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1 Spatial Distribution and Air-Water Exchange of Organic Flame

2 Retardants in the Lower Great Lakes

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14 **ABSTRACT**

15 Organic flame retardants (OFRs) such as polybrominated diphenyl ethers (PBDEs) and novel halogenated flame retardants
16 (NHFRs) are ubiquitous, persistent, and bioaccumulative contaminants that have been used in consumer goods to slow combustion. In
17 this study, polyethylene passive samplers (PEs) were deployed throughout the lower Great Lakes (Lake Erie and Lake Ontario) to
18 measure OFRs in air and water, calculate air-water exchange fluxes, and investigate spatial trends. Dissolved Σ_{12} BDE was greatest in
19 Lake Ontario near Toronto (18 pg/L), while gaseous Σ_{12} BDE was greatest on the southern shoreline of Lake Erie (11 pg/m³). NHFRs
20 were generally below detection limits. Air-water exchange was dominated by absorption of BDEs 47 and 99, ranging from -964
21 pg/m²/day to -30 pg/m²/day. Σ_{12} BDE in air and water was significantly correlated with surrounding population density, suggesting
22 that phased-out PBDEs continued to be emitted from population centers along the Great Lakes shoreline in 2012. Correlation with
23 dissolved Σ_{12} BDE was strongest when considering population within 25 km, while correlation with gaseous Σ_{12} BDE was strongest
24 when using population within 3 km to the south of each site. Bayesian kriging was used to predict dissolved Σ_{12} BDE over the lakes,
25 illustrating the utility of relatively highly spatially resolved measurements in identifying potential hot spots for future study.

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30 **INTRODUCTION**

31 Organic flame retardants (OFRs) such as the polybrominated diphenyl ethers (PBDEs) and novel halogenated flame retardants
32 (NHFRs) are persistent bioaccumulative contaminants that have been liberally added to polymers used in consumer goods to slow
33 combustion in the event of a fire.^{1,2} While PBDEs are no longer manufactured or used in North America, they are ubiquitous in the
34 environment and continually leach out of in-use products, especially furniture, casings for electronics, and automotive upholstery.³
35 Numerous studies have shown that PBDEs, as well as many NHFRs, accumulate in humans⁴⁻⁶ and wildlife,⁷⁻¹¹ and that concentrations
36 are elevated in North American cities.¹²⁻¹⁴ Some studies have suggested that various NHFRs are increasingly being added to
37 consumer products due to the PBDE phase-out, but there is uncertainty regarding which chemicals are being used in which
38 applications, and at what production volumes.^{2,14-16}

39 Previous studies have identified densely populated areas, central business districts, and indoor environments as sources of
40 OFRs to the atmosphere via volatilization from consumer goods.^{13,14,17,18} Atmospheric wet and dry deposition have been identified as
41 important pathways for these contaminants to reach the Great Lakes,^{19,20} though recent work has shown inputs from storm water,

42 tributaries, and wastewater also play a significant role.^{21,22} Some studies have identified absorption of gaseous PBDEs from air as a
43 potentially significant source of some PBDEs to the Great Lakes,^{23,24} though others have demonstrated that volatilization from surface
44 water can be a significant loss process for semi-volatile organic compounds, especially as atmospheric concentrations decline
45 following changes in regulation.^{25,26} The direction of air-water diffusive exchange for OFRs can be deduced by simultaneous
46 measurement of dissolved and gaseous concentrations, which has not been undertaken previously in the lower Great Lakes (Lake Erie
47 and Lake Ontario).

48 While some recent studies have measured concentrations of PBDEs and NHFRs in air,^{14,18,27,28} rain,¹⁹ and surface water²⁹ of
49 the lower Great Lakes, there are no published studies of regional spatial trends, nor are there reported measurements of air-water
50 exchange fluxes. This information is critical to track whether changes in regulation and usage of OFRs lead to future changes in
51 spatial distributions and air-water exchange. Deployment of polyethylene passive samplers (PEs) in air and water is a convenient way
52 to deduce fugacity ratios at the air-water interface and a cost-effective approach to time-averaged monitoring at numerous sites. PEs
53 have been used to measure PBDEs in a handful of previous studies,^{24,30-32} but their use to detect NHFRs has not been previously
54 reported.

55 In this study, extracts from PEs deployed in the air and water throughout Lake Erie and Lake Ontario were analyzed for twelve
56 PBDEs and nine NHFRs to (i) determine baseline concentrations of PBDEs and NHFRs at a variety of shoreline, nearshore, and
57 offshore sites, (ii) determine whether the lower Great Lakes were acting as sinks or secondary sources of PBDEs via air-water

58 exchange, (iii) investigate spatial trends of PBDEs and their relation to population centers, and (iv) build a geostatistical interpolation
59 model to provide estimates of dissolved PBDE concentrations across the lakes.

