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1 **Gaseous and Freely-Dissolved PCBs in the Lower Great Lakes**
2 **based on Passive Sampling: Spatial Trends and Air-water**
3 **Exchange.**

4
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23 **ABSTRACT**

24 Polyethylene passive sampling was applied to quantify gaseous and
25 freely-dissolved polychlorinated biphenyls (PCBs) in the air and water of Lakes
26 Erie and Ontario during 2011-2012. In view of differing physical characteristics
27 and the impacts of historical contamination by PCBs within these lakes, spatial
28 variation of PCB concentrations and air-water exchange across these lakes may
29 be expected. Both lakes displayed statistically similar aqueous and atmospheric
30 PCB concentrations. Total aqueous concentrations of 29 PCBs ranged from 1.5 pg
31 L⁻¹ in the open lake of Lake Erie (site E02) in 2011 spring to 105 pg L⁻¹ in Niagara
32 (site On05) in 2012 summer, while total atmospheric concentrations were
33 7.7-634 pg m⁻³ across both lakes. A west-to-east gradient was observed for
34 aqueous PCBs in Lake Erie. River discharge and localized influences (e.g.,
35 sediment resuspension and regional alongshore transport) likely dominated
36 spatial trends of aqueous PCBs in both lakes. Air-water exchange fluxes of
37 Σ_7 PCBs ranged from -2,420 ($\pm 1,870$) pg m⁻² day⁻¹ (deposition) in Sheffield (site
38 E03) to 9,030 ($\pm 3,070$) pg m⁻² day⁻¹ (volatilization) in Niagara (site On05). Net
39 volatilization of PCBs was the primary trend across most sites and periods.
40 Almost half of variation in air-water exchange fluxes was attributed to the
41 difference in aqueous concentrations of PCBs. Uncertainty analysis in fugacity
42 ratios and mass fluxes in air-water exchange of PCBs indicated that PCBs have
43 reached or approached equilibrium only at the eastern Lake Erie and along the
44 Canadian shore of Lake Ontario sites, where air-water exchange fluxes
45 dominated atmospheric concentrations.

46 INTRODUCTION

47 The manufacture and import of polychlorinated biphenyls (PCBs) was banned
48 in Canada and the United States in 1977 and 1979,^{1,2} respectively. In Canada,
49 PCB use was illegal in any electrical products manufactured after 1980, but
50 electrical equipment manufactured prior to 1980 were permitted for continued
51 use.³ As persistent organic pollutants, however, PCBs are still being detected in
52 environmental compartments such as water,⁴ air,⁵ sediment,^{6,7} and biota.^{8,9} Due
53 to the concern for the environmental and health effects of PCBs,¹⁰ they have been
54 frequently monitored and detected in the Great Lakes ecosystem, particularly
55 through the International Atmospheric Deposition Network (IADN).^{11,12}

56 Atmospheric deposition (dry deposition, wet deposition and air-water
57 diffusive fluxes) is a significant source of POPs to large inland lakes, and its
58 importance for PCBs has already been demonstrated in the Great Lakes.¹³
59 Results from IADN have illustrated the role of atmospheric deposition (gas and
60 particulate)^{14,15} and volatilization¹⁶ in the atmospheric pathway of PCBs at few
61 designated locations. To improve the knowledge on environmental fate of PCBs
62 in the Great Lakes, more atmospheric and aqueous sampling sites are useful.
63 Although atmospheric PCBs have been extensively investigated in the Great
64 Lakes,¹⁷ limited information is available about the spatial trend of gaseous and
65 freely-dissolved PCBs. There is a scarcity of recently published data, although a
66 recent survey reported dissolved concentrations for the Great Lakes.^{4,18} This
67 prompted us to deploy passive samplers at more locations across the lakes, to
68 investigate environmental fate of PCBs in air-water exchange processes, and to
69 determine whether the Great Lakes have become an important secondary source
70 of PCBs to the atmosphere. Alternatively, primary emissions continue to deposit

71 PCBs into the Lakes, either via atmospheric deposition, or from direct discharges
72 from rivers, wastewater treatment plants and potentially historically
73 contaminated sites.¹⁹⁻²² By working on Lakes Erie and Ontario, we also aimed to
74 better understand whether the lake characteristics affected concentrations and
75 trends of PCBs.

76 Lakes Erie and Ontario constitute the “lower” Great Lakes having the smallest
77 surface area, mean depth and water residence times. Lake Erie has a mean depth
78 of 19 m and a water residence time of 2.6 years, while Lake Ontario has a mean
79 depth of 86 m and a water residence time of 6 years.²³ Lake Erie mainly receives
80 water from Lake Huron via the Detroit River and outflows to Lake Ontario
81 through the Niagara River. Major urban areas include Detroit, Toledo, Cleveland
82 and Buffalo around Lake Erie, and Hamilton, Toronto, Rochester and Kingston
83 around Lake Ontario. It is expensive to conduct active sampling at such a large
84 scale, restricting the assessment of spatial variation of atmospheric and aqueous
85 PCBs and their air-water exchange flux. One way around the restriction is to
86 deploy passive samplers. Published literatures indicated that POPs
87 concentrations from passive atmospheric sampling were in good agreement with
88 those measured with active sampling.²⁴⁻²⁶ In previous work, we performed
89 source apportionment and correlation with urban area of gaseous and
90 freely-dissolved PCBs in the lower Great Lakes covering summer and fall 2011.²⁷
91 In this study, spatial trends of atmospheric and aqueous PCB concentrations and
92 their air-water exchange fluxes are presented and discussed, with a stronger
93 statistical power based on the two years of data (2011-2012).

