{-3}), and eastern open lake (0.95 ng m^{-3}) were all at background levels similar to Eagle Harbor of around 1 ng m^{-3} . The central and western open lake samples displayed lower PAHs concentrations, as could be assumed for overwater sites. This comparison also serves to support the choice of Eagle Harbor as a rural background site for IADN; yet it might not be a good representation of overwater concentrations.

Spatial Distributions in Water. PAH concentrations in the water followed similar spatial patterns as the atmospheric PAH distributions (Figure 1B, Table SI 11). Seasonally averaged $\Sigma_{21}\text{PAH}$ concentrations in Lake Superior were greatest at Sault Ste. Marie (June–October 65 ng L^{-1}), followed by Ashland (26 ng L^{-1}). Concentrations at Sault Ste. Marie were dominated by phenanthrene, fluoranthene and pyrene (all $>10 \text{ ng L}^{-1}$). Methyl phenanthrenes, pyrene, phenanthrene, and fluoranthene also contributed to Ashland concentrations ($3\text{--}5 \text{ ng L}^{-1}$, respectively), however the greatest PAH present was retene (7.5 ng L^{-1}), possibly due to biomass burning and the degradation of wood from lumber production and treatment. Retene also accounted for ca. 35–60% of the dissolved PAHs at Foster Island, Sturgeon Bay, and Station 139 and ca. 40–70% at the open-water sites. Methyl phenanthrenes were typically $>1 \text{ ng L}^{-1}$, reaching $>5.0 \text{ ng L}^{-1}$ at Sault Ste. Marie, Sturgeon Bay, Ashland, and Michipicoten Bay, as well as accounting for 60% of the dissolved PAHs at Foster Island. Concentrations of dissolved PAHs were lower than expected at Station 221 ($\Sigma_{21}\text{PAH } 4.8 \text{ ng L}^{-1}$), east of Duluth, however, the sampler was deployed approximately 3 km offshore and may not have received a direct urban signal. At coastal sites, dissolved $\Sigma_{21}\text{PAH}$ water concentrations changed significantly between deployments, but without a clear trend. Dissolved concentrations at Ashland and Michipicoten Bay increased from June–August to August–October (8.0 to 28 and 2.8 to 12 ng L^{-1} , respectively), but decreased at Duluth from June–October ($7.3\text{--}0.58 \text{ ng L}^{-1}$).

Dissolved Retene. Although PAH concentrations near urban, industrial, and shipping centers were generally characterized by fossil fuel emissions, total dissolved concentrations of PAHs across most sites were dominated by retene. It is the combustion byproduct of abietic acid, a natural product mainly found in coniferous trees.^{32,40} Retene can be produced

in urban areas from municipal waste incinerators, tire burning, and incineration of building waste; however, it is primarily emitted by burning wood.⁴¹ Rural households consume about three times more wood than urban homes.³² It is therefore not surprising that retene accounts for ca. 20–60% of the total PAHs at the northern coastal sites and ca. 40–70% of total PAHs present in open lake waters. Atmospheric retene concentrations typically peak in the winter months when wood is burned for residential heating, but lower-magnitude spikes can occur between April and September due to naturally occurring wildfires.³²

Several sites exhibited elevated retene concentrations in both air and water during deployment 3 (August–October) relative to deployment 2 (June–August) (Figure 2). Dissolved retene

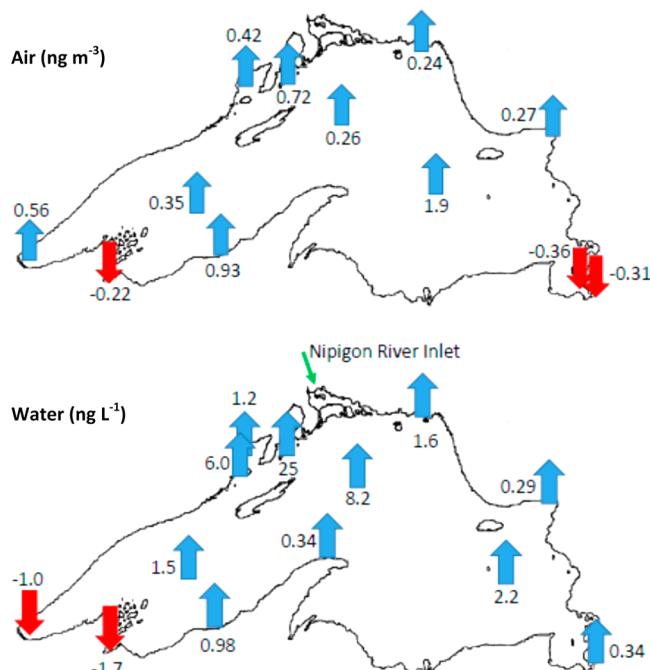


Figure 2. Changes in retene concentration (Δ) between June–August and August–October 2011.

increased strongly at Sturgeon Bay (from 0.92 to 26 ng L^{-1}), station 113 (from 0.13 to 8.3 ng L^{-1}), and Station 139 (from 0.92 to 6.9 ng L^{-1}). Because PE sampling was limited to one season, we cannot confirm whether these trends occur in annual cycles or are due to unique events. However, sites with the greatest retene concentrations (Sturgeon Bay and Station 113) were northern and central lake locations, which probably received enhanced retene inputs following elevated forest fire intensity from July–September 2011 northwest of the Lake (see Figure SI 3).⁴² Retene could also enter the Lake's water through tributaries, but Sturgeon Bay and Station 113 were not close to river plumes.