60

61 **METHODS**

62 **Sampler Preparation and Deployment.** Air and water PEs were deployed throughout the lower Great Lakes region from April to
63 November of 2012. Air concentrations were monitored at 22 locations (14 shoreline sites, 5 nearshore sites (<5 km from the
64 shoreline), and 3 offshore sites), while water concentrations were monitored at 20 locations (8 shoreline sites, 7 nearshore sites, and 5
65 offshore sites). Air samplers were also deployed during the 2011/2012 winter (generally from October 2011 to April 2012).
66 Deployment time ranged from 4-30 weeks. The sampling schedule, locations, and site characteristics are summarized in the
67 Supporting Information (SI) along with the length of deployment time at each site (Table S1). Nearby meteorological buoys used to
68 determine average temperature and wind speed during deployments are listed in Table S2.

69 Details of sampler preparation and deployment have been summarized previously in McDonough et al. and Liu et al.^{33,34}
70 Briefly, 50 µm-thick PEs were pre-cleaned with solvent and loaded with performance reference compounds (PRCs), which included
71 deuterated polycyclic aromatic hydrocarbons (PAHs; naphthalene-*d8*, pyrene-*d12*, and benzo(a)pyrene-*d12*) and bromobiphenyls
72 (PBB 9, PBB52, and PBB 103). Shoreline air PEs were secured within protective chambers constructed from two metal bowls and
73 hung from trees or structures, generally at about 1.5 meters height. Shoreline water PEs were fastened to rope and anchored about 1

74 meter below the water's surface. Nearshore/offshore air PEs were fastened into protective chambers secured to buoys about 2 meters
75 above the water's surface, and water PEs were placed in perforated stainless steel cages and secured to subsurface floats at a depth of
76 about 4 meters. After PEs were recovered, they were mailed back to the laboratory overnight on ice and frozen until extraction.

77 **Extraction and Analysis.** PEs from 56 air and 39 aqueous deployments were spiked with non-native PBDEs (BDE 35, BDE 77,
78 BDE 118, BDE 128, and BDE 190) and extracted for about 24 hours in pentane, then concentrated to ~50 μ L and spiked with
79 injection standard (BDE 71). Water extracts were passed through silica gel/sodium sulfate cleanup columns and eluted with 60:40
80 pentane:DCM. Concentrations were corrected for internal standard recoveries.

81 Extracts were analyzed for twelve mono- to octa-brominated PBDE congeners (BDE 2, 8, 15, 30, 28, 47, 49, 100, 99, 154, 153,
82 and 183) and nine NHFRs (tetrabromo-p-xylene (pTBX), pentabromobenzene (PBBz), pentabromotoluene (PBT),
83 pentabromoethylbenzene (PBEB), hexabromobenzene (HBBz), hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO), 1,2-
84 bis(2,4,6-tribromophenoxy)ethane (BTBPE), and *anti*- and *syn*-isomers of Dechlorane Plus (ADP and SDP)) on an Agilent 6890N gas
85 chromatograph coupled to a Waters Quattro Micro mass spectrometer (GC-MS/MS) in electron ionization mode (EI, 70 eV) using
86 multiple reaction monitoring (MRM). Extracts were injected in splitless mode with helium carrier gas at 2 mL/min onto an Agilent
87 J&W DB-5MS fused silica capillary column (30 m x 0.25 mm I.D.).

88 **Quality Control.** Every batch of PEs was extracted alongside a method blank and two spiked blanks to control for compound losses
89 during extraction, concentration, and clean-up steps. Average spike recoveries ranged from 67 \pm 15% for BDE 2 to 101 \pm 19% for BDE

90 100 (Table S3). Concentrations were blank-subtracted using the most relevant field blank and detection limits were defined as the
91 upper limit of the 95% confidence interval for 11 laboratory blanks.

92 Detection limits per gram PE are summarized in Table S4, and are converted to typical ambient air or water concentrations in
93 Table S5. Percent detection for each compound is shown in Table S6. Concentrations below detection limits were replaced with zero.
94 More details on detection limits and repeatability of replicate sampler extractions are in the SI.

95 **Sampling Rates & Ambient Concentrations.** PRC loss data was entered into a generalized exponential model for PE uptake to
96 derive best-fit values for the thickness of the diffusive boundary layer (δ_{DBL}). The best-fit δ_{DBL} value for each PE was then used to
97 determine the percent equilibration (f) reached by each compound during sampler deployment. f values were used to convert
98 concentrations in PEs to ambient concentrations, which is described in detail in the SI. Physico-chemical properties of target
99 compounds used in these calculations are presented in Table S7. Average f values for each compound in air and water are in Table S8.
100 Mono- to dibrominated PBDEs were generally equilibrated or nearly equilibrated in all PEs while tetra- to octa-brominated PBDEs
101 remained <50% equilibrated in the majority of samples.