94 To gain more knowledge about the trends and cycling of PCBs in the lower
95 Great Lakes, low density polyethylene (LDPE) passive samplers were deployed

96 in the air and water at Lake Ontario and Lake Erie during 2011-2012. Our goals
97 were to a) investigate spatial trend of gaseous and freely-dissolved PCBs in Lakes
98 Erie and Ontario, b) identify their possible sources, c) estimate spatially resolved
99 air–water exchange fluxes, and d) explore the primary factors influencing
100 variability in magnitude and direction of the fluxes in the both lakes.

101

102 **MATERIALS AND METHODS**

103 **Passive Sampling.** Detailed information on sampling sites and temporal
104 coverage is provided in the Supporting Information (Figure S1 and Tables S1-2).
105 A 50.8 µm-thick LDPE commercial sheeting was cut into strips of 10 × 40 cm. The
106 strips were cleaned and spiked with performance reference compounds (PRCs)
107 via a method adapted from Booij et al.²⁸ The LDPE passive samplers were
108 deployed in the air and water of the Great Lakes region by trained volunteers.
109 Water and air passive samplers were deployed in the same locations whenever
110 possible. Shoreline air samplers were mounted inside two inverted bowls and
111 deployed 1-2 m above the ground or water surface to shelter LDPE samplers
112 from direct radiation and rainfall. Coastal water samplers were fastened to an
113 anchored rope and suspended in water ~1 m below the surface. Air samplers
114 nearshore (1-2 km from shore) northern Lake Ontario sites were mounted
115 within stainless steel bowl housings ~2 m above the water surface on buoys.
116 Co-located (within 200 m of air sites) water samplers were suspended below a
117 sub-surface float at 4 m depth in perforated stainless steel cages anchored at
118 lake-bottom to a stainless steel cable. Mid-lake deployments involved securing
119 the stainless steel wire holding the PEs to rods inside a perforated (1.5 cm
120 diameter holes) 10 cm diameter stainless steel or copper tube (see Figure S2).

121 Depending on the location, one to four sampling campaigns of 4-34 weeks were
122 conducted from April of 2011 to October of 2012. Due to logistical constraints,
123 in-lake deployments had fewer sampling deployments than on-land.

124

125 **Sample Analysis and QA/QC.** LDPE samples were processed according to the
126 published method.^{29,30} Briefly, all LDPE sheets contained PRCs and were spiked
127 with surrogate standards (¹³C labeled PCB 8, 28, 52, 118, 138, 180, and 209) and
128 then extracted overnight in pentane for 18 - 24 hours. After extracts were
129 concentrated to ~100 µL, an injection standard (tribromobiphenyl) was added
130 before analysis. No additional sample clean-up was performed for air samples,
131 while water samples were passed through a silica gel and sodium sulfate column
132 for cleanup. PCBs (29 congeners) were analyzed using Agilent GC 6890N with
133 DB-5 MS fused silica capillary column equipped with a Quattro micro GC tandem
134 MS (Waters), including dichlorobiphenyl (PCB 8 and 11), trichlorobiphenyl (PCB
135 18 and 28), tetrachlorobiphenyl (PCB 44, 52, 66, 77, and 81),
136 pentachlorobiphenyl (PCB 101, 105, 114, 118, 123, and 126),
137 hexachlorobiphenyl (PCB 128, 138, 153, 156, 157, 167, and 169),
138 heptachlorobiphenyl (PCB 170, 180, 187, and 189), octachlorobiphenyl (PCB
139 195), nonachlorobiphenyl (PCB 206) and decachlorobiphenyl (PCB 209). PCB
140 concentrations in LDPE samplers were corrected for surrogate standard
141 recoveries and blank-subtracted using the field blank relevant to the sampling
142 location. The PCB concentrations in field blanks were less than 5% of the
143 measured concentrations in samples, except PCB 8 and 11 (6-23%). PRC
144 concentrations in field and method blanks from each batch were used to
145 determine initial PRC concentrations in deployed samplers from the same batch.

146 Measured concentrations in LDPE were used to calculate ambient concentrations
147 using sampler-matrix partition coefficients corrected to ambient temperatures
148 for each PCB. The calculation is based on an assumption that the uptake rate of
149 target compounds from ambient environment to the LDPE sheet is equal with the
150 loss rate of PRCs from the LDPE sheet to ambient matrix.³¹ Equilibrium
151 percentages of target PCBs were calculated from the quantities of PRCs
152 remaining in each sample. Further analytical details and calculations are
153 provided in the Supporting Information.

154 Procedural blanks, field blanks, matrix spikes, and replicate samples were
155 performed periodically for quality assurance. Limits of detection were 0.5-13.1
156 pg m⁻³ and 0.2-1.5 pg L⁻¹ in air and water, respectively. Average recoveries of the
157 surrogate standards ranged from 52-108%. Average relative standard deviation
158 percentages of target PCBs and sampling rates ranged from 9.2-36.4% and
159 0.5-31.8%. More information on quality assurance and quality control is in the
160 Supporting Information (Tables S6-S7).

161

162 **Fugacity Ratio between Air and Water and Bivariate Analysis.** The
163 fugacity ratio (f_a/f_w) was calculated based on PCB concentrations in air (C_a) and
164 water (C_w ; both in pg m⁻³) and (air) temperature-corrected air-water partition
165 coefficient (K_{aw}), as shown in Equation 1.

$$166 \quad \log(f_a/f_w) = \log C_a - \log C_w - \log K_{aw} \quad (1)$$

167 The log-transformed fugacity ratios are listed in Table S11 and those of ICES 7
168 PCBs observed across the Lakes were analyzed via bivariate Pearson correlation
169 (result in Table S14) using SPSS statistical software packages (SPSS 13.0 for
170 windows).