Comparison to Active Sampling. Venier et al. (2014)⁴³ reported apparently dissolved water concentrations of various POPs, including PAHs across the Great Lakes using active GFF-XAD sampling in 2011/2012. For the open Lake Superior, apparently dissolved PAH concentrations were, on average, dominated by fluoranthene (310 pg L^{-1}), followed by pyrene (140 pg L^{-1}), benz(a)anthracene (100 pg L^{-1}) and retene (50 pg L^{-1}). These concentrations were much lower than what we determined here. Venier et al. (2014) collected

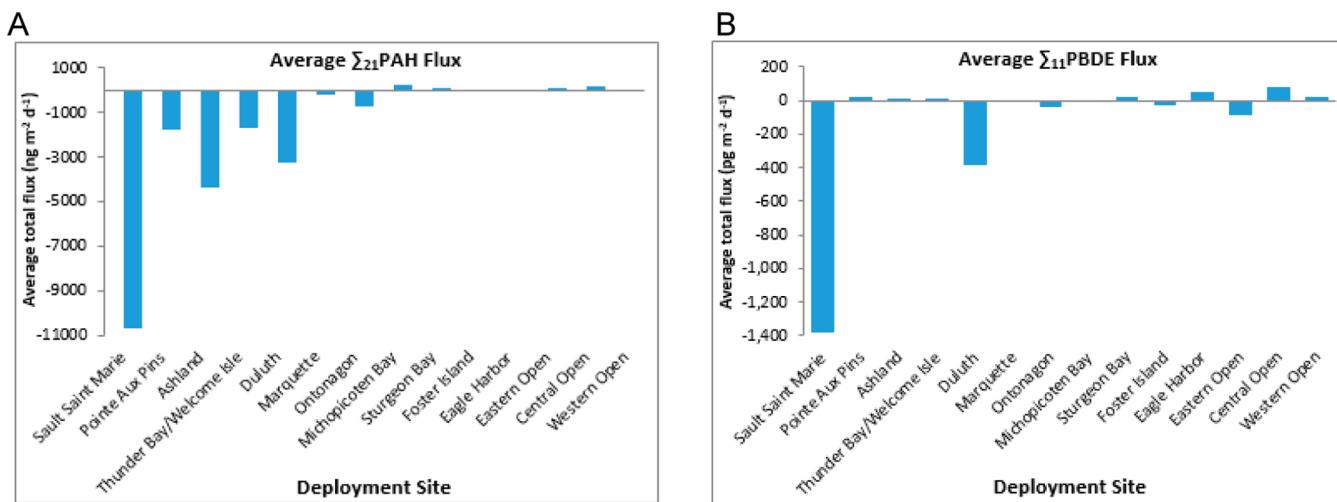


Figure 3. (a) PAH and (b) PBDE fluxes (Σ_{21} PAHs as per Table 1, Σ_{11} PBDE as per Table 2) across the air–water interface of Lake Superior. Positive values indicate volatilization from the surface water, while negative values indicate atmospheric deposition. Only values from significant C_{PEa}/C_{PEw} ratios were averaged. PAH averages (Figure 3A) from June to October 2011 for all stations except Marquette and Eagle Harbor which only account for the second deployment (June–August 2011), and Pointe Aux Pins which only accounts for the third deployment (August–October 2011). Eastern refers to buoys Station 23 and ODAS45004, Central is Station 113 and ODAS45001, and Western is Station 169 and ODAS45006. PBDE averages (Figure 3B) from June to October 2011 for all stations except Marquette which was from June–August 2011.

samples during the spring season, before Lake Superior stratified during the summer (see temperature profiles for May and July in Figure S12). Most likely, PAH concentrations across Lake Superior increased strongly during the summer of 2011, probably due to wildfires, which peaked in July (see Figure S13): retene was present in the ng L⁻¹ range at all sites during this study, while Venier et al. (2014) only reported 50 pg L⁻¹. The comparison between active and passively sampled PBDEs (see below) similarly displayed significant differences between both sampling approaches.

PAH Air–Water Exchange. Atmospheric deposition is a major source of pollutants to the Great Lakes.^{44,45,12} Chemical exchange across the air–water interface is a key process controlling concentrations and residence times of semivolatile pollutants in these water bodies.^{46,47,34} PE sampling improves upon previous estimates of air–water PAH exchange by (i) a greater spatial coverage; (ii) simultaneously measured time-averaged concentrations for both the air and water dampening diurnal effects and minimizing anomalous signals; (iii) by only measuring gas- or dissolved-phase compounds directly available for exchange across the air–water interface, and (iv) by providing concentrations from open Lake locations. To our knowledge these are the first open lake passive measurements for PAHs in the Great Lakes.