102 Best-fit δ_{DBL} values and BDE 47 sampling rates are shown in Tables S9 and S10. Average δ_{DBLS} for air boundary layers (δ_{ABL})
103 were lower for offshore/nearshore PEs (0.2 ± 0.1 mm; average \pm stdev) than for shoreline PEs (1.8 ± 1.4 mm in summer and 1.4 ± 0.5 mm
104 in winter). Average water boundary layer thickness (δ_{WBL}) was 170 ± 63 μ m at shoreline sites and 82 ± 25 μ m at offshore sites. For air
105 PEs, average sampling rates for BDE 47 were 9 ± 3 m³/day for winter PEs, 10 ± 6 m³/day for shoreline summer PEs, and 83 ± 36 m³/day

106 for offshore PEs. For water PEs, average BDE 47 sampling rates were 27 ± 8 L/day for shoreline PEs and 14 ± 10 L/day for offshore
107 PEs, in-line with expectations based on relative flow strengths at these locations.

108 **Air-water exchange calculations.** 32 pairs of co-deployed air and water PEs were used to investigate PBDE air-water exchange.
109 Details on the procedure for calculating fugacity ratios, air-water exchange fluxes, and associated error propagation are presented in
110 the SI. Fugacity ratios and air-water exchange fluxes were only calculated in instances where the congener was detected in both air
111 and water. In cases where the compound was not detected in air and/or water, or where fugacity ratios were not significantly different
112 from equilibrium after error propagation, the net air-water exchange flux was assumed to be zero.

113 To determine whether PE-derived air-water exchange fluxes were representative of average exchange fluxes in non-steady-
114 state conditions over time periods relevant to this study, a model was built in R³⁵ to compare simulated air-water exchange fluxes to
115 PE-derived exchange fluxes. This is described further in the SI (Figures S1, S2; Table S11).

116 **Correlation with population density.** Average summertime concentrations of PBDEs were compared to population within 2 - 60 km
117 of each site using population data from the Columbia University Center for International Earth Science Information Network
118 (CIESIN) Global Rural-Urban Mapping Project (GRUMP).³⁶ To determine which radius around the sites yielded the strongest linear
119 correlation, ordinary least squares regression was performed for each congener, as well as the sum of all congeners, at a series of
120 different radii in R³⁵ to identify the model with the minimum residual standard error (RSE) in each case. This procedure was repeated

121 for population data within 180° wedges to the north, south, east, and west of each sampling site to determine whether population
122 density within one general direction was more significant in driving spatial distributions of PBDEs.

123 **Bayesian kriging.** Bayesian kriging is a geostatistical interpolation technique that automates the parameter estimation needed to build
124 a kriging model, which makes it the most appropriate approach for datasets with very limited spatial resolution.³⁷ More details on this
125 approach are in the SI.

126

127 **RESULTS & DISCUSSION**

128 **Dissolved PBDEs in the Great Lakes.** Average concentrations of dissolved PBDEs are summarized in Table 1 for shoreline
129 (deployed directly from shoreline), nearshore (< 5 km from shore), and offshore sites. BDEs 100, 99, 47, 28, and 49 were detected in
130 >70% of all water PEs. BDE 154 was detected in 53%, BDE 153 in 43%, and the remaining congeners in ≤15%. Average dissolved
131 Σ_{12} BDE ranged from 0.6 pg/L at Dunkirk (DUN) on the southern shoreline of Lake Erie to 18 pg/L at a nearshore buoy site west of
132 central Toronto (WTOR). All dissolved PBDE concentrations for all deployments are displayed in Table S9.

133 Average concentration and composition for summer dissolved Σ_{12} BDE at each site is shown in Figure 1. BDEs 47 and 99
134 were the dominant congeners at most sites, making up 41±15% and 29±14% of Σ_{12} BDE, respectively. Composition of the major BDE
135 congeners (BDE 47, 99, and 100) was quite consistent among sites with Σ_{12} BDE>3 pg/L, but more variable at sites with lower

136 concentrations. This was most likely due to some congeners being <DL at these sites. Figure S3 provides a closer look at mean
137 percent composition at each location.