171

172 **Quantification of Air-Water Exchange Flux.** Air-water mass flux ($F_{a/w}$, in pg
173 $m^{-2} day^{-1}$) is driven by the difference in compound's chemical activity between
174 two matrixes,³² see Equation 2.

$$175 \quad F_{a/w} = v_{a/w} \times (C_w - C_a/K_{aw}) \quad (2)$$

176 where $v_{a/w}$ is overall mass transfer velocity (in $m day^{-1}$) and K_{aw} is the air
177 temperature-corrected air-water partition coefficient. Details on estimating $v_{a/w}$
178 from wind speed for different temperature are provided in the Supporting
179 Information. The calculated $v_{a/w}$ values are presented in Table S10, and the flux
180 ($F_{a/w}$) values are in Table S8.

181

182 **Error propagation analysis.** Uncertainties in air-water fugacity ratios and
183 calculated mass fluxes were estimated, by taking measured uncertainties in air
184 and water analysis, partitioning coefficients (including temperature and the
185 Henry's law constant, H_c) and air-water transfer velocity ($v_{a/w}$) into account.
186 More details are shown in the Supporting Information. Uncertainties of
187 log-transformed fugacity ratios ranged from 0.53 (CB 153) to 0.60 (CB 128), and
188 the flux uncertainties are listed in Table S9.

189

190 **RESULTS AND DISCUSSION**

191 **Concentrations of Gaseous and Freely-Dissolved PCBs.** In this study, higher
192 molecular weight (octa-, nona- and deca-PCB) congener concentrations in both
193 air and water were typically below their limits of detection, while the other
194 congeners (di-PCBs: 8 and 11; tri-PCBs: 18 and 28; tetra-PCBs: 44, 52, and 66;
195 penta-PCBs: 101, 105, and 118; hexa-PCBs: 138, 153; hepta-PCBs: 180, and 187)

196 were detected in most samples. Several, mostly co-planar congeners (PCBs: 77,
197 81, 114, 123, 126, 128, 156, 157, 167, 169, 170, and 189), were only detected in a
198 few of the samples (for details, see Table S6).

199 In active sampling, the ‘apparently dissolved’ concentration is defined as the
200 fraction passing a fiber filter (e.g. below 0.5 micrometers).⁴ Dissolved
201 concentration is hence an operational classification in active sampling, whereas
202 LDPE passive sampling results reported here represent the freely dissolved
203 concentration (as dissolved organic carbon-bound compounds are not sampled).

204 In the water, total freely-dissolved concentrations of 29 PCBs were 1.50-83.8
205 pg L^{-1} (average and median values: 30.8 and 23.8 pg L^{-1}) in Lake Erie and
206 6.00-105 pg L^{-1} (average and median values: 33.9 and 29.1 pg L^{-1}) in Lake
207 Ontario. In the air, total gaseous concentrations of 29 PCBs were 19.0-421 pg m^{-3}
208 (average and median values: 111 and 80.3 pg m^{-3}) across Lake Erie and 7.70-634
209 pg m^{-3} (average and median values: 105 and 80.9 pg m^{-3}) across Lake Ontario.

210 The descriptive statistics of the total concentration of freely-dissolved and
211 gaseous 29 PCBs are illustrated in Figure 1.a and b, respectively. The
212 concentrations of PCBs were not significantly different in the both lakes by
213 Student’s *t* test ($p = 0.83$), in spite of their differences in size, depth and
214 residence time. Similarly, atmospheric PCB concentrations were not significantly
215 different between the two lakes ($p = 0.61$). Anderson et al. reported apparently
216 dissolved phase PCB concentrations ranging from 52-330 pg L^{-1} and 110-190 pg
217 L^{-1} in Lake Erie and Ontario, respectively.³³ Venier et al. also reported that
218 apparently dissolved phase PCB concentrations (reporting 84 PCBs) were $582 \pm$
219 127 pg L^{-1} and $623 \pm 113 \text{ pg L}^{-1}$ in Lakes of Eric and Ontario, respectively.⁴ All
220 studies agree, though, that Lakes Erie and Ontario display similar PCB

221 concentrations in the water.

222 The seven ICES (International Council for the Exploration of the Sea) PCBs
223 were recommended as monitoring indicators by the European Union Community
224 Bureau of Reference, due to their relatively high concentrations and wide
225 chlorination range (3-7 chlorine atom per molecule), including PCB 28, 52, 101,
226 118, 138, 153, and 180.³⁴ Linear regression analyses of total concentrations of
227 ICES 7 PCBs (abbreviated as Σ_7 PCBs) against those of 29 PCBs in air and water
228 were examined, and strongly significant positive correlations between them
229 were observed ($R = 0.952$ and 0.889 in air and water, respectively and $p < 0.001$,
230 see Figure S3). This confirms that the choice of the 7 congeners as representative
231 for a large suite of PCBs (29 congeners in this study). The 7 congeners are
232 selected as representative PCBs for the following analysis.

233

234 **Spatial distribution of Σ_7 PCBs.**

235 *Freely-dissolved PCBs in Water.* In the water, freely-dissolved concentrations of
236 the 7 PCBs in Lake Erie were comparable with those in Lake Ontario.
237 Freely-dissolved Σ_7 PCBs were 0.8 - 39.1 pg L^{-1} (average and median values: 13.7
238 and 12.0 pg L^{-1}) in Lake Erie and 1.7 - 43.7 pg L^{-1} (average and median values:
239 12.9 and 7.5 pg L^{-1}) in Lake Ontario. The freely-dissolved PCB levels varied with
240 sampling locations (Figure 2.a). In general, total concentrations along the shore,
241 e.g., 30 pg L^{-1} in Erie (site E07) and 44 pg L^{-1} in Niagara (site On05), were
242 relatively higher than those in the open lakes, e.g., < 10 pg L^{-1} in lakes of Erie (site
243 E08) and Ontario (site On07). Open-lake freely-dissolved PCBs were mainly
244 influenced by atmospheric deposition (see below). The onshore-offshore
245 gradient generally reflected anthropogenic land uses in adjacent urban areas and