The direction of air–water exchange was determined by the ratio of the concentration of an analyte in the PE at equilibrium with the air to the concentrations of the analyte in the PE at equilibrium with the water:

$$\text{flux direction} = C_{PEa}/C_{PEw} \quad (5)$$

Uncertainty propagation indicated that ratios needed to be <0.14 and >3.9 to determine net deposition or volatilization (see SI page 9). Hence, a ratio >3.9 indicated a higher activity in the air, and therefore, net deposition, while a ratio <0.14 resulted in net volatilization.

Net air–water exchange of gas-phase PAHs was generally into the lake near populated or industrialized (point) sources, however fluxes were low at most sites (<1000 ng m⁻² d⁻¹) (Table S12). Sault Ste. Marie displayed the greatest fluxes for

several of the PAHs (Figure 3A, Table S13). At this site average deposition was dominated by six PAHs: fluorene, phenanthrene, methyl phenanthrenes, fluoranthene, and pyrene; however, only phenanthrene (6900 ng m⁻² d⁻¹) and fluoranthene (2700 ng m⁻² d⁻¹) underwent net deposition significantly different ($P < 0.05$) from equilibrium as defined above. Retene was deposited at most sites, with notable exceptions at the central open lake site and Sturgeon Bay, where retene concentrations in the water were exceptionally high; air–water exchange was near equilibrium from August–October. As previously discussed, retene inputs may have been elevated due to high wildfire activity in the region that season, resulting in net volatilization of retene into the atmosphere at the central open lake and Sturgeon Bay. This volatilization was in contrast to the eastern and western open lake sites where retene was being deposited.

Polybrominated Diphenylethers (PBDEs). *Spatial Distributions.* Σ_{11} BDE concentrations in air were more than 3 orders of magnitude lower than PAHs across Lake Superior (Figure 4A, Table S19). BDE-47 was generally the most abundant congener present (approximately 20 to 60% in air and 40–75% in water samples) throughout the sampling period, followed by BDE-28, 49, 99, and 100. BDE-153 concentrations were low or below detection at all most sites and BDE-154 was not detected in any samples. Changes in atmospheric and aqueous PBDE concentrations between deployments at a given site were smaller than variations among sites. In other words, the proximity to emission sources was more important than geochemical variations (currents, winds, temperature).

Atmospheric PBDE concentrations were greatest at Marquette (June–October average 15 pg m⁻³) (Table 2). This station was located at a dock for a coal-fired power plant and in proximity to a number of sites registered with the EPA Toxic Release Inventory, including facilities that manufacture polyurethane and explosives,⁴⁸ where PBDEs might have been used in the past. Sault Ste. Marie and Duluth also had elevated atmospheric PBDE concentrations from June–October, 7.4 and 5.7 pg m⁻³, respectively. Atmospheric concentrations at