138 Along the southern shore of Lake Erie, Σ_{12} BDE ranged from 0.6 pg/L on the Dunkirk shoreline (DUN) to 11 pg/L in Presque
139 Isle Bay (ERI). Concentrations at the three sites near Cleveland (CLE, SHF, and FH) were similar, with average summertime Σ_{12} BDE
140 of 4.3–5.5 pg/L. Along the southern shore of Lake Ontario, Σ_{12} BDE was greater than what was seen on Lake Erie, ranging from 11–
141 12 pg/L. The Cape Vincent shoreline site (CV) had a lower average Σ_{12} BDE (3.8 pg/L), possibly due to dilution, as the site was along
142 the St. Lawrence River, the major outflow from Lake Ontario, while the three shoreline sites in Niagara (NIA), Oswego (OSW), and
143 Rochester (ROC) were located near the mouths of tributaries.

144 Σ_{12} BDE at offshore/nearshore sites was generally < 3 pg/L, significantly lower than shoreline concentrations ($p < 0.05$ two-
145 tailed t test with unequal variance), excluding the three nearshore Toronto sites. The greatest offshore concentrations were observed at
146 the westernmost offshore sites on each lake, with Σ_{12} BDE of 2.8 pg/L in western Lake Erie and 3.2 pg/L in western Lake Ontario.
147 These western sites were the closest offshore sites to the major rivers feeding each lake (the Detroit River and Niagara River) and may
148 have been influenced by inputs from these rivers.

149 Generally, dissolved PBDEs in this study were lower than in previous studies. This may be because the PEs used for sampling
150 were selective for the truly dissolved phase. In previous active sampling studies on the Great Lakes, Venier et al. measured average
151 BDE 28, 47, 99, and 100 at a total concentration of 117 pg/L in Lake Ontario and 62 pg/L in Lake Erie surface waters during a 2011-

152 2012 springtime sampling campaign²⁹ and Streets et al. measured a mean value for total dissolved Σ_6 BDE of 18 pg/L in offshore Lake
153 Michigan in 2004.¹⁰ In other regions, Zarnadze & Rodenburg reported dissolved PBDE concentrations of 44, 5.5, and 35 pg/L for
154 BDE 47, 100, and 99 in Raritan Bay in 2001-2002³⁸ and Yang et al. measured dissolved Σ_{10} BDE from 13 – 26 pg/L in 9 English
155 freshwater lakes from 2008 to 2012.³⁹ In contrast, studies using PEs to measure total truly dissolved PBDEs in Narragansett Bay in
156 2009 and Lake Superior in 2011 found concentrations <3 pg/L at all sites, similar to offshore/nearshore concentrations in this
157 study.^{18,24} Booij et al. measured BDEs 47, 99, and 153 in the Western Scheldt Estuary in 1999 using semi-permeable membrane
158 devices (SPMDs) and found that total concentrations generally did not exceed 2 pg/L.⁹

159 We investigated whether the discrepancy between concentrations reported by Venier et al.²⁹ and our own could be due to the
160 presence of dissolved organic carbon (DOC) that was likely co-sampled by Venier's active sampling method. As detailed further in
161 the SI (Table S12), the DOC concentrations that would be needed to explain the discrepancy were quite high for the open-lake Great
162 Lakes sites (> 3 mg/L), suggesting that the inclusion of the colloidal phase in the active sampling study was not sufficient to explain
163 the difference between concentrations. Seasonal differences in dissolved PBDE concentrations may explain some of the additional
164 discrepancy, as Venier et al. sampled in April-May, while PEs from this study were representative of average summer concentrations.
165 Another possible contributor to the discrepancy is uncertainty in quantifying the affinity of BDEs for DOC (K_{iDOC}). Similar
166 discrepancies were observed in a comparison by Ruge et al. in Lake Superior.²⁴

167 **Gaseous PBDEs above the Great Lakes.** BDEs 99, 100, and 47 were detected in >75% of air PEs. BDE 28 was in 54%, BDE 49 in
168 34%, and the remaining congeners were in $\leq 15\%$ (Table S6). Mean summer gaseous $\Sigma_{12}\text{BDE}$ ranged from 0.1 pg/m^3 near the
169 northeastern shore of Lake Ontario to 11 pg/m^3 on the Cleveland shoreline (CLE). BDEs 47 and 99 were the dominant congeners,
170 making up $39\pm 21\%$ and $34\pm 18\%$ of $\Sigma_{12}\text{BDE}$, respectively. As with dissolved PBDEs, composition of the major congeners (BDE 47,
171 99, and 100) was similar at most sites, with the exception of one in northern Lake Ontario (CHB), where the difference in composition
172 was most likely because concentrations were very low and BDE 99 and 47 were <DL, and two other locations with atypical
173 compositions, Sheffield Lake (SHL) and Rochester Site 1 (ROC1), where the reason for the absence of BDE 99 was not known
174 (Figure S4).