246 watersheds. Burniston et al. found that PCBs, mercury, PAHs and some
247 chlorobenzenes exhibited elevated nearshore concentrations in surface water,
248 compared to open lakes and the elevation was indicative of watershed sources.³⁵

249

250 *Freely-dissolved PCBs in Lake Erie.* A west-to-east gradient was observed in
251 Lake Erie (Data in Table S12), and PCBs gradually decreased from $\sim 30 \text{ pg L}^{-1}$ in
252 the western, to $\sim 20 \text{ pg L}^{-1}$ in the central, and to $<10 \text{ pg L}^{-1}$ in the eastern basin.
253 Venier et al. also reported greater PCB concentrations in the western basin than
254 those in the central and eastern basins.⁴ Similar trends were described for
255 freely-dissolved endosulfans, and to a lesser degree for DDTs and chlordanes.²⁹
256 Such west-to-east gradient was also found for PCBs in mink, and could be linked
257 to the Detroit River, a primary source of PCBs to the western basin.³⁶ Marvin et al.
258 indicated the influence of the Trenton Channel in the Detroit River as source of
259 dioxin-like PCBs to western Lake Erie via investigating suspended sediment.¹⁹
260 Discharge of the Detroit River probably resulted in the high level of
261 freely-dissolved PCBs at site E02 (open lake).¹⁹ Although nearly 90 percent of
262 total inflow to Lake Erie comes from the Detroit River,³⁷ inflow from stream and
263 tributaries draining agricultural lands also delivered PCBs to the western basin.
264 For example, the higher concentrations of PCBs at Toledo (E01) could be
265 attributed to the discharge of Maumee River.

266

267 *Freely-dissolved PCBs in Lake Ontario.* Total concentrations along the US shore,
268 e.g., $20\text{-}40 \text{ pg L}^{-1}$ in Niagara (site On05), Rochester (site On09) and Oswego (site
269 On11) sites, were greater than those on the Canadian shore, e.g., $<10 \text{ pg L}^{-1}$ in
270 Mississauga (site On01), Toronto (site On03), Pickering (site On06) and Cobourg

271 (site On08) sites. This US versus Canada comparison might be the result from the
272 Canadian deployments being conducted 1 km off shore, while the US
273 deployments were truly coastal (in Table S2). A west-to-east gradient was
274 observed along the US shore of Lake Ontario. The Σ_7 PCB concentrations
275 decreased from 44 pg L⁻¹ in Niagara (site On05), to 40 pg L⁻¹ in Rochester (site
276 On09), to 24.2 pg L⁻¹ in Oswego (site On11), and 15 pg L⁻¹ in Cape Vincent (site
277 On12). The main sources of PCBs into Lake Ontario were the Niagara River and
278 its watershed in western New York.^{38, 39} The gradient possibly resulted from
279 outflow of the Niagara River and water circulation patterns of Lake Ontario, as
280 shown in Figure 2.a. Helm et al. indicated regional alongshore transport when
281 examining the influence of land based source to lakes and coastal areas.⁴⁰

282 Along the US coast, the PCB distributions seems to be related to the presence
283 of waste water treatment plants (WWTPs) and urban centers, while along the
284 Canadian shore, there was no obvious correlation to them, as shown in Figure S4.
285 This is likely caused by the Lake Ontario deployments being ca 1 km offshore and
286 the US deployments being truly coastal. The influence of WWTPs is likely to be
287 very limited on the intra-lake distributions of dissolved PCBs. Helm et al.
288 captured the distribution of wastewater-related contaminants in a nearshore
289 zone of Lake Ontario and found the influence of WWTP was quickly diluted out
290 to 'background' level on the order of less than a kilometer.⁴⁰ Alongshore currents
291 and upwelling seemed to contribute to concentration variation. Historically
292 contaminated resuspended sediment could serve as an additional loading to the
293 lakes, according to an extremely similar spatial pattern of sedimentary PCBs
294 reported by Forsythe and Marvin (in Figure S6).⁴¹ Compared with Lake Ontario,
295 Lake Erie is shallow and undergoes active resuspension of sediment, which could

296 explain the similar west-to-east gradients of aqueous and sedimentary PCBs in
297 Lake Erie.

298

299 *PCBs in air.* Concentrations of gaseous PCBs across Lake Erie were similar to
300 those across Lake Ontario. Gaseous Σ_7 PCBs were 6.7-205 pg m^{-3} (average and
301 median values: 41.4 and 30.3 pg m^{-3}) across Lake Erie and 5.2-306 pg m^{-3}
302 (average and median values: 36.4 and 20.2 pg m^{-3}) across Lake Ontario. As
303 shown in Figure 2.b, across Lake Erie, atmospheric concentrations were greatest
304 in the urban area of Cleveland (sites E03 and E05), and lowest at the open lake
305 sites (E04 and E08), while concentrations across Lake Ontario were dominated
306 by elevated concentrations at Cape Vincent (site On12). The distribution of
307 atmospheric PCBs differed significantly from that in the water (Figure 2),
308 indicating that there are different sources contributing to either phase. Air-water
309 exchange gradients indicate net volatilization across most sites and seasons (see
310 below). A possible reason is due to PCB volatilization from (contaminated)
311 terrestrial sites. Greater concentrations of gaseous PAHs were also found in
312 Cleveland, and urban centers were considered as their main source.³⁰ As PCBs
313 have been banned in USA and Canada for a long time, their emissions are
314 different from ongoing PAHs emission. It seems reasonable to assume that legacy
315 PCBs in soils along the lakes volatilize back to atmosphere and have become a
316 (secondary) source of gaseous PCBs. Yet Melymuk et al.⁴² also suggested that a
317 major city such as Toronto still has plenty of PCBs in-use in transformers and
318 other uses. Similarly, Khairy et al.²⁹ detected a correlation between land use
319 pattern and atmospheric concentrations of several banned OCPs in the region,
320 and suggested that agriculture soils and urban centers were major sources of the

321 banned OCPs to the air. In their recent work,²⁷ approximately 45% of PCB
322 sources around Lakes Erie and Ontario resemble ‘fresh’ Aroclor mixtures, while
323 27% resemble ‘weathered’ Aroclors; the latter could be attributed to
324 volatilization from contaminated soils/sites, while the former could imply their
325 leaching from in-use equipments.