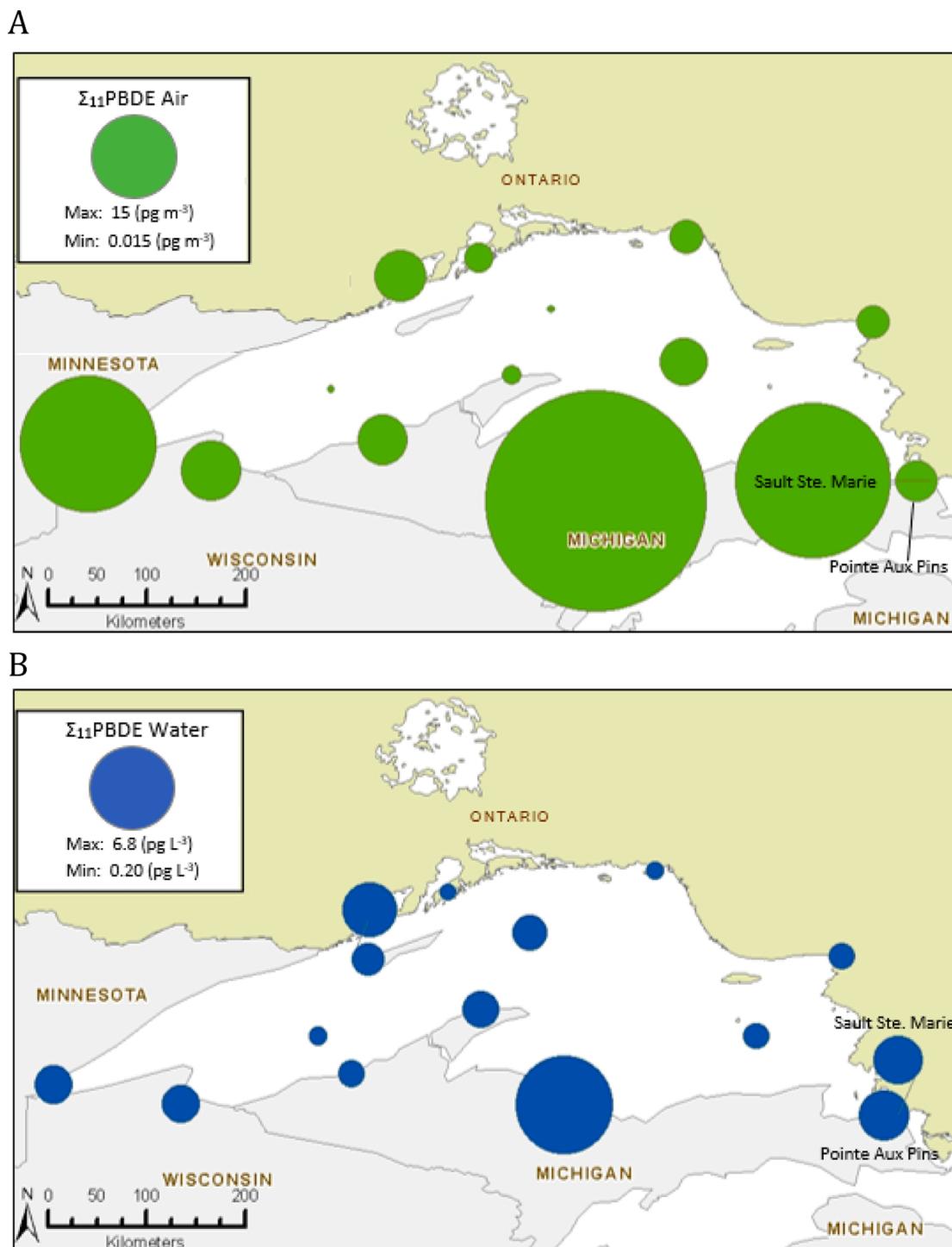


Figure 4. Average $\Sigma_{11}\text{PBDE}$ (as defined by Table 2) concentrations at each station. (A) Air concentrations (pg m^{-3}) are averaged from June to October 2011. (B) Water concentrations (pg L^{-1}) are averaged from June to October 2011 for all stations except Marquette, which represents June–August.

nearly all other sites were $<1 \text{ pg m}^{-3}$. The eastern open lake site (ODAS45004) exhibited concentrations >10 times higher than the other open lake sites, perhaps receiving input downwind from Marquette.

Water concentrations had similar spatial distributions as air concentrations (Figure 4B, Table SI20). Concentrations were greatest at Marquette (June–August average 6.8 pg L^{-1}), followed by Thunder Bay/Welcome Island, Pointe Aux Pins, and Sault Ste. Marie (June–October average 2.1, 1.8, and 1.7 pg L^{-1} ,

pg L^{-1} , respectively). Dissolved PBDE concentrations were lowest at rural Canadian sites: Sturgeon Bay (0.20 pg L^{-1}), Foster Island (0.21 pg L^{-1}), and Michipicoten Bay (0.46 pg L^{-1}). Eastern and western open lake sites exhibited PBDE concentrations similar to coastal rural sites (0.46 and 0.24 pg L^{-1} , respectively), with the exception of Eagle Harbor (0.97 pg L^{-1}). Average central open lake PBDE concentrations were slightly higher than the other open lake sites (0.86 pg L^{-1}),

Table 2. \sum_{11} PBDE Concentrations in Air (pg m^{-3}) and Water (pg L^{-1}) by Deployment Period^a

site	air (pg m^{-3})				water (pg L^{-1})			
	April–June	June–August	August–October	June–October average	April–June	June–August	August–October	June–October average
Sault Ste. Marie	1.4	12	2.6	7.4	3.7	1.4	1.9	1.7
Pointe Aux Pins		0.54	0.49	0.51		1.8	1.8	1.8
Ashland	0.56	1.5	0.77	1.1	2.7	0.93	1.1	1.0
Thunder Bay/Welcome Isle		0.77	0.84	0.80		3.0	1.3	2.1
Station 139						0.73	0.76	0.75
Duluth	1.4	6.0	5.3	5.7		1.2	0.86	1.1
Marquette	0.92	24	6.3	15	3.5	6.8	N/A	N/A
Ontonagon		1.3	0.26	0.75		0.37	0.64	0.50
Michipicoten Bay		0.27	0.38	0.32		0.69	0.23	0.46
Sturgeon Bay		0.14	0.38	0.26		0.31	0.086	0.20
Foster Island		0.25	0.44	0.35		0.19	0.23	0.21
Eagle Harbor	0.046	0.21	bd	0.11		0.99	0.94	0.97
Eastern Open Lake		0.48	0.87	0.68		0.34	0.58	0.46
Central Open Lake		0.030	bd	0.015		0.53	1.2	0.86
Western Open Lake		0.031	bd	0.015		0.42	0.065	0.24

^a \sum_{11} PBDE = sum of BDE-2, 8, 15, 28, 30, 47, 49, 99, 100, 153, 154. bd = below detection limit of GC/MS. N/A = not available due to lost polyethylene samplers.

similar to Station 139 (0.75 pg L^{-1}) near Thunder Bay/Welcome Isle.