175 Summertime concentrations of total gaseous PBDEs are summarized in Table 2 for shoreline, nearshore, and offshore sites.
176 Gaseous $\Sigma_{12}\text{BDE}$ was significantly greater at the shoreline than offshore and nearshore sites ($p < 0.005$, two-tailed t test with unequal
177 variance), and shoreline gaseous $\Sigma_{12}\text{BDE}$ was greater in summer than winter ($p < 0.005$, two-tailed paired t test). Concentrations of all
178 compounds from all deployments are presented in Table S10.

179 Average summer gaseous PBDE concentration and composition at each site are shown in Figure 1. Gaseous $\Sigma_{12}\text{BDE}$ was
180 lower than concentrations from previous studies in the region, possibly due to declining concentrations over time. Su et al. reported
181 mean gaseous $\Sigma_{12}\text{BDE}$ of 17 pg/m^3 at a clearing in Ontario during 2001-2002.⁴⁰ Ma et al. measured average gaseous $\Sigma_{34}\text{BDEs}$ ranging
182 from 5 pg/m^3 in Eagle Harbor, a remote site on the shore of Lake Superior, to 25 pg/m^3 in Cleveland and 32 pg/m^3 in Chicago via

183 active sampling with XAD resin.¹⁴ They observed a significant decreasing trend from 2005 to 2011 for BDE 47 in Cleveland and
184 Chicago, though concentrations increased or showed little change at other locations.¹⁴

185 During 2007-2008, Melymuk et al. monitored PBDEs throughout the greater Toronto area and found mean Σ_{25} BDE of 3 pg/m^3
186 at their southernmost site, near the northern Lake Ontario shoreline. This was about two to three times greater than total mean
187 Σ_{12} BDE measured at the nearshore Toronto sites in this study (1.1 – 1.4 pg/m^3).²⁸ The site monitored by Melymuk et al. was closer to
188 the city center and polyurethane foam passive samplers (PUFs) were used, which capture both gaseous and some fraction of particle-
189 sorbed PBDEs.²⁸ During 2012-2013, Peverly et al. measured Σ_{27} BDE ranging from 11-150 pg/m^3 in the Chicago region, also using
190 PUFs, and observed a significant contribution from BDE 209, which was not measured here.⁴¹ In the only previous study to use PEs
191 to measure truly gaseous PBDEs in the Great Lakes region, Ruge et al. measured average summer gaseous Σ_7 BDE of 0.02-5.5 pg/m^3
192 in Lake Superior in 2011, similar to the range of values in this study.²⁴

193 **Gaseous and Dissolved NHFRs in the Great Lakes.** Ambient concentrations of gaseous NHFRs are presented in Table S10. When
194 detected, estimated gaseous bromobenzene concentrations (PBBz, PBT, PBEB, and HBBz) were similar in magnitude to those
195 measured by Venier et al. in the Great Lakes atmosphere by high-volume active sampling with XAD, with all concentrations <2
196 pg/m^3 .²⁷ However, these compounds were only detected intermittently in this study and were near detection limits, so estimated
197 concentrations are somewhat uncertain.

198 Venier et al. measured dissolved and colloidal NHFRs in Great Lakes water by active sampling and found mean PBEB
199 concentrations in Lake Ontario to be 32 ± 18 pg/L, while in this study PBEB concentrations were < 2 pg/L (Table S9).²⁹ No other
200 NHFRs were detected in more than two aqueous PEs.

201 Percent detection was low for all NHFRs. As the NHFRs are low-volatility compounds that are expected to be found primarily
202 in the particulate phase, it may be that concentrations in the truly gaseous or dissolved phase were too low to be detected here using
203 passive samplers.

204 **Air-water exchange of PBDEs.** Fugacity ratios (f_w/f_a), which indicate the direction of air-water exchange, are presented in Table S13
205 for all PBDE congeners. In all cases where fugacity ratios were significantly different from equilibrium after error propagation, they
206 indicated absorption into surface waters.

207 Exchange fluxes for all available air-water PE pairs at each site were averaged to yield mean summer air-water exchange
208 fluxes for each location, which are shown in Figure 2. Mean absorptive fluxes ranged from -964 pg/m²/day on the shoreline of Cape
209 Vincent (CV) to -30 pg/m²/day at an offshore site in central Lake Erie (CERI). Absorption of BDEs 47 and 99 dominated air-water
210 exchange fluxes at the majority of sites, with greatest absorption fluxes at shoreline sites and little to no significant exchange flux in
211 either direction at most offshore/nearshore sites. It should be noted that aqueous PEs at Cleveland Edgewater (CLE) and Fairport
212 Harbor (FH) were placed on nearshore buoys, while air measurements were taken at the shoreline, which may have resulted in
213 calculation of stronger absorption fluxes than if dissolved concentrations were monitored directly at the shoreline.

