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

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1 **Concentrations, trends, and air-water exchange of PAHs and PBDEs**
2 **derived from passive samplers in Lake Superior in 2011**

3 Zoe Ruge¹, Derek Muir², Paul Helm³, Rainer Lohmann^{1*}

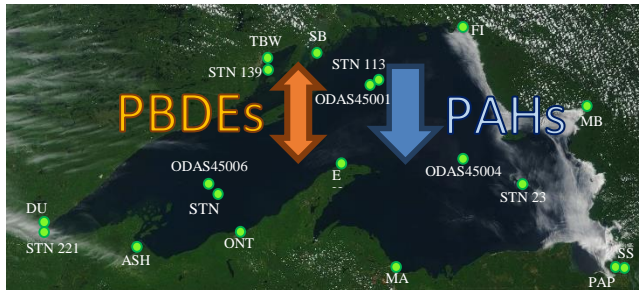
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13 **Graphical TOC**



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(TOC map from

17 [http://coastwatch.glerl.noaa.gov/modis/modis.php?region=s&page=4&template=sub&](http://coastwatch.glerl.noaa.gov/modis/modis.php?region=s&page=4&template=sub&image=t1.15206.1638.LakeSuperior.143.250m.jpg)
18 [image=t1.15206.1638.LakeSuperior.143.250m.jpg](http://coastwatch.glerl.noaa.gov/modis/modis.php?region=s&page=4&template=sub&image=t1.15206.1638.LakeSuperior.143.250m.jpg))

19

20 **Abstract**

21 Polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenylethers
22 (PBDEs) are both currently released into the environment from anthropogenic activity.
23 Both are hence primarily associated with populated or industrial areas, although
24 wildfires can be an important source of PAHs, as well. Polyethylene passive samplers
25 (PEs) were simultaneously deployed in surface water and near surface atmosphere to
26 determine spatial trends and air-water gaseous exchange of 21 PAHs and 11 PBDEs at
27 19 sites across Lake Superior in 2011. Surface water and atmospheric PAH
28 concentrations were greatest at urban sites (up to 65 ng L^{-1} and 140 ng m^{-3} , respectively,
29 averaged from June to October). Near populated regions, PAHs displayed net air-to-
30 water deposition, but were near equilibrium off-shore. Retene, probably depositing
31 following major wildfires in the region, dominated dissolved PAH concentrations at
32 most Lake Superior sites. Atmospheric and dissolved PBDEs were greatest near urban
33 and populated sites (up to 6.8 pg L^{-1} and 15 pg m^{-3} , respectively, averaged from June to
34 October), dominated by BDE-47. At most coastal sites, there was net gaseous deposition
35 of BDE-47, with less brominated congeners contributing to Sault Ste. Marie and eastern
36 open lake fluxes. Conversely, the central open lake and Eagle Harbor sites generally
37 displayed volatilization of PBDEs into the atmosphere, mainly BDE-47.

38

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42

43 **Introduction**

44 Polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenylethers
45 (PBDEs) are two classes of persistent organic pollutants (POPs) that have been
46 monitored in the Great Lakes' atmosphere over the past two decades as part of the
47 International Atmospheric Deposition Network (IADN) program.^{1,2,3} POPs are
48 resistant to natural degradation, bioaccumulate, elicit adverse effects on human health
49 and the environment, and undergo long-range transport.⁴ Another Great Lakes
50 program has monitored the time trends of POPs in lake trout across the Great Lakes.^{5,6}
51 The IADN program, with its single master station per Great Lake has been
52 instrumental in understanding time trends of airborne organic contaminants across the
53 Great Lakes region.

54 Yet, IADN has not been designed to understand spatial trends, nor was it
55 designed to determine the trends and cycling of organic pollutants in the waters of the
56 Great Lakes themselves. To be able to answer questions linked to air-water exchange
57 and loadings of POPs to the Great Lakes, spatially resolved air and water
58 measurements are required. The study described here is part of our effort to enhance
59 our understanding of POPs cycling by deploying passive samplers in air and water at
60 numerous sites around the Great Lakes, in this case Lake Superior. Samplers covered a
61 range of sites – urban, remote coastal and open-lake sites across Lake Superior to help
62 discern trends and fluxes.

63 Passive samplers integrate contaminant concentrations over time, representing
64 time-weighted averages over their accumulation period.^{7,8} In general, passive- and
65 active-sampler derived concentrations agree within a factor of two to three.^{8,9} When

66 using the same passive sampler, in our case polyethylene, in air and water, the
67 compound's air-water activity (or fugacity) gradient can be directly assessed.¹⁰

68 Of the known PAHs, seven are identified as probable human carcinogens.¹¹
69 PAHs are composed of two or more fused aromatic rings released as the result of
70 incomplete combustion of both anthropogenic (fossil fuels) and natural (biomass)
71 sources.^{12,13} They can also result from petrogenic releases (oil spills) and
72 volatilization from polluted soils.^{14,15} PAHs are actively emitted to the environment
73 through car exhaust, industrial activity, residential heating, and wildfires,¹⁶ leading to
74 a ubiquitous presence and continued atmospheric deposition across the Great Lakes.¹³

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

89 industrial applications and landfills,²⁴ suggesting continued release to the environment
90 and deposition into Lake Superior.