326

327 **Air-water exchange.**

328 *Fugacity ratios.* Air-water exchange gradients of PCBs are described using
329 their fugacity ratios between air and water. Log-transformed fugacity ratios of
330 selected PCBs are cross plotted in Figure 3 and full data are listed in Table S11.
331 Fluxes not significantly different from equilibrium were defined based on error
332 propagation from PCB and temperature measurement and Henry’s law constant
333 estimation, detailed in the Supporting Information. In Figure 3, air-water fugacity
334 ratios for most congeners were scattered across the ‘evaporation’ or ‘equilibrium’
335 area, namely $\log(f_a/f_w) < 0$, while a few of ratios were located at the area of
336 ‘deposition’, that is $\log(f_a/f_w) \geq 0$. This implies that the primary trend of
337 air-water exchange of PCBs is volatilization from water to air across most sites
338 and seasons. Deposition trends of PCBs at sites E03 (Sheffield), E09 (Dunkirk)
339 and On12 (Cape Vincent) were mostly observed during the 2012 autumn,
340 indicating that atmospheric PCBs are still a source to the Lakes at specified sites
341 and periods. It is worth pointing out that the air-water exchange trends at site
342 E09 (Dunkirk) in 2012 depended mainly on the temperature, namely,
343 volatilization during the warming spring, approaching equilibrium in the
344 summer and deposition in the cooling autumn. Furthermore, we observed a
345 strong temperature dependence of atmospheric PCB concentrations at that site

346 (data in Table S13). These results imply that site E09 is dominated by secondary
347 sources, which changes in flux direction depending on the temperature. Site E09
348 was characterized by low concentrations in both air and water, relative to other
349 sites, supporting the absence of dominant primary sources; this could mean that
350 air-water exchange dominated atmospheric concentration of PCBs at this site.

351 In Figure 3, the $\log(f_a/f_w)$ of PCB 118 is significantly correlated with those of
352 PCB 52, 101, 153 and 180. And such cross-correlation was also widely observed
353 among the 7 PCBs. The Pearson correlation coefficients are listed in Table S14
354 indicating similar transport trends and proportional fugacity gradients in
355 air-water exchange of different congeners. Furthermore, there is a separation
356 between lighter and heavier PCBs. The correlations are weaker between the
357 lighter and heavier PCB. The correlation coefficients depend on similarity of
358 PCBs.

359
360 *Air-water exchange fluxes.* Air-water exchange mass transfer velocities and
361 fluxes of PCBs ($\text{pg m}^{-2} \text{ day}^{-1}$) are listed in Tables S8 and S10, respectively. Mass
362 transfer velocities of PCBs primarily depend on wind speed, temperature, and
363 PCB volatility. The transfer velocity range was 14-98 cm day^{-1} in this study and
364 comparable with the PAH transfer velocities (0.2-73 cm day^{-1}) that McDonough
365 et al. reported.³⁰ Net volatilization fluxes were observed across most sites and
366 deployment periods, indicating discharge of rivers and sediment resuspension
367 were more significant sources of freely-dissolved PCBs than atmospheric
368 deposition. Jeremiason et al. indicated that decreases in aqueous PCB
369 concentrations reflected volatilization loss across Lake Superior.¹⁶ In our work,
370 volatilization fluxes of lighter PCBs were greater than heavier ones (Table S8),

371 and the flux patterns primarily depended on volatility of PCB congeners. Total
372 fluxes of the 7 PCBs during deployment periods are presented in Figure 4. The
373 maximum values of volatilization and deposition flux were observed at site On05
374 (Niagara) in the summer ($9,030 \pm 3070 \text{ pg m}^{-2} \text{ day}^{-1}$) and E03 (Sheffield) in the
375 autumn ($-2,420 \pm 1870 \text{ pg m}^{-2} \text{ day}^{-1}$), respectively. Hornbuckle et al. reported
376 much greater air-water exchange fluxes of 77 PCBs from $-18 \text{ ng m}^{-2} \text{ day}^{-1}$ (net
377 deposition) to $60 \text{ ng m}^{-2} \text{ day}^{-1}$ (net volatilization) in Lake Michigan during
378 1991-1993.⁴³ The significant differences in the fluxes were partly attributed to
379 the difference in wind speeds used by Hornbuckle et al. (5.1 m s^{-1} on average)⁴³
380 and this study (4.2 m s^{-1}). Higher wind speeds yielded higher overall mass
381 transfer velocities which significantly increased the calculated flux. In addition,
382 Hornbuckle et al. used active sampling, which, particularly in the water phase
383 might lead to increased 'apparent' dissolved concentrations, which would also
384 increase derived water-to-air fluxes.

385 Strong deposition fluxes were observed only at sites of E03 (Sheffield) and
386 On12 (Cape Vincent) and were driven by the higher concentrations of
387 atmospheric PCBs at the two sites.

388 In Lake Ontario, higher volatilization fluxes were mostly observed along the
389 US shores ($2,220-9,030 \text{ pg m}^{-2} \text{ day}^{-1}$ with average value of $4,690 \text{ pg m}^{-2} \text{ day}^{-1}$),
390 compared with those in Canada ($97-7,390 \text{ pg m}^{-2} \text{ day}^{-1}$ with average of $1,390 \text{ pg}$
391 $\text{m}^{-2} \text{ day}^{-1}$). The surprising difference of fluxes at site On08 (Cobourg) was
392 primarily related to differences of wind speeds (4.4 and 6.0 m s^{-1}) and
393 concentrations of freely-dissolved PCBs (1.9 and 9.6 pg L^{-1}) during two
394 deployment periods. The difference in wind speed translated in a ~ 2.7 times
395 difference in mass transfer velocities at the two deployment periods. Air-water

396 exchange was approaching equilibrium at the sites with lower concentrations of
397 gaseous and freely-dissolved PCBs, e.g., at the eastern basin of Lake Erie and the
398 Canadian shores in Lake Ontario, implying air-water exchange dominated
399 atmospheric PCB concentrations at these regions. The (near) equilibrium
400 conditions could be related to the deeper water at those sites which weakened
401 the PCB contribution from sediment resuspension.