214 Previous measurements of PBDE air-water exchange fluxes are scarce. Xie et al. and Lohmann et al. both observed net
215 absorption of gaseous PBDEs on transects of the Atlantic Ocean, dominated by BDEs 47 and 99.^{31,42} Lohmann et al. calculated
216 median air-water exchange fluxes of about -325 pg/m²/day for BDE 47 and about -260 pg/m²/day for BDE 99. Xie et al. calculated
217 fluxes ranging from -28 to -875 pg/m²/day for BDE 47 and -3 to -170 pg/m²/day for BDE 99. In contrast to the offshore Great Lakes
218 sites, where fluxes were mostly near equilibrium, these studies were conducted in remote regions with lower concentrations of
219 dissolved PBDEs where atmospheric deposition was expected to be the primary source of PBDEs.

220 Ruge et al. observed absorption of gaseous PBDEs at shoreline sites and volatilization offshore on Lake Superior in 2011, with
221 the greatest total absorption flux at Sault Ste. Marie (-2,700 pg/m²/day).²⁴ The occurrence of offshore volatilization in that study,
222 compared to near-equilibrium conditions at offshore sites in this study, may have been due to the smaller surface areas and more
223 urbanized shorelines of Lake Erie and Lake Ontario in comparison with Lake Superior.

224 Liu et al. observed volatilization of polychlorinated biphenyls (PCBs) at the majority of the same sites discussed here³⁴ ,
225 suggesting that the lakes may be acting as secondary sources of legacy pollutants, but continue to absorb PBDEs.

226 **Correlation between PBDE congeners and other compound groups.** Dissolved concentrations of the seven PBDEs found in >30%
227 of water samples (BDEs 28, 47, 49, 99, 100, 154, and 153) were significantly linearly correlated with each other ($p < 0.05$, $0.24 \leq r^2 \leq$
228 0.73), with the exception of BDEs 49 and 153. Correlations between the two hexabrominated congeners, BDEs 154 and 153, and
229 other congeners were generally weaker than correlations between lower-brominated congeners. This may be because PBDEs 28, 49,

230 47, 99, and 100 share a common source: the Penta-BDE commercial formulation, while BDEs 154 and 153 are associated with Octa-
231 BDE.⁴³ BDEs 154 and 153 were strongly correlated with each other in the dissolved phase ($p < 0.001$, $r^2=0.63$). Gaseous
232 concentrations of the five PBDEs found in >30% of air samples (BDEs 28, 47, 49, 99, and 100) were also significantly linearly
233 correlated with each other ($p < 0.05$, $0.30 \leq r^2 \leq 0.80$). Only samples in which both congeners were found >DL were used in the
234 correlation analysis for each pair.

235 In addition to comparisons between PBDE congeners, Σ_{12} BDE concentrations in air and water were compared to total
236 concentrations of polycyclic musks (PCMs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs)
237 measured in the same extracts. PCB data was published previously by Liu et al.,³⁴ PCM data is currently in review, and mean PAH
238 concentrations are available in Tables S14 and S15. Dissolved Σ_{12} BDE exhibited a significant positive linear correlation with total
239 dissolved PCMs (Σ_5 PCM; $p < 0.01$; $r^2 = 0.34$; SE = 4.2; N = 39), but was not correlated with dissolved Σ_{14} PAH or Σ_7 PCB, suggesting
240 that dissolved PBDEs may share more common sources with PCMs than with PAHs or PCBs in the lower Great Lakes region.
241 Previous work by Melymuk et al. suggested that wastewater may be an important source of both PBDEs and PCMs in Lake Ontario,
242 while not as significant for PCBs or PAHs.²²

243 In contrast, gaseous Σ_{12} BDE was weakly but significantly correlated with gaseous Σ_{14} PAH ($p < 0.01$; $r^2=0.13$; SE = 3.8; N =
244 56) and Σ_7 PCB ($p < 0.01$; $r^2=0.16$; SE = 3.8; N = 54), but not correlated with Σ_5 PCM, possibly due to scarcity of data, as gaseous
245 PCMs were detected above blank levels less frequently than the other compound groups. Previous studies in the Great Lakes region

246 have also reported significant correlation between atmospheric PBDEs and PCBs due to their elevated emissions in urban and
247 industrial areas.⁴⁴

248 Results of this correlation analysis suggest that PBDEs and PCMs share common sources to the aquatic environment. They
249 may also share common sources to the atmosphere, but results for air were inconclusive.