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

98

99 **Materials and Methods**

100 *Sampling Methodology*

101 Low density PE (2 mil) was cut into approximately 10x40 cm strips from
102 commercial sheeting (Berry Plastics Corporation, Evansville, IN) yielding passive
103 samplers ~2 g each. PEs were cleaned successively in dichloromethane and hexane
104 for 24 h each. PEs were spiked with performance reference compounds (PRCs) to
105 account for mass-transfer limitations during deployment. Deuterated PAHs
106 (naphthalene-d₈, pyrene-d₁₀), brominated biphenyls (dibromobiphenyl,
107 tetrabromobiphenyl, pentabromobiphenyl) and octachloronaphthalene (Ultra
108 Scientific, North Kingstown, RI, USA; Cambridge Isotopes, Andover, MA, USA)
109 were equilibrated with the PEs in 80:20 methanol:water on a shaker table for 4 weeks
110 based on the procedure reported by Booij et al. (2002).²⁵ PEs were woven onto
111 stainless steel wire and distributed to collaborators and volunteers. Air PEs were

112 deployed in inverted bowl stations at 11 coastal and three open-lake sites (see TOC).
113 Surface water PEs (unprotected) were deployed in tandem with the coastal air
114 samplers, as well as at three open-lake sites (slightly offset from air deployments) and
115 two additional coastal sites (in-cage deployments, see SI for details). Samples were
116 collected in three deployment periods to evaluate temporal trends: April-June, June-
117 August, and August-October 2011 (Table SI 3). Duplicate air samples and triplicate
118 water samplers were deployed at two sites during each deployment. Field blanks were
119 taken from 2-3 sites per deployment period. After retrieval, samplers were wrapped in
120 foil, shipped to the lab and stored at 4°C until analysis.

121

122 *Analytical Methodology*

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

131

132 *Quality Assurance/Quality Control*

133 PE matrix spikes were prepared in each batch of approximately 20 samples.
134 Analyte concentrations were recovery corrected. Average surrogate recoveries for

135 PAHs were generally >50- 60% and spiked matrix recoveries of unlabeled PAHs were
136 typically around 100% (Table SI 9). Average surrogate recoveries for PBDEs ranged
137 from 80-150% and spiked matrix recoveries were typically 80-90% (Table SI 18).
138 Method blanks were prepared with each batch of samples to monitor for laboratory
139 contamination. Method blanks ranged from 280 – 3,400 pg/g PE for PAHs and bd –
140 140 pg/g PE for PBDEs (see SI for details). Samples were blank-corrected by
141 subtracting the average of the method and field blank concentrations. Only
142 concentrations greater than three times the standard deviation of the average blank
143 values are reported (Table SI 8, Table SI 17). Standard checks were analyzed every
144 ten samples to monitor instrument performance.

145

146 *Calculations/Data Analysis*

147 At each site, 21 PAHs and 11 PBDEs were determined (for details, see SI page
148 6). Truly dissolved concentrations of POPs in water, C_w (pg L⁻¹), were calculated as ²⁶:

$$149 \quad C_w = C_{PEW}/K_{PEW} \quad (1)$$

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

$$154 \quad K_{PEW(T)} = K_{PEW(298K)} * e^{-(\Delta H_{vap}/R)*[(1/298K)-(1/T)]} \quad (2)$$

155 where ΔH_{vap} is the enthalpy of vaporization (kJ mol⁻¹) (Table SI 5, Table SI 14), R is
156 the gas constant (kJ/K*mol) and T is the average water temperature during
157 deployment (Kelvin) (Table SI 4). Gas-phase atmospheric POP concentration, C_A ,

158 was determined with the same calculations, substituting the air-PE partitioning
159 coefficient, K_{PEA} , for K_{PEW} .

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

$$163 \quad \% \text{ equilibrium} = 1 - e^{-(R_s * t) / (V * K_{PE})} \quad (3)$$

164 where

165 R_s is the (fitted) sampling rate ($L \text{ day}^{-1}$),

166 t is the sampling time (days), and

167 V is the PE volume (L).

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

171 The direction of air-water exchange is determined by the ratio of the
172 equilibrium concentration of the POP in air (C_{PEa} , $ng \text{ m}^{-3}$) to the equilibrium
173 concentrations of the POP in water (C_{PEw} , $ng \text{ L}^{-1}$), where a ratio >1 indicates
174 atmospheric deposition and a ratio <1 indicates volatilization from the water to the air.
175 Net air-water fluxes ($ng \text{ m}^{-2} \text{ day}^{-1}$) were calculated by modifying the equation²⁸ Flux =
176 $k_{ol} * (C_w - C_a / K_{AW})$ to

$$177 \quad \text{Flux} = k_{ol} * [(C_{PEw} - C_{PEa} / 10^3) / K_{PEW}] \quad (4)$$

178 where k_{ol} is mass transfer coefficient ($m \text{ day}^{-1}$) (see SI page 7) and K_{PEW} is the POP's
179 temperature-corrected PE-water partitioning coefficient ($L \text{ kg}^{-1}$). Equation (4) derives

180 air-water exchange gradients without needing to rely on Henry's Law Constants,
181 which are arguably the least constrained physico-chemical constants.^{10,29}

182

183 **Results and Discussion**

184 *Polycyclic Aromatic Hydrocarbons (PAHs)*

185 **Spatial Distributions in Air:** Averaged Σ_{21} PAH gas-phase concentrations
186 (June – October) ranged from <1 to >100 ng m⁻³ (Figure 1A, Table SI 10).

187 Concentrations were always greatest at Sault Ste. Marie, (June-October mean 140 ng
188 m⁻³), and lowest at Eagle Harbor, MI (June-August 0.054 ng m⁻³) and the open lake
189 sites (mean 0.13-0.95 ng m⁻³) (Table 1). An urban-rural gradient, as observed in this
190 study, can occur due to particle scavenging near urban sources, precipitation
191 scrubbing, and OH radical degradation.^{30,31} PAHs tend to have a strong urban
192 signature from vehicle emissions, power generation plants, and industrial
193 activity.^{31,32,33} At some locations, atmospheric concentrations increased with
194 increasing temperature; yet mostly the changes were within the overall uncertainty of
195 the passive sampling (factor of 2; see Table SI 4 and Table SI 10). Atmospheric
196 concentrations of semi-volatile compounds generally have a seasonal component due
197 to the effect of ambient temperature on the direction of pollutant transfer across the
198 air-water interface.³⁴ It has been suggested, however, that atmospheric PAH
199 concentrations are a function of emissions source rather than temperature³⁵, in-line
200 with the results presented here.