Comparison to Active Sampling. Ma et al. (2013) reported average gas-phase concentrations of PBDEs in Great Lakes air samples from IADN sites covering 2003–2011.⁴⁹ For Eagle Harbor, concentrations were reported as $2\text{--}3 \text{ pg m}^{-3}$ for BDEs 47 and 99, which dominated total PBDEs. Our 2011 gas-phase concentrations displayed lower concentrations, though dominated by similar congeners. There is evidence that PBDE concentrations have begun decreasing across the Great Lakes.¹⁷ In general, active and passive results for gas-phase air sampling yield fairly similar results.¹⁵

Venier et al. (2014) also reported dissolved PBDE concentrations (water filtered through glass fiber cartridges removing $>90\%$ of particles $>0.5 \mu\text{m}$) for several sites across Lake Superior in the pg L^{-1} range.⁴³ On average, BDE-47 dominated at 6 pg L^{-1} , followed by BDEs 100 and 153 ($\sim 1 \text{ pg L}^{-1}$) and BDE-28 (0.5 pg L^{-1}). These concentrations were between 10-fold (BDEs 28 and 47) and 100-fold (BDEs 100 and 153) greater than what was measured in this study. Such discrepancy has often been attributed to the inadvertent sampling of dissolved organic carbon (DOC)-bound compounds by active sampling approaches. DOC concentrations of around 1.2 mg L^{-1} have been reported for the open Lake Superior.⁵⁰ A typical affinity of PBDEs to DOC is one tenth of their octanol–water partitioning coefficients.⁵¹ Yet this DOC-correction was not sufficient to eliminate the discrepancy between active and passive sampling (on average, concentrations reported by Venier et al. (2014) were still greater than our passive sampler-derived concentrations by 10–80-fold.⁴³ As sampling was conducted at different times, different locations and different laboratories, perfect agreement cannot be expected. Yet the strong discrepancy suggests that dissolved PBDE concentrations display some temporal dynamics (which might have led to elevated active sampling results), and the efficient retention of PBDEs associated with DOC and possibly small particles by active sampling.

PBDE Air–Water Exchange. Air–water exchange ratios varied greatly between sites and for PBDE congeners (Table SI21). Where present, BDE-2,8,15, and 30 were deposited,

possibly from photodegradation.⁵² Eagle Harbor and open lake site ratios suggested mainly net volatilization for tetra and penta BDEs, as well as BDE-28. By and large, BDE-47 underwent net deposition during the first two deployments. Exceptions were the open lake sites where BDE-47 volatilized, and some coastal sites during August–October.

PBDEs were deposited into Lake Superior at half of the coastal sites as indicated by significant air-to-water ratios. The greatest net gas-phase deposition fluxes during June–August were at Sault Ste. Marie ($-2700 \text{ pg m}^{-2} \text{ d}^{-1}$), Duluth ($-770 \text{ pg m}^{-2} \text{ d}^{-1}$), and Ontonagon ($-140 \text{ pg m}^{-2} \text{ d}^{-1}$) (Figure 3B, Table SI22). During August–October, overall net fluxes were lower, with the greatest fluxes at the central open water site ($120 \text{ pg m}^{-2} \text{ d}^{-1}$) and the eastern open lake site ($-180 \text{ pg m}^{-2} \text{ d}^{-1}$).

Gaseous deposition fluxes were primarily composed of BDE-47 with less brominated congeners contributing to Sault Ste. Marie and eastern open lake fluxes. Conversely, the central open lake and Eagle Harbor sites generally displayed volatilization of PBDEs into the atmosphere, mainly BDE-47. Interestingly, the eastern open lake site (Station 23) exhibited strong deposition of di- and tribromodiphenyl ethers (170 and $44 \text{ pg m}^{-2} \text{ d}^{-1}$, respectively) from August–October, perhaps indicating an upwind source during that time period.

PBDE Sources. PBDE concentrations in both the air and water were correlated with industrial and urban sites, reflecting their origin as flame retardants used widely in consumer, commercial, and industrial products. Atmospheric deposition is an important source of PBDEs to Lake Superior and is probably the main pathway to open-lake sites.⁴⁵ Physico-chemical properties indicate that lighter (less brominated) congeners will travel farther from PBDE sources.¹⁸ Tri-, tetra-, and pentaBDEs were most commonly detected at Lake Superior sites, whereas lighter and heavier congeners were typically below detection. These congeners would typically stem from the penta-BDE commercial mixture. We cannot exclude that this is a reflection of the environmental fractionation of BDEs, their use, and our sampling approach.

Waning PBDE sources may explain the reduced atmospheric PBDE concentrations found in this study compared to IADN-

derived measurements. Σ_7 BDE gas-phase concentrations from 2005 to 2006 were $2.8 \pm 0.28 \text{ pg m}^{-3}$.² Our atmospheric concentrations were an order of magnitude lower at Eagle Harbor, possibly indicating the positive effect of reduced emissions in the region. Likewise, our Eagle Harbor fluxes indicate reduced gas deposition (1.5 kg y^{-1}) since 2005–2006 ($18 \pm 9.5 \text{ kg y}^{-1}$),² however, urban locations may contribute to greater deposition. It should be noted that the passive samplers deployed in our study only detect truly gas-phase compounds, while IADN operates high-volume samplers. The observed decrease in PBDE concentrations over time could thus at least partially be due to methodological differences.

