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Spatial Distribution and Air-Water Exchange of Organic Flame Retardents in the Lower Great Lakes

Carrie A. McDonough

Gavino Puggioni
University of Rhode Island

See next page for additional authors

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Authors

Carrie A. McDonough, Gavino Puggioni, Paul A. Helm, Derek Muir, and Rainer Lohmann

1 # Spatial Distribution and Air-Water Exchange of Organic Flame

2 # Retardants in the Lower Great Lakes

3 *Carrie A. McDonough[1], Gavino Puggioni[2], Paul A. Helm[3], Derek Muir[4], Rainer Lohmann[1*]*

4 [1]University of Rhode Island Graduate School of Oceanography, 215 South Ferry Road, Narragansett, RI, USA 02882

5 [2] University of Rhode Island Department of Computer Science and Statistics, 45 Upper College Road, Kingston, RI, USA 02881

6 [3] Ontario Ministry of the Environment and Climate Change, 125 Resources Road, Toronto, Ontario, Canada M9P 3V6

7 [4] Environment Canada, Aquatic Contaminants Research Division, 867 Lakeshore Road, Burlington, Ontario, Canada L7S 1A1

8 [*]Corresponding Author; Email: rlohmann@ uri.edu; Phone: 401-874-6612; Fax: 401-874-6811

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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/m^3). NHFRs

20   were generally below detection limits. Air-water exchange was dominated by absorption of BDEs 47 and 99, ranging from -964

21   pg/m^2/day to -30 pg/m^2/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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INTRODUCTION

Organic flame retardants (OFRs) such as the polybrominated diphenyl ethers (PBDEs) and novel halogenated flame retardants (NHFRs) are persistent bioaccumulative contaminants that have been liberally added to polymers used in consumer goods to slow 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 environment and continually leach out of in-use products, especially furniture, casings for electronics, and automotive upholstery.[3] Numerous studies have shown that PBDEs, as well as many NHFRs, accumulate in humans[4–6] and wildlife,[7–11] and that concentrations are elevated in North American cities.[12–14] Some studies have suggested that various NHFRs are increasingly being added to consumer products due to the PBDE phase-out, but there is uncertainty regarding which chemicals are being used in which applications, and at what production volumes.[2,14–16]

Previous studies have identified densely populated areas, central business districts, and indoor environments as sources of OFRs to the atmosphere via volatilization from consumer goods.[13,14,17,18] Atmospheric wet and dry deposition have been identified as 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 water[29] 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

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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.

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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 μL 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±15% for BDE 2 to 101±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±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 μm at shoreline sites and 82±25μm at offshore sites. For air

105 PEs, average sampling rates for BDE 47 were 9±3 m^3/day for winter PEs, 10±6 m^3/day for shoreline summer PEs, and 83±36 m^3/day

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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 R[35] 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 R[35] to identify the model with the minimum residual standard error (RSE) in each case. This procedure was repeated

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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 $\leq$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 campaign[29] and Streets et al. measured a mean value for total dissolved Σ_6BDE 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 2001-2002[38] 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 Σ_{12}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±21% and 34±18% of Σ_{12}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 Σ_{12}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 Σ_{12}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 Σ_{12}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 Σ_{12}BDE of 17 pg/m^3 at a clearing in Ontario during 2001-2002.[40] Ma et al. measured average gaseous Σ_{34}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_7BDE 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/m^2/day on the shoreline of Cape

209   Vincent (CV) to -30 pg/m^2/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/m^2/day for BDE 47 and about -260 pg/m^2/day for BDE 99. Xie et al. calculated

217   fluxes ranging from -28 to -875 pg/m^2/day for BDE 47 and -3 to -170 pg/m^2/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/m^2/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 here[34] ,

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,

15

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_5PCM; $p < 0.01$; $r^2 = 0.34$; SE = 4.2; N = 39), but was not correlated with dissolved Σ_{14}PAH or Σ_7PCB, 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_7PCB ($p < 0.01$; $r^2=0.16$; SE = 3.8; N = 54), but not correlated with Σ_5PCM, 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 $\Sigma_{12}BDE$ 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 $\Sigma_{12}BDE$ and $\Sigma_{14}PAH$ 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(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.

AUTHOR INFORMATION

Corresponding Author

* Rainer Lohmann: rlohmann@uri.edu

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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	$\Sigma_{12}BDE$
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 ^{a}N is the number of sites of each type.

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Table 2. Average Gaseous PBDEs (pg/m^3) ± Standard Deviation.

	N^a	BDE 28	BDE 49	BDE 47	BDE 100	BDE 99	$\Sigma_{12}BDE$
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

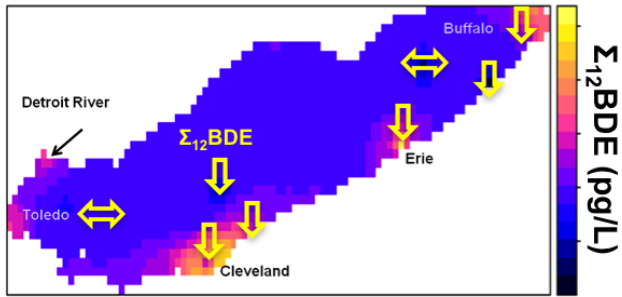446   [a]N is the number of sites of each type.

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452 **GRAPHICAL ABSTRACT**

453

454   For Table of Contents only

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