201 A previous sediment study measured the greatest PAH concentrations near
202 Lake Superior's second largest city, Duluth, MN,¹² however, the study did not include

203 Sault Ste. Marie. Although not the largest city along the Lake Superior shoreline,
204 Sault Ste. Marie is located on the Soo Locks, which sees >70,000,000 net tons of
205 cargo annually.³⁶ Shipping traffic may significantly contribute to local PAH
206 concentrations, though there is also a steel mill burning coal in Sault Ste. Marie,
207 Canada, 3 km northwest of our sampling site. Atmospheric PAH concentrations at
208 Sault Ste. Marie were dominated by the more volatile two- and three-ring compounds,
209 including phenanthrene (57 ng m⁻³), acenaphthene (24 ng m⁻³), fluorene (21 ng m⁻³),
210 fluoranthene (17 ng m⁻³), methyl phenanthrenes (8.3 ng m⁻³), plus the four-ringed
211 pyrene (7.1 ng m⁻³). These compounds are emitted from gasoline engines, coal
212 combustion, and coke ovens.³¹ At the nearby Pointe Aux Pins sites, atmospheric
213 concentrations were much smaller (see Table SI 10), pointing towards urban and
214 industrial activities as major sources of PAHs .

215 The second greatest atmospheric PAH concentrations were at Ashland, WI
216 (June-October average 29 ng m⁻³), a major industrial port with a history of iron ore
217 processing, manufactured natural gas from coal, and lumber mills. It is now
218 designated as a U.S. EPA Superfund site polluted with benz(a)anthracene and
219 benzo(a)pyrene (Figure SI 1, Table SI 2).³⁷ Our samplers were deployed near the Soo
220 Line Ore dock, a now unused jetty originally serving ships and trains with iron ore.
221 Acenaphthene (13 ng m⁻³), phenanthrene (6.0 ng m⁻³), fluorene (5.2 ng m⁻³), and
222 fluoranthene (1.6 ng m⁻³) contributed to Ashland PAH concentrations. Retene, a PAH
223 resulting from biomass burning and the decomposition of conifer trees, was also
224 significantly present (ca. 4% of Σ_{21} PAHs, 1.1 ng m⁻³). Retene is associated with wood

225 varnish and lumber treatment,³² therefore, the lumber industry in Ashland could be
226 contributing to the retene signal in that region.

227 Atmospheric PAH concentrations at other urban locations, while a tenth and a
228 third, or less, of those at Sault Ste. Marie and Ashland, respectfully, were still ca. two-
229 to ten-times greater than rural coastal sites, and several times the open-water air
230 concentrations. Duluth had a lower atmospheric PAH concentrations (June-October
231 average 12 ng m⁻³) than Sault Ste. Marie and Ashland despite being an urban center
232 and possible emissions linked to shipping traffic in the Duluth/Superior harbor, the
233 busiest port in the Great Lakes system.³⁸ This may be because the PE was deployed at
234 the regional EPA office northeast (upwind) of the city center. Following Duluth at
235 slightly lower PAH concentrations were Marquette (June-August average 10 ng m⁻³)
236 and Thunder Bay/Welcome Isle (June-October average 5.4 ng m⁻³). The sampler at
237 Thunder Bay was also several km removed from the city center. Concentrations were
238 characterized by many of the same petroleum- and biomass-derived PAHs measured at
239 shipping sites: phenanthrene, methyl phenanthrenes, fluoranthene, and pyrene.
240 Thunder Bay and Duluth have relatively modest populations (110,000 and 100,000
241 people, respectively), and these samples demonstrate the effect even small cities have
242 on local atmospheric PAH concentrations.

243 Eagle Harbor, MI atmospheric PAH concentrations were below the detection
244 limit for April-June and <0.1 ng m⁻³ for June-August; August-October data were not
245 available, however, temporal trends for other sites suggest atmospheric concentrations
246 may have been greater during the late summer. The IADN master station for Lake
247 Superior is located at Eagle Harbor and has been collecting high volume air samples

248 of PAHs since 1990.³² The site is used as the background atmosphere standard for
249 Lake Superior and the entire Great Lakes region.³⁵ Typical annual IADN gas+particle
250 PAH concentrations are ca. 1 ng m⁻³ (monthly averages were not available for
251 comparison).^{35,16} Gas-phase PAHs concentrations measured in this study may be
252 lower than IADN values due to differences in sampling procedure and the sampling
253 period. PEs were deployed from April to October, when PAH emissions are lowest.
254 IADN samplers collect air samples throughout the entire year and results are reported
255 as annual means, including the winter months when residential heating causes a spike
256 in PAH emissions.^{32,39} IADN relies on active sampling using a glass fiber filter
257 coupled with XAD/PUF for sampling gas-phase compounds, whereas PEs only
258 sample the truly gas phase fraction of atmospheric PAHs. A recent comparison
259 between PUF- and passive sampler-collected gas-phase PAHs implied good agreement
260 between both methods.¹⁵

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

267 **Spatial Distributions in Water:** PAH concentrations in the water followed
268 similar spatial patterns as the atmospheric PAH distributions (Figure 1B, Table SI 11).
269 Seasonally averaged Σ_{21} PAH concentrations in Lake Superior were greatest at Sault
270 Ste. Marie (June-October 65 ng L⁻¹), followed by Ashland (26 ng L⁻¹). Concentrations