250 **Gaseous PBDEs and population density.** Population data within a 180° wedge to the south of each site resulted in stronger
251 correlation with gaseous Σ_{12} BDE than population within a circle around each site or population to the north, east, or west. This was
252 also generally true for individual BDE congeners. Correlations found using a circular radius or 180° southern wedge are compared for
253 Σ_{12} BDE and Σ_{14} PAH in Figure S5.

254 In previous studies investigating relationships between atmospheric pollutant concentrations and population, sites have often
255 been characterized using a circular area with a specific radius (often 20 – 25 km).⁴⁶ However, some studies have shown that
256 directional terms should be considered when investigating trends of atmospheric pollutants in the Great Lakes, especially for
257 compound groups with significant local atmospheric emissions.⁴⁵ Previous studies have also demonstrated that coastal effects can
258 disrupt population trends when offshore air dilutes the urban plume.⁴⁶ The work described here included mostly shoreline sites which
259 had very different nearby population densities to the north and south. Furthermore, the lower Great Lakes region was generally
260 subject to prevailing southwesterly winds during the deployment period, as is demonstrated by wind direction data from
261 meteorological buoys and predicted mean wind directions at the sampling sites, shown in Tables S16 and S17 and Figures S6 and S7.

262 Average gaseous Σ_{12} BDE exhibited significant ($p < 0.05$) linear correlation with population within 1-10 km south of each site,
263 with the strongest correlation at 3 km ($p < 0.005$; $r^2 = 0.36$; $SE = 2.9$; $N = 22$). Significant linear correlation with population was also seen
264 for four of the five commonly detected individual congeners (BDE 28, 47, 99, and 100), with strongest correlations between 3-15 km.
265 This suggests PBDE concentrations were significantly influenced by local sources, consistent with their low vapor pressures and
266 significant loss via deposition. Melymuk et al. observed a swift decline in PBDE concentrations with 5 km south of the Toronto city
267 center, supporting the importance of nearby populated areas in influencing distributions of these compounds.²⁸ BDE 49 did not
268 exhibit significant correlation with population at any distance, perhaps due to its low frequency of detection (34%) compared to the
269 other congeners (>50%).

270 The maximum radius where a significant ($p < 0.05$) linear correlation was observed between gaseous concentration and
271 population density was plotted against $\log p_L$ at 298 K for four PBDE congeners, as well as several PAHs, PCBs, and PCMs, in Figure
272 3. As compound vapor pressure increased, the maximum distance where significant correlation was observed expanded, suggesting
273 that spatial distributions of more volatile compounds like the PCMs and lower molecular weight PAHs were influenced more strongly
274 by distant emissions, while local emissions were more important in determining spatial distributions of PBDEs.

275 Previous data from PEs collected on the lower Great Lakes in 2011 suggested that PAHs with sub-cooled liquid vapor pressure
276 $\log p_L(\text{Pa}) < -3$ at 298 K most strongly correlated with population within a radius of 3 km, while PAHs with greater vapor pressures
277 correlated more strongly with population within a radius of 20 km.³³ In this study, PAHs, PCBs, and PCMs with $\log p_L > -2$ remained

278 significantly correlated with population within radii >25 km, while less volatile compounds generally did not. BDEs 47 and 99 fell
279 farther below the regression line in Figure 3 than the other compounds, with significant correlation occurring only to a radius of 5-6
280 km. This may be due to their short lifetimes with respect to photolysis and OH radical degradation (4.0 – 8.7 hours) compared to BDE
281 100 and 28 (26 – 48 hours).²⁰

282 **Dissolved PBDEs and population density.** Dissolved Σ_{12} BDE exhibited a significant positive linear correlation with population
283 within a 25 km radius of each site ($r^2=0.52$; $p<0.01$; $SE=0.27$; $N=20$), as shown in Figure 4. The correlation was driven primarily by
284 the seven nearshore sites, which exhibited the broadest range in surrounding population densities. In this case, use of population
285 extracted from wedges north, south, east, or west of each site did not result in stronger correlations.

286 Four shoreline sites (OSW, NIA, ROC, and ERI) exhibited low surrounding population and elevated dissolved Σ_{12} BDE relative
287 to the regression line, suggesting they may be influenced by nearby point sources. The Niagara River site (NIA) was likely
288 representative of the Niagara River plume and the Oswego site (OSW) may have been influenced by two nearby (within 1.5 km)
289 wastewater treatment plants that discharged directly into Lake Ontario, both identified as major dischargers in the US Environmental
290 Protection Agency (US EPA) National Pollutant Discharge Elimination System (NPDES) 2012 Discharge Monitoring Report.⁴⁷

291 **Geostatistical Interpolation of Dissolved PBDE Concentrations.** Using passive samplers enabled a much improved spatial
292 coverage over past studies of the region (though still limited on the scale of the Great Lakes). This dataset thus provided an
293 opportunity to more accurately predict surface water concentrations over the lakes. Maps of predicted aqueous Σ_{12} BDE across Lake

294 Erie and Lake Ontario are presented in Figure 5 and variance for these predictions is presented in Figure S8. Posterior distributions
295 for the estimated parameters used in the kriging model are shown in Figure S9 and results of cross validation are shown in Figure S10.