402 Pearson correlation analysis was performed between total fluxes of the 7
403 PCBs and wind speeds, temperatures, atmospheric and aqueous concentrations.
404 Results show that the total fluxes showed a strongly significant negative
405 correlation with atmospheric concentrations, and a strongly significant positive
406 correlation with aqueous concentrations. Hence, stepwise multiple linear
407 regression analysis was conducted to explore primary factors influencing the
408 variability in the magnitude and direction of fluxes in this case. Standardized
409 normal deviations of wind speeds, temperatures, atmospheric and aqueous
410 concentrations and the total fluxes were used as independent and dependent
411 variables, respectively. Variability of the total flux was explained by the four
412 factors (R square = 0.86, $p < 0.001$). The major contributor was aqueous
413 concentration, accounting for 47%. Contributions of atmospheric concentration,
414 wind speed and temperature were 23%, 20% and 10%, respectively. Accordingly,
415 spatial variation of air-water exchange fluxes of PCBs primarily depended on
416 aqueous concentrations. Nevertheless, all factors caused changes in direction
417 and the magnitude of air-water exchange to different extent.

418

419 **IMPLICATIONS**

420 This study demonstrated that monitoring concentrations of PCBs based on

421 passive sampling method is useful to better understand their spatial distribution
422 and behavior, and quantify fluxes between air and water in the lower Great
423 Lakes. Although there may be differences in atmospheric concentrations
424 between passive and active sampling methods, enhanced passive sampling
425 deployments are a logical choice for establishing spatial pattern of atmospheric
426 PCBs. The passive sampling method can be considered as one of complementary
427 methods of active sampling already occurring in the IADN project, enabling a
428 high geospatial resolution and easy storage of duplicate samples as historical
429 record (multiple LDPE sheets in same sampler). In the same vein, utilizing
430 passive samplers for measuring freely-dissolved concentrations will help screen
431 on-going emissions of PCBs to the Great Lakes. Spatial distribution patterns of
432 freely-dissolved PCBs were attributed to river discharge, water circulation
433 pattern and sediment resuspension. Both Lakes display fairly similar PCB
434 concentrations, based on the results presented here, and supported by previous
435 studies, air-water exchange fluxes were either near equilibrium or favored net
436 volatilization. In light of these results, the similarity in freely-dissolved PCB
437 concentrations in both lakes could be fortuitous, driven by contaminated sites
438 and river discharges, rather than resulting from atmospheric deposition.
439 Meanwhile, more sampling sites are needed along Canada shores in Lake Erie
440 and in open lakes to improve knowledge on occurrence, source and transport of
441 semi-volatile organic compounds in the lower Great Lakes.

442

443 **ASSOCIATED CONTENT**

444 **Supporting Information**

445 Detailed information on sampler deployment, PCB properties can be found along
446 with calculated sampling rates and overall mass transfer velocities, atmospheric
447 and aqueous concentrations. This material is available free of charge via the
448 Internet at [Http://pubs.acs.org](http://pubs.acs.org).

449

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453 **Notes**

454 The authors declare no competing financial interest.

455

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463 Analytical Laboratories, and Research Support group (Environment Canada
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465 Environment for near-shore deployments along Lake Ontario.

466

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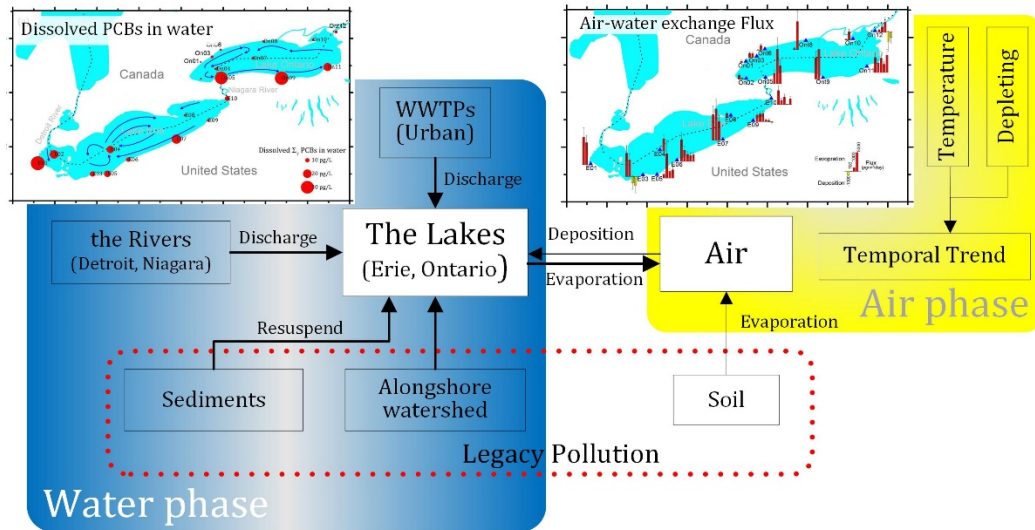
588 **FIGURE CAPTIONS**

589 Figure 1. Comparison of aqueous (a) and atmospheric (b) total concentrations of
590 29 PCBs in Lakes Erie and Ontario.