■ IMPLICATIONS

Although long-range atmospheric transport is a major pathway for PAH and PBDE distribution across Lake Superior, point sources along the lake perimeter significantly impact local and regional concentrations. Fluxes for both currently emitted POPs were generally into the lake near industrial and urban sources, whereas the open lake sites appeared to volatilize POPs back into the atmosphere at much lower rates. Thus, Lake Superior combines primary source-driven deposition of POPs at its periphery with serving as a secondary source of POPs back to the atmosphere in its interior. Enhancing spatial and temporal coverage of the Great Lakes region will provide meaningful trends in PAH and PBDE concentrations and fluxes as use and regulations change. We anticipate PAH concentrations to remain constant or even increase with time, but PBDE concentrations may decrease as use is phased out. Changes in atmospheric concentrations could lead to an equilibrium reversal and the volatilization of PBDEs out of Lake Superior into the atmosphere. Such trends can be monitored effectively and affordably with passive samplers. There is evidence of a strong discrepancy between active and passive sampling results for POPs in water, which will impact our ability to derive air–water fluxes accurately.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.5b02611](https://doi.org/10.1021/acs.est.5b02611).

Additional information on sampling locations, physico-chemical constants, sampling rates, QA/QC, analysis, calculations and concentrations of PAHs and PBDEs and their air–water exchange available free of charge via the Internet at <http://pubs.acs.org/> (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 401-874-6612; fax: 401-874-6811; e-mail: lohmann@gso.uri.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge funding from the U.S. EPA Great Lakes Restoration Initiative GLAS No. 00E00597-0, Project Officer Todd Nettlesheim, and from the Great Lakes Air Deposition Program, No. GLAD 2010-5. We thank Peter August (URI) for GIS assistance, David Adelman (URI) for organizing deployments, Camilla Teixeira and the field staff of the Emergencies, Operational Analytical Laboratories, and Research Support

group (Environment Canada Burlington) for open-lake deployments, Great Lakes Unit technical staff (Ontario Ministry of the Environment) for Canadian nearshore deployments, Allison Pugh (Environmental Canada Burlington, Water Quality Monitoring and Surveillance Division) for water temperature data, Dr. Mohammed Khairy (URI) for assistance with data analysis and interpretation, and all of the volunteers who deployed PEs in the region.

■ REFERENCES

- (1) Venier, M.; Hites, R. A. Time trend analysis of atmospheric POPs concentrations in the Great Lakes region since 1990. *Environ. Sci. Technol.* **2010**, *44*, 8050–8055.
- (2) Venier, M.; Hites, R. A. Atmospheric deposition of PBDEs to the Great Lakes featuring a Monte Carlo analysis of errors. *Environ. Sci. Technol.* **2008**, *42*, 9058–9064.
- (3) Integrated Atmospheric Deposition Network, IADN. *Atmospheric Deposition of Toxic Substances to the Great Lakes: IADN results through 2005*.
- (4) United Nations Economic Commission for Europe: Stockholm Convention, Listing of POPs. <http://www.chm.pops.int> (accessed July 24, 2013).
- (5) Luross, J. M.; Alaee, M.; Sergeant, D. B.; Cannon, C. M.; Whittle, D. M.; Solomon, K. R.; Muir, D. C. Spatial distribution of polybrominated diphenyl ethers and polybrominated biphenyls in lake trout from the Laurentian Great Lakes. *Chemosphere* **2002**, *46*, 665–672.
- (6) Carlson, D. L.; De Vault, D. S.; Swackhamer, D. L. On the rate of decline of persistent organic contaminants in lake trout (*Salvelinus namaycush*) from the Great Lakes, 1970–2003. *Environ. Sci. Technol.* **2010**, *44*, 2004–2010.
- (7) Stuer-Lauridsen, F. Review of passive accumulation devices for monitoring organic micropollutants in the aquatic environment. *Environ. Pollut.* **2005**, *136*, 503–524.
- (8) Shaw, M.; Mueller, J. F. Time integrative passive sampling: how well do chemcatchers integrate fluctuating pollutant concentrations? *Environ. Sci. Technol.* **2009**, *43*, 1443–1448.
- (9) Lohmann, R.; Booij, K.; Smedes, F.; Vrana, B. Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water. *Environ. Sci. Pollut. Res.* **2012**, *19*, 1885–1895.
- (10) Morgan, E.; Lohmann, R. Detecting air-water and surface-deep water gradients of PCBs using polyethylene passive samplers. *Environ. Sci. Technol.* **2008**, *42*, 7248–7253.
- (11) Massachusetts Energy and Environmental Affairs. *Polycyclic Aromatic Hydrocarbons (PAHs)* <http://www.mass.gov/eea/agencies/massdep/toxics/reports/polycyclic-aromatic-hydrocarbons-pahs.html> (accessed 2012).
- (12) Gewurtz, S. B.; Shen, L.; Helm, P. A.; Waltho, J.; Reiner, E. J.; Painter, S.; Brindle, I. D.; Marvin, C. H. Spatial distribution of legacy contaminants in sediments of Lakes Huron and Superior. *J. Great Lakes Res.* **2008**, *34*, 153–168.
- (13) Slater, G. F.; Benson, A. A.; Marvin, C.; Muir, D. PAH fluxes to Siskiwit revisited: Trends in fluxes and sources of pyrogenic PAH and perylene constrained via radiocarbon analysis. *Environ. Sci. Technol.* **2013**, *47*, 5066–5073, DOI: 10.1021/es400272z.
- (14) Sabin, L. D.; Maruya, K. A.; Lao, W.; Diehl, D.; Tsukada, D.; Stolzenbach, K. D.; Schiff, K. C. Exchange of polycyclic aromatic hydrocarbons among the atmosphere, water, and sediment in coastal embayments of southern California, USA. *Environ. Toxicol. Chem.* **2010**, *29*, 265–275.
- (15) Khairy, M. A.; Lohmann, R. Field validation of polyethylene passive air samplers for parent and alkylated PAHs in Alexandria, Egypt. *Environ. Sci. Technol.* **2012**, *46*, 3990–3998.
- (16) Buehler, S. S.; Basu, I.; Hites, R. A. A comparison of PAH, PC, and pesticide concentrations in air at two rural sites on Lake Superior. *Environ. Sci. Technol.* **2001**, *35*, 2417–2422.
- (17) Crimmins, B. S.; Pagano, J. J.; Xia, X.; Hopke, P. K.; Milligan, M. S.; Holsen, T. M. Polybrominated biphenyl ethers (PBDEs): Turning