296 Predictions for Lake Erie identified the area near Detroit at the western end of the lake as a possible unmonitored “hot spot”,
297 and highlighted areas around Buffalo, Cleveland, and Dunkirk as having the greatest concentrations (around 10 ± 4 pg/L) on the lake.
298 Predictions for Lake Ontario highlighted the significance of the Toronto conurbation as a source of PBDEs to the lake, with elevated
299 concentrations of 10-18 pg/L extending about 15 km away from the shoreline.

300 The use of Bayesian kriging coupled with PE-derived concentrations to predict dissolved Σ_{12} BDE over the lakes illustrates the
301 utility of relatively highly spatially resolved data in identifying potential hot spots for further study, like the area around Detroit.
302 Concentrations in this area would likely be greater than predicted by the model, as they would be influenced by the Detroit River,
303 which is the major tributary to Lake Erie. Elevated gaseous and dissolved PBDEs near population centers highlight the need to
304 continually monitor concentrations of phased-out persistent organic pollutants in urbanized areas.

305 **ASSOCIATED CONTENT**

306 **Supporting Information.** Additional figures and tables, as well as details on sampling rate estimation and air-water exchange flux
307 calculations, are available in the Supporting Information. This material is available free of charge via the Internet at
308 <http://pubs.acs.org>.

309

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320

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- 433
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435 **FIGURES AND TABLES**

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438

439 **Table 1. Average Dissolved PBDEs (pg/L) ± Standard Deviation.**

	N ^a	BDE 28	BDE 49	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	Σ ₁₂ BDE
Toronto Nearshore	3	0.48±0.12	0.22±0.02	5.4±1.3	1.8±0.76	5.0±1.8	0.42±0.22	0.20±0.07	14±4.1
Lake Erie Shoreline/Nearshore	6	0.23±0.22	0.20±0.17	2.0±1.2	0.93±0.46	1.9±1.4	0.11±0.11	0.03±0.04	5.5±3.4
Lake Ontario Shoreline/Nearshore	6	0.28±0.16	0.23±0.21	3.0±2.2	0.95±0.68	2.0±1.8	0.13±0.15	0.06±0.05	6.8±5.0
Lake Erie Offshore	3	0.17±0.15	0.13±0.11	0.55±0.48	0.30±0.27	0.63±0.74	0.07±0.07	0.02±0.04	1.9±0.91
Lake Ontario Offshore	2	0.08±0.11	0.11±0.06	1.1±0.18	0.40±0.21	0.85±0.36	0.09±0.12	< DL	2.6±0.81

440 ^aN is the number of sites of each type.

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445 **Table 2. Average Gaseous PBDEs (pg/m³) ± Standard Deviation.**

	N ^a	BDE 28	BDE 49	BDE 47	BDE 100	BDE 99	Σ ₁₂ BDE
Summer Sites (May to November)							
Offshore	3	0.09±0.10	0.03±0.02	0.22±0.09	0.05±0.03	0.25±0.12	0.74±0.15
Nearshore	5	0.14±0.09	0.03±0.02	0.28±0.24	0.11±0.05	0.22±0.18	0.79±0.56
Shoreline	14	0.25±0.29	0.06±0.07	2.9±1.3	0.59±0.25	2.6±1.7	6.7±2.1
Winter Sites (November to May)							
Shoreline	9	0.03±0.07	0.01±0.02	0.55±0.62	0.21±0.15	1.7±0.88	2.7±1.4

446 ^aN is the number of sites of each type.

447

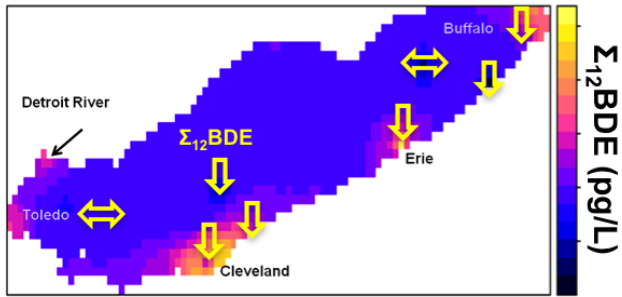
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452 **GRAPHICAL ABSTRACT**



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