591 Figure 2. Average aqueous (a) and atmospheric (b) concentrations of Σ_7 PCBs in
592 lakes of Erie and Ontario. Water circulation as described by Beletsky et
593 al.,⁴⁴ and prevailing wind direction provided by Wind History.⁴⁵

594 Figure 3. Cross plots of log-transformed fugacity ratios between air (f_a) and
595 water (f_w) in different sampling sites.

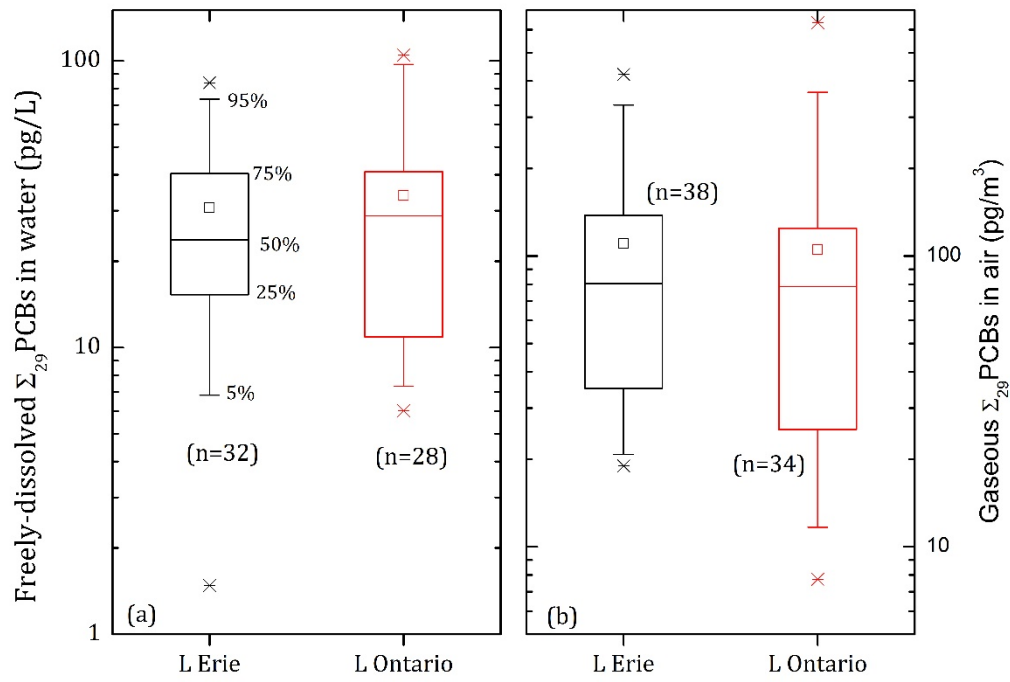
596 Figure 4. Air-water exchange flux of Σ_7 PCBs.



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598 ABSTRACT ART

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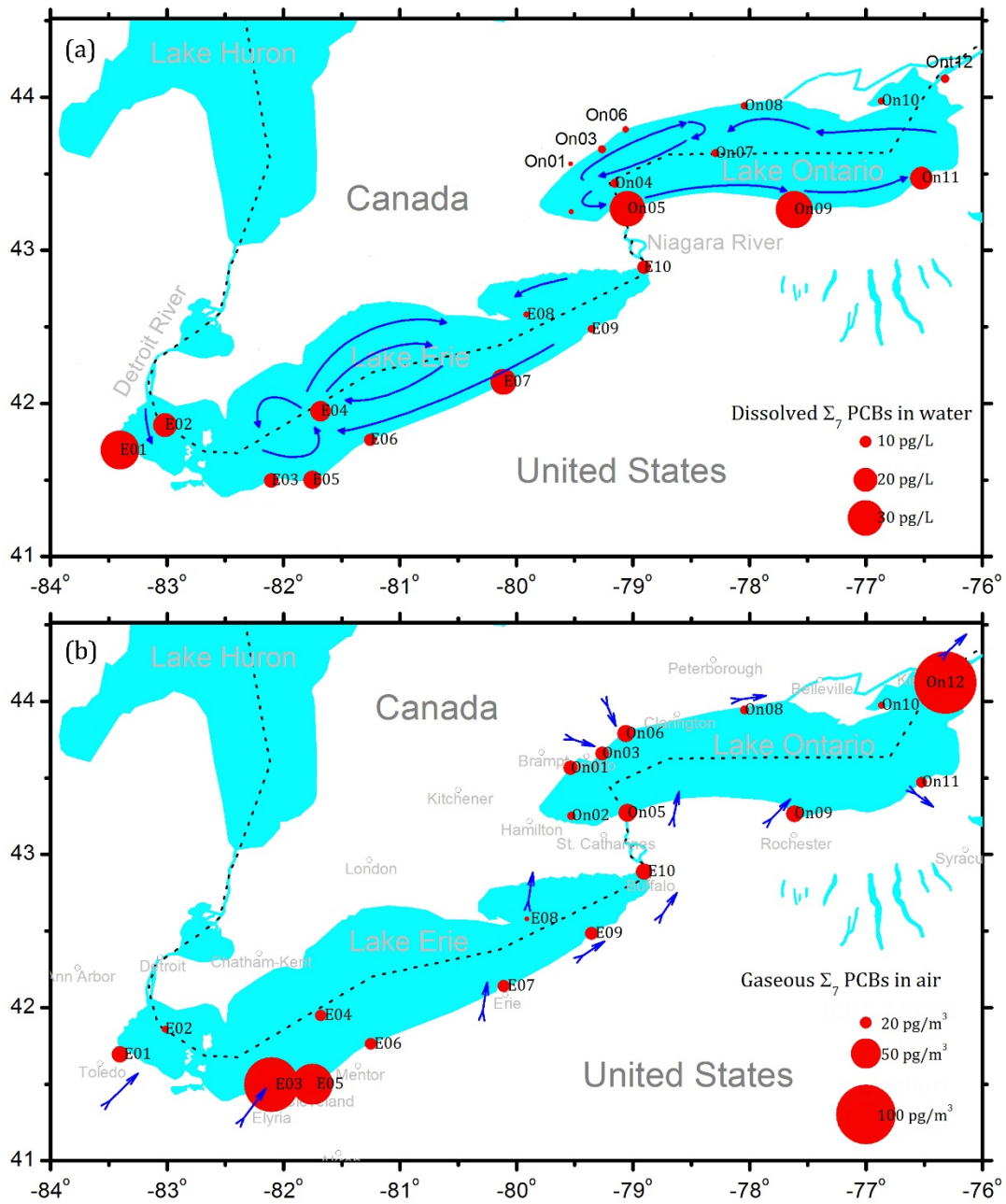


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 603 29 PCBs in Lakes Erie and Ontario.