271 at Sault Ste. Marie were dominated by phenanthrene, fluoranthene and pyrene (all
272 $>10 \text{ ng L}^{-1}$). Methyl phenanthrenes, pyrene, phenanthrene, and fluoranthene also
273 contributed to Ashland concentrations ($3\text{-}5 \text{ ng L}^{-1}$, respectively), however the greatest
274 PAH present was retene (7.5 ng L^{-1}), possibly due to biomass burning and the
275 degradation of wood from lumber production and treatment. Retene also accounted
276 for ca. 35-60% of the dissolved PAHs at Foster Island, Sturgeon Bay, and Station 139
277 and ca. 40-70% at the open-water sites. Methyl phenanthrenes were typically $>1 \text{ ng L}^{-1}$,
278 reaching $>5.0 \text{ ng L}^{-1}$ at Sault Ste. Marie, Sturgeon Bay, Ashland, and Michipicoten
279 Bay, as well as accounting for 60% of the dissolved PAHs at Foster Island.
280 Concentrations of dissolved PAHs were lower than expected at Station 221 ($\Sigma_{21}\text{PAH}$
281 4.8 ng L^{-1}), east of Duluth, however, the sampler was deployed approximately 3 km
282 offshore and may not have received a direct urban signal. At coastal sites, dissolved
283 $\Sigma_{21}\text{PAH}$ water concentrations changed significantly between deployments, but without
284 a clear trend. Dissolved concentrations at Ashland and Michipicoten Bay increased
285 from June-August to August-October (8.0 to 28 and 2.8 to 12 ng L^{-1} , respectively), but
286 decreased at Duluth from June-October (7.3 to 0.58 ng L^{-1}).

287 **Dissolved retene:** Although PAH concentrations near urban, industrial, and
288 shipping centers were generally characterized by fossil fuel emissions, total dissolved
289 concentrations of PAHs across most sites were dominated by retene. It is the
290 combustion byproduct of abietic acid, a natural product mainly found in coniferous
291 trees.^{32,40} Retene can be produced in urban areas from municipal waste incinerators,
292 tire burning, and incineration of building waste; however, it is primarily emitted by
293 burning wood.⁴¹ Rural households consume about three times more wood than urban

294 homes.³² It is therefore not surprising that retene accounts for ca. 20-60% of the total
295 PAHs at the northern coastal sites and ca. 40-70% of total PAHs present in open lake
296 waters. Atmospheric retene concentrations typically peak in the winter months when
297 wood is burned for residential heating, but lower-magnitude spikes can occur between
298 April and September due to naturally occurring wildfires.³²

299 Several sites exhibited elevated retene concentrations in both air and water
300 during deployment 3 (August-October) relative to deployment 2 (June-August)
301 (Figure 2). Dissolved retene increased strongly at Sturgeon Bay (from 0.92 to 26 ng
302 L⁻¹), station 113 (0.13 to 8.3 ng L⁻¹), and Station 139 (0.92 to 6.9 ng L⁻¹). Because PE
303 sampling was limited to one season, we cannot confirm whether these trends occur in
304 annual cycles or are due to unique events. However, sites with the greatest retene
305 concentrations (Sturgeon Bay and Station 113) were northern and central lake
306 locations, which probably received enhanced retene inputs following elevated forest
307 fire intensity from July – September 2011 northwest of the Lake (see Figure SI 3).⁴²
308 Retene could also enter the Lake's water through tributaries, but Sturgeon Bay and
309 Station 113 were not close to river plumes.

310 **Comparison to active sampling:** Venier et al. (2014)⁴³ reported apparently
311 dissolved water concentrations of various POPs, including PAHs across the Great
312 Lakes using active GFF - XAD sampling in 2011/12. For the open Lake Superior,
313 apparently-dissolved PAH concentrations were, on average, dominated by
314 fluoranthene (310 pg L⁻¹), followed by pyrene (140 pg L⁻¹), benz(a)anthracene (100 pg
315 L⁻¹) and retene (50 pg L⁻¹). These concentrations were much lower than what we
316 determined here. Venier et al. (2014) collected samples during the spring season,

340 a higher activity in the air, and therefore, net deposition, while a ratio <0.14 resulted in
341 net volatilization.

342 Net air-water exchange of gas-phase PAHs was generally into the lake near
343 populated or industrialized (point) sources, however fluxes were low at most sites
344 ($<1,000 \text{ ng m}^{-2} \text{ d}^{-1}$) (Table SI 12). Sault Ste. Marie displayed the greatest fluxes for
345 several of the PAHs (Figure 3A, Table SI 13). At this site average deposition was
346 dominated by six PAHs: fluorene, phenanthrene, methyl phenanthrenes, fluoranthene,
347 and pyrene; however, only phenanthrene ($6,900 \text{ ng m}^{-2} \text{ d}^{-1}$) and fluoranthene ($2,700 \text{ ng}$
348 $\text{m}^{-2} \text{ d}^{-1}$) underwent net deposition significantly different ($P < 0.05$) from equilibrium as
349 defined above. Retene was deposited at most sites, with notable exceptions at the
350 central open lake site and Sturgeon Bay, where retene concentrations in the water were
351 exceptionally high; air-water exchange was near equilibrium from August-October. As
352 previously discussed, retene inputs may have been elevated due to high wildfire
353 activity in the region that season, resulting in net volatilization of retene into the
354 atmosphere at the central open lake and Sturgeon Bay. This volatilization was in
355 contrast to the eastern and western open lake sites where retene was being deposited.

356
357 *Polybrominated Diphenylethers (PBDEs)*

358 **Spatial Distributions:** Σ_{11} BDE concentrations in air were more than three
359 orders of magnitude lower than PAHs across Lake Superior (Figure 4A, Table SI 19).
360 BDE-47 was generally the most abundant congener present (approximately 20 to 60%
361 in air and 40-75% in water samples) throughout the sampling period, followed by
362 BDE-28, 49, 99, and 100. BDE-153 concentrations were low or below detection at all
363 most sites and BDE-154 was not detected in any samples. Changes in atmospheric and

364 aqueous PBDE concentrations between deployments at a given site were smaller than
365 variations among sites. In other words, the proximity to emission sources was more
366 important than geochemical variations (currents, winds, temperature).