- the corner in Great Lakes trout 1980–2009. *Environ. Sci. Technol.* **2012**, *46*, 9890–9897.
- (18) Melymuk, L.; Robson, M.; Csiszar, S. A.; Helm, P. A.; Kaltenecker, G.; Backus, S.; Bradley, L.; Gilbert, B.; Blanchard, P.; Jantunen, L.; Diamond, M. From the city to the lake: loadings of PCBs, PBDEs, PAHs and PCMs from Toronto to Lake Ontario. *Environ. Sci. Technol.* **2014**, *48*, 3732–3741.
- (19) United States Environmental Protection Agency. *Emerging Contaminant—Polybrominated Biphenyl Ethers (PBDE) and Polybrominated Biphenyls (PBB). Solid Waste and Emergency Response (S106P)*, EPA 505-F-007. April 2008.
- (20) Norwegian Pollution Control Authority. *SFT, Guidance on Alternative Flame Retardants to the Use of Commercial Pentabromodiphenylether (c-PentaBDE)*; SFT: Oslo, February 2009.
- (21) Arinaitwe, K.; Muir, D. C.; Kiremire, B. T.; Fellin, P.; Li, H.; Teixeira, C. Polybrominated diphenyl ethers and alternative flame retardants in air and precipitation samples from the northern Lake Victoria region, East Africa. *Environ. Sci. Technol.* **2014**, *48*, 1458–1466.
- (22) Raff, J. D.; Hites, R. A. Deposition versus photochemical removal of PBDEs from Lake Superior air. *Environ. Sci. Technol.* **2007**, *41*, 6725–6731.
- (23) Hites, R. A. Polybrominated diphenyl ethers in the environment and people: a meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, *38*, 945–956.
- (24) Abbasi, G.; Buser, A. M.; Soehl, A.; Murray, M. W.; Diamond, M. L. Stocks and flows of PBDEs in products from use to waste in the U.S. and Canada from 1970 to 2020. *Environ. Sci. Technol.* **2015**, *49*, 1521–1528.
- (25) Booij, K.; Smedes, F.; van Weerlee, E. M. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere* **2002**, *46*, 1157–1161.
- (26) Adams, R. G.; Lohmann, R.; Fernandez, L. A.; Macfarlane, J. K.; Gschwend, P. M. Polyethylene devices: Passive samplers for measuring dissolved hydrophobic organic compounds in aquatic environments. *Environ. Sci. Technol.* **2007**, *41*, 1317–1323.
- (27) Lohmann, R. Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environ. Sci. Technol.* **2012**, *46*, 606–618.
- (28) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. Chapter 20: Air-water exchange. In *Environmental Organic Chemistry*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2003.
- (29) Bruhn, R.; Lakaschus, S.; McLachlan, M. S. Air/sea gas exchange of PCBs in the southern Baltic Sea. *Atmos. Environ.* **2003**, *37*, 3445–3454.
- (30) Offenberg, J. H.; Baker, J. E. Precipitation scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons along an urban to over-water transect. *Environ. Sci. Technol.* **2002**, *36*, 3763–3771.
- (31) Hafner, W. D.; Hites, R. A. Potential sources of pesticides, PCBs, and PAHs to the atmosphere of the Great Lakes. *Environ. Sci. Technol.* **2003**, *37*, 3764–3773.
- (32) Sun, P.; Backus, S.; Blanchard, P.; Hites, R. A. Annual variation of polycyclic aromatic hydrocarbon concentrations in precipitation collected near the Great Lakes. *Environ. Sci. Technol.* **2006**, *40*, 696–701.
- (33) McDonough, C. A.; Khairy, M. A.; Muir, D. C. G.; Lohmann, R. Significance of population centers as sources of gaseous and dissolved PAHs in the lower Great Lakes. *Environ. Sci. Technol.* **2014**, *48*, 7789–7797.
- (34) Hillery, B. R.; Simcik, M. F.; Basu, I.; Hoff, R. M.; Strachan, W. M. J.; Burniston, D.; Chan, C. H.; Brice, K. A.; Sweet, C. W.; Hites, R. A. Atmospheric deposition of toxic pollutants to the Great Lakes as measured by the Integrated Atmospheric Deposition Network. *Environ. Sci. Technol.* **1998**, *32*, 2216–2221.