367 Atmospheric PBDE concentrations were greatest at Marquette (June-October
368 average 15 pg m^{-3}) (Table 2). This station is located at a dock for a coal-fired power
369 plant and in proximity to a number of sites registered with the EPA Toxic Release
370 Inventory, including facilities that manufacture polyurethane and explosives,⁴⁸ where
371 PBDEs might have been used in the past. Sault Ste. Marie and Duluth also had
372 elevated atmospheric PBDE concentrations from June-October, 7.4 and 5.7 pg m^{-3} ,
373 respectively. Atmospheric concentrations at nearly all other sites were $<1 \text{ pg m}^{-3}$. The
374 eastern open lake site (ODAS45004) exhibited concentrations >10 times higher than
375 the other open lake sites, perhaps receiving input downwind from Marquette.

376 Water concentrations had similar spatial distributions as air concentrations
377 (Figure 4B, Table SI 20). Concentrations were greatest at Marquette (June-August
378 average 6.8 pg L^{-1}), followed by Thunder Bay/Welcome Island, Pointe Aux Pins, and
379 Sault Ste. Marie (June-October average 2.1 , 1.8 , and 1.7 pg L^{-1} , respectively).
380 Dissolved PBDE concentrations were lowest at rural Canadian sites: Sturgeon Bay
381 (0.20 pg L^{-1}), Foster Island (0.21 pg L^{-1}), and Michipicoten Bay (0.46 pg/L). Eastern
382 and western open lake sites exhibited PBDE concentrations similar to coastal rural
383 sites (0.46 and 0.24 pg L^{-1} , respectively), with the exception of Eagle Harbor (0.97 pg
384 L^{-1}). Average central open lake PBDE concentrations were slightly higher than the
385 other open lake sites (0.86 pg L^{-1}), similar to Station 139 (0.75 pg L^{-1}) near Thunder
386 Bay/Welcome Isle.

387 **Comparison to active sampling:** Ma et al. (2013) reported average gas-phase
388 concentrations of PBDEs in Great Lakes air samples from IADN sites covering 2003-
389 2011.⁴⁹ For Eagle Harbor, concentrations were reported as 2-3 pg m⁻³ for BDEs 47
390 and 99, which dominated total PBDEs. Our 2011 gas-phase concentrations displayed
391 lower concentrations, though dominated by similar congeners. There is evidence that
392 PBDE concentrations have begun decreasing across the Great Lakes.¹⁷ In general,
393 active and passive results for gas-phase air sampling yield fairly similar results.¹⁵

394 Venier et al. (2014) also reported dissolved PBDE concentrations (water
395 filtered thru glass fiber cartridges removing >90% of particles >0.5 µm) for several
396 sites across Lake Superior in the pg L⁻¹ range.⁴³ On average, BDE-47 dominated at 6
397 pg L⁻¹, followed to BDEs 100 and 153 (~ 1 pg L⁻¹) and BDE-28 (0.5 pg L⁻¹). These
398 concentrations were between 10-fold (BDEs 28 and 47) and 100-fold (BDEs 100 and
399 153) greater than what was measured in this study. Such discrepancy has often been
400 attributed to the inadvertent sampling of dissolved organic carbon (DOC)-bound
401 compounds by active sampling approaches. DOC concentrations of around 1.2 mg L⁻¹
402 have been reported for the open Lake Superior.⁵⁰ A typical affinity of PBDEs to DOC
403 is one tenth of their octanol-water partitioning coefficients.⁵¹ Yet this DOC-correction
404 was not sufficient to eliminate the discrepancy between active and passive sampling
405 (on average, concentrations reported by Venier et al. (2014) were still greater than our
406 passive sampler-derived concentrations by 10 – 80 –fold.⁴³ As sampling was
407 conducted at different times, different locations and different laboratories, perfect
408 agreement cannot be expected. Yet the strong discrepancy suggests that dissolved
409 PBDE concentrations display some temporal dynamics (which might have led to

410 elevated active sampling results), and the efficient retention of PBDEs associated with
411 DOC and possibly small particles by active sampling.

412 **PBDE Air-Water Exchange:** Air-water exchange ratios varied greatly
413 between sites and for PBDE congeners (Table SI 21). Where present, BDE-2,8,15,
414 and 30 were deposited, possibly from photodegradation.⁵² Eagle Harbor and open
415 lake site ratios suggested mainly net volatilization for tetra and penta BDEs, as well as
416 BDE-28. By and large, BDE-47 underwent net deposition during the first two
417 deployments. Exceptions were the open lake sites where BDE-47 volatilized, and
418 some coastal sites during August-October.

419 PBDEs were deposited into Lake Superior at half of the coastal sites as
420 indicated by significant air-to-water ratios. The greatest net gas-phase deposition
421 fluxes during June-August were at Sault Ste. Marie (-2,700 pg m⁻² d⁻¹), Duluth (-770
422 pg m⁻² d⁻¹), and Ontonagon (-140 pg m⁻² d⁻¹) (Figure 3B, Table SI 22). During
423 August-October, overall net fluxes were lower, with the greatest fluxes at the central
424 open water site (120 pg m⁻² d⁻¹) and the eastern open lake site (-180 pg m⁻² d⁻¹).

425 Gaseous deposition fluxes were primarily composed of BDE-47 with less
426 brominated congeners contributing to Sault Ste. Marie and eastern open lake fluxes.
427 Conversely, the central open lake and Eagle Harbor sites generally displayed
428 volatilization of PBDEs into the atmosphere, mainly BDE-47. Interestingly, the
429 eastern open lake site (Station 23) exhibited strong deposition of di- and
430 tribromodiphenyl ethers (170 and 44 pg m⁻² day, respectively) from August-October,
431 perhaps indicating an upwind source during that time period.

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

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

454

455 **Implications**

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

472

473 **Supporting Information Available**

474 Additional information on sampling locations, physicochemical constants, sampling
475 rates, QA/QC, analysis, calculations and concentrations of PAHs and PBDEs and their
476 air-water exchange available free of charge via the Internet at <http://pubs.acs.org/>.

477

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490

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- 642

643 **Tables and Figures**644 **Table 1:** Σ_{21} PAH concentrations in air (ng m^{-3}) and water (ng L^{-1}) by deployment period

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		4.5	6.4	5.4		6.0	5.9	6.0
Welcome Isle						4.0	11	7.6
Station 139						8.7	0.95	4.8
Duluth/Station 221	2.3	11	13	12		9.4	N/A	N/A
Marquette	3.5	10	N/A	N/A	10	3.4	4.1	3.7
Ontonagon		0.71	4.7	2.7		3.2	13	8.0
Michipicoten Bay		0.15	1.2	0.69		3.8	39	22
Sturgeon Bay		0.61	2.2	1.4		2.4	6.0	4.2
Foster Island		0.99	0.79	0.89		0.0041	0.34	0.17
Eagle Harbor	bd	0.054	N/A	N/A		0.93	4.2	2.6
Eastern Open Lake		bd	1.9	0.95		1.6	11	6.3
Central Open Lake		bd	0.26	0.13		0.52	1.5	1.0
Western Open Lake		0.0014	0.35	0.17				

645 Σ_{21} PAH = sum of biphenyl, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, methyl phenanthrenes, fluoranthene, pyrene, retene, benz(a)anthracene, chrysene, benzo(b)fluoranthene,
646 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
647 bd = below detection limit of GC/MS
648 N/A = not available due to lost polyethylene samplers

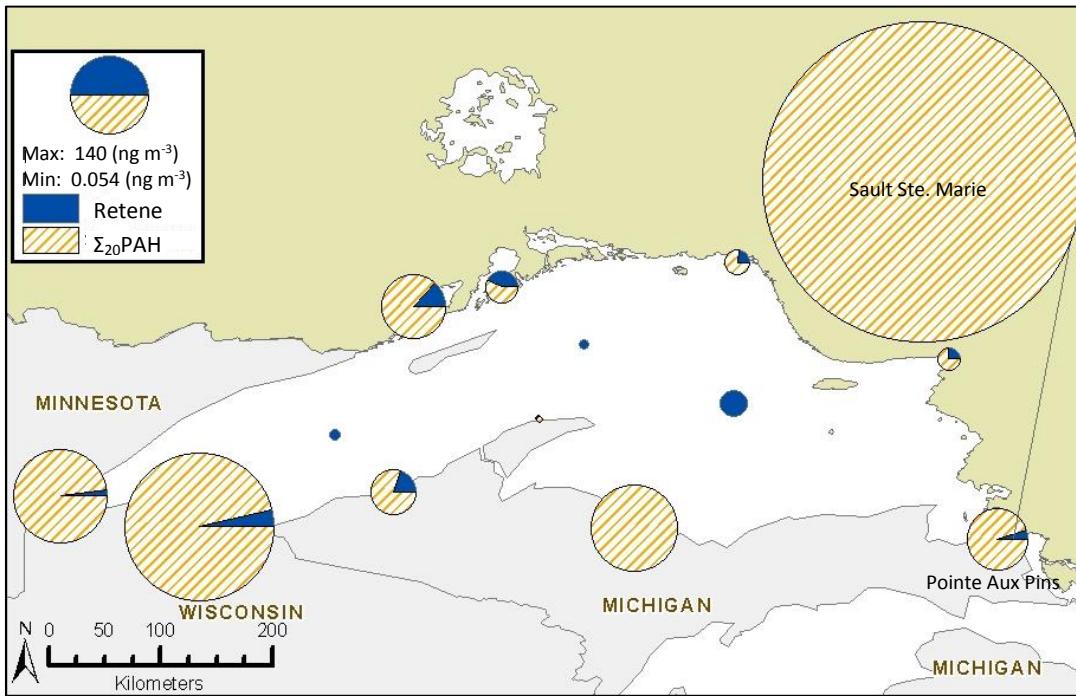
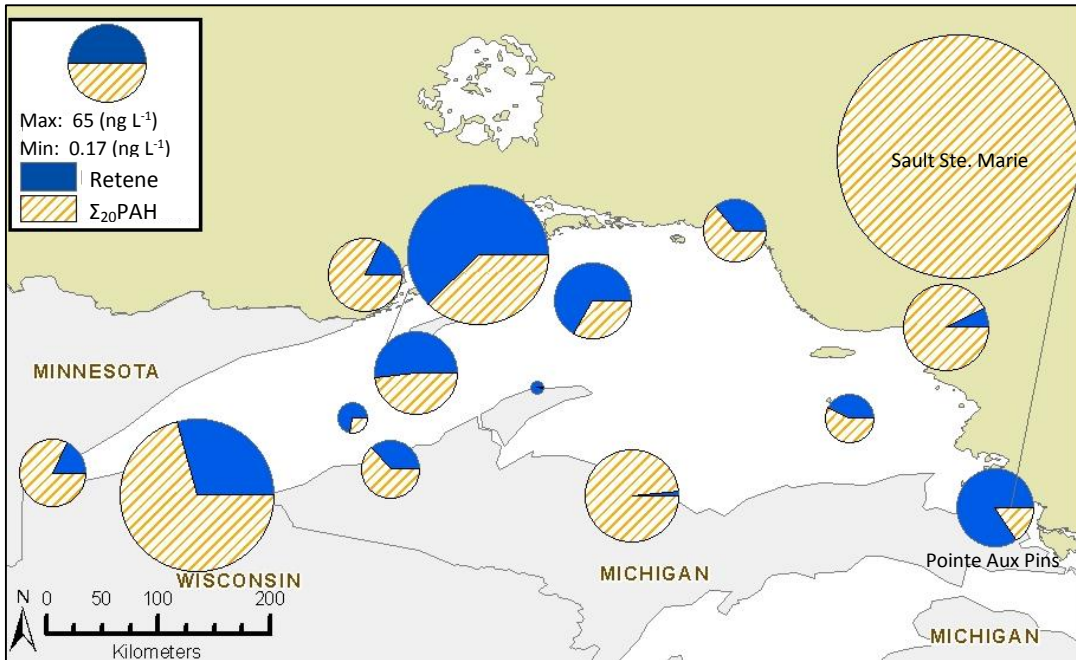
A**B**

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.