- (35) Cortes, D. R.; Basu, I.; Sweet, C. W.; Hites, R. A. Temporal trends in and influence of wind on PAH concentrations measured near the Great Lakes. *Environ. Sci. Technol.* **2000**, *34*, 356–360.
- (36) United States Army Corps of Engineers. *St. Marys Falls Canal, Michigan: Statistical Report of Lake Commerce Passing through St. Marys Falls Canal Sault Ste Marie during 2010 Navigation Season*; United States Army Engineer District, Detroit, Sault Ste. Marie Area Office, 2011.
- (37) NPL Site Narrative for Ashland/Northern States Power Lakefront <http://www.epa.gov/superfund/sites/npl/nar1616.htm> (accessed September 20, 2015).
- (38) Duluth Seaway Port Authority <http://www.duluthport.com/port.php> (accessed September 15, 2015).
- (39) Liu, L. Y.; Kukučka, P.; Venier, M.; Salamova, A.; Klánová, J.; Hites, R. A. Differences in spatiotemporal variations of atmospheric PAH levels between North America and Europe: data from two air monitoring projects. *Environ. Int.* **2014**, *64*, 48–44.
- (40) Ramdahl, T. Retene – a molecular marker of wood combustion in ambient air. *Nature* **1983**, *306*, 580–583.
- (41) Shen, G.; Tao, S.; Wei, S.; Zhang, Y.; Wang, R.; Wang, B.; Li, W.; Shen, H.; Huang, Y.; Yang, Y.; Wang, W.; Wang, X.; Massey Simonich, S. L. Retene emission from residential solid fuels in China and evaluation of retene as a unique marker for soft wood combustion. *Environ. Sci. Technol.* **2012**, *46*, 4666–4672.
- (42) Ontario Ministry of Natural Resources. 2012. <http://www.mnr.gov.on.ca> (accessed 2012).
- (43) Venier, M.; Dove, A.; Romanak, K.; Backus, S.; Hites, R. Flame retardants and legacy chemicals in Great Lakes' water. *Environ. Sci. Technol.* **2014**, *48*, 9563–9572.
- (44) Buckley, D. R.; Rockne, K. J.; Li, A.; Mills, W. J. Soot deposition in the Great Lakes: implications for semi-volatile hydrophobic organic pollutant deposition. *Environ. Sci. Technol.* **2004**, *38*, 1732–1739.
- (45) Li, A.; Rockne, K. J.; Sturchio, N.; Song, W.; Ford, J. C.; Buckley, D. R.; Mills, W. J. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 4. Influencing factors, trends, and implications. *Environ. Sci. Technol.* **2006**, *40*, 7528–7534.
- (46) Baker, J. E.; Eisenreich, S. J. Concentrations and fluxes of polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface of Lake Superior. *Environ. Sci. Technol.* **1990**, *24*, 342–352.
- (47) Gevao, B.; Hamilton-Taylor, J.; Jones, K. C. Polychlorinated biphenyl and polycyclic aromatic hydrocarbon deposition to and exchange at the air-water interface of Esthwaite Water, a small lake in Cumbria, UK. *Environ. Pollut.* **1998**, *102*, 63–75.
- (48) United States Environmental Protection Agency, U.S. EPA, EnviroMapper <http://www.epa.gov/emeedata/em4ef.home> (accessed July 24, 2013).
- (49) Ma, Y.; Salamova, A.; Venier, M.; Hites, R. A. Has the phase-out of PBDEs affected their atmospheric levels? Trends of PBDEs and their replacements in the Great Lakes atmosphere. *Environ. Sci. Technol.* **2013**, *47*, 11457–11464.
- (50) Zigah, P. K.; Minor, E. C.; Werne, J. P.; McCallister, S. L. Radiocarbon and stable carbon isotopic insights into provenance and cycling of carbon in Lake Superior. *Limnol. Oceanogr.* **2011**, *56*, 867–886.
- (51) Burkhard, L. P. Estimating dissolved organic carbon partition coefficients for nonionic organic chemicals. *Environ. Sci. Technol.* **2000**, *34*, 4663–4668.
- (52) Zeng, X.; Massey Simonich, S. L.; Robrock, K. R.; Korytár, P.; Alvarez-Cohen, L.; Barofsky, D. F. Development and validation of a congener-specific photodegradation model for polybrominated diphenyl ethers. *Environ. Toxicol. Chem.* **2008**, *27*, 2427–2435.