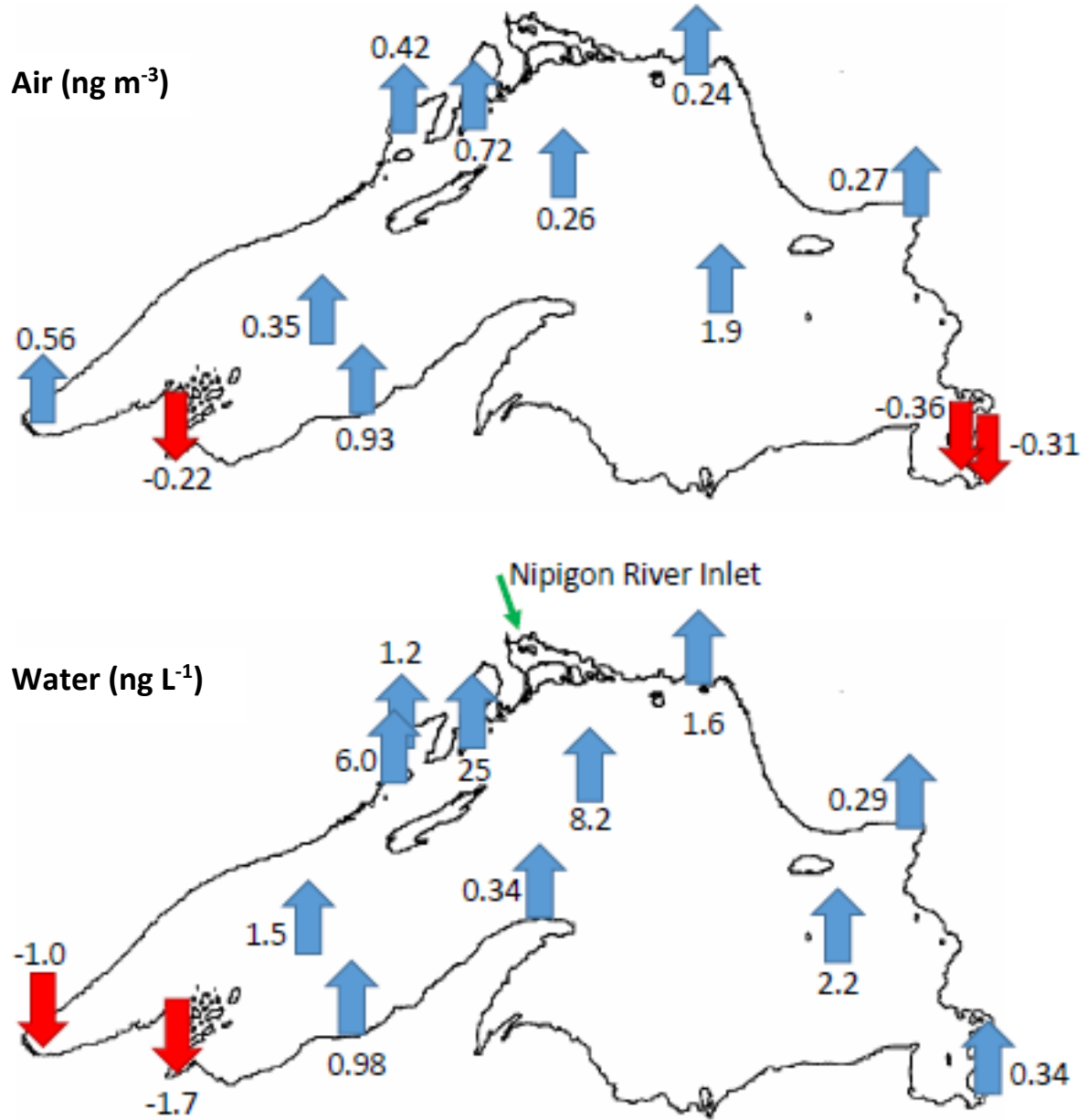


Figure 2: Changes in retene concentration (Δ) between June-August and August-October 2011.

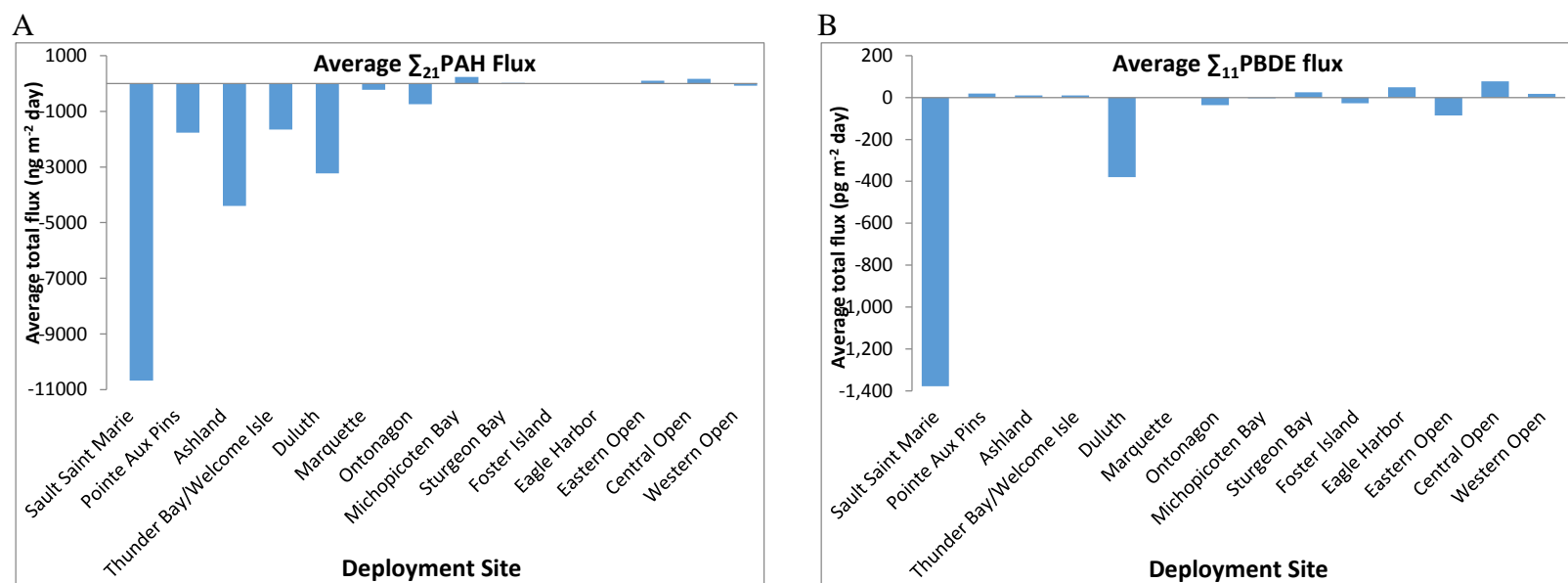


Figure 3: (a) PAH and **(b)** PBDE fluxes (Σ_{21} PAHs as per Table 1, Σ_{11} PBDE as per Table 2) across the air-water interface of Lake Superior. Positive values indicate volatilization from the surface water, while negative values indicate atmospheric deposition. Only values from significant C_{PEa}/C_{PEw} 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.

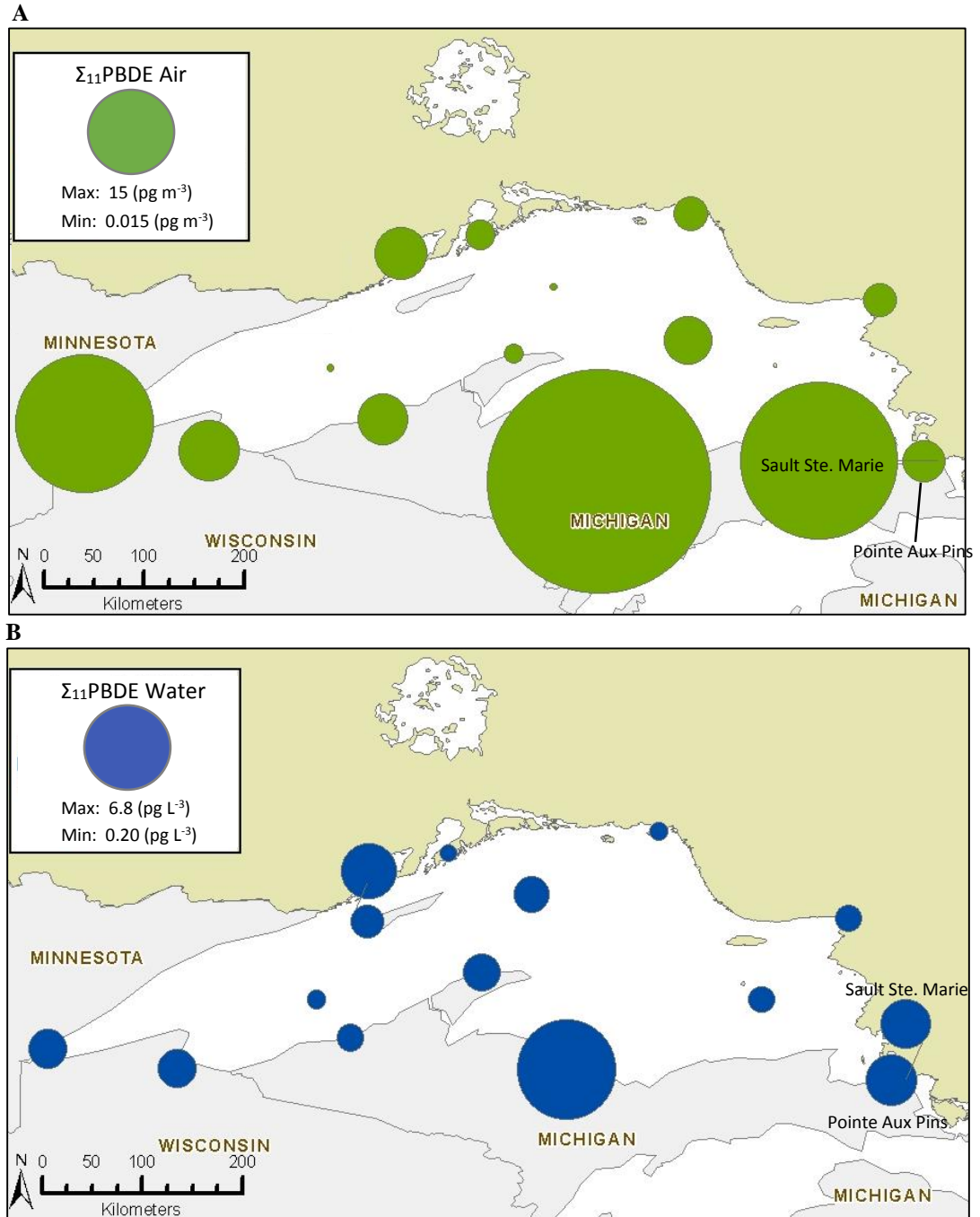


Figure 4: Average $\Sigma_{11}\text{PBDE}$ (as defined by Table 2) concentrations at each station. (A) Air concentrations (pg m^{-3}) are averaged from June to October 2011. (B) Water concentrations (pg L^{-1}) are averaged from June to October 2011 for all stations except Marquette, which represents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

Table 2: Σ_{11} PBDE concentrations in air ($\mu\text{g m}^{-3}$) and water ($\mu\text{g L}^{-1}$) by deployment period

Site	Air ($\mu\text{g m}^{-3}$)				Water ($\mu\text{g L}^{-1}$)			
	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

Σ_{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