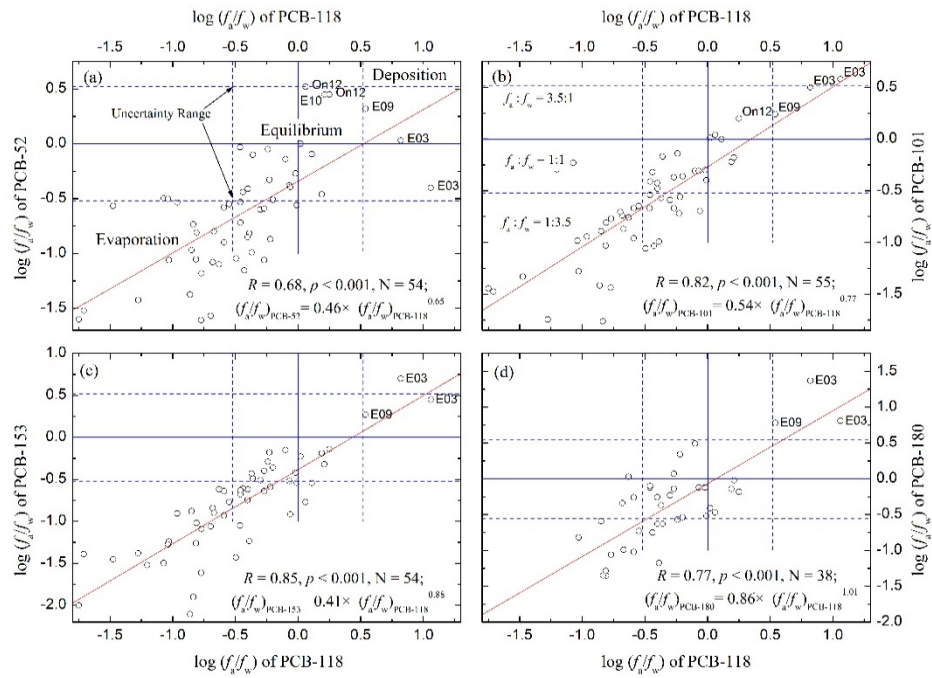
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607 Figure 2. Average aqueous (a) and atmospheric (b) concentrations of Σ_7 PCBs in
 608 Lake Erie and Ontario. Water circulation as described by Beletsky et
 609 al.,⁴⁴ and prevailing wind direction provided by Wind History.⁴⁵

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Figure 3. Cross plots of log-transformed fugacity ratios between air (f_a) and water (f_w) in different sampling sites. The blue line represents equilibrium, and the dashed blue lines represent the uncertainty range around the equilibrium.

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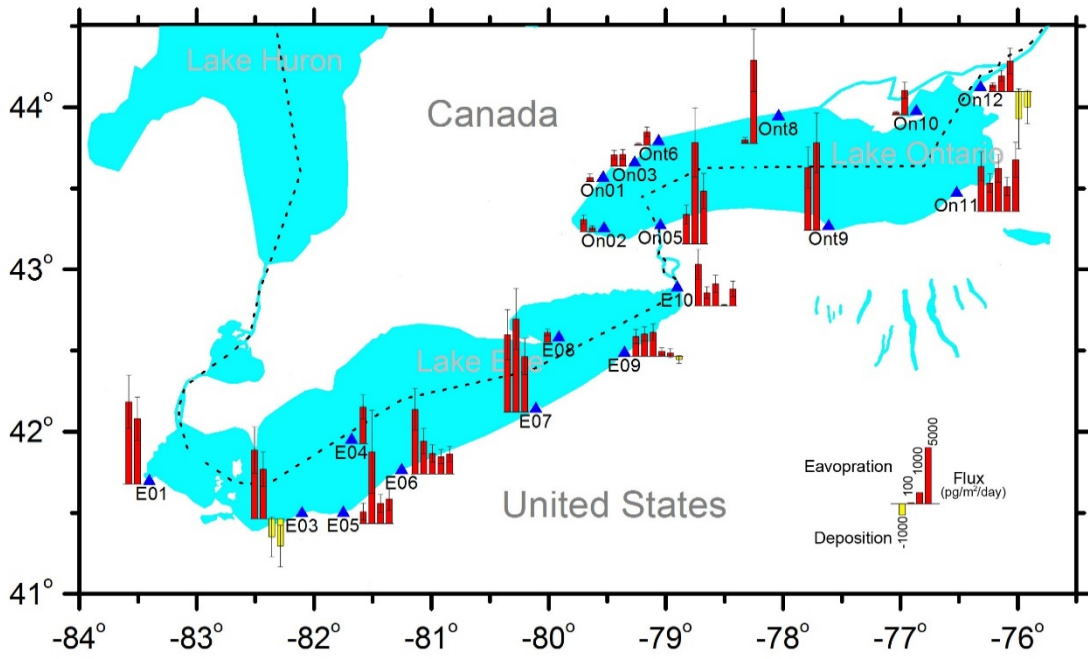
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621 Figure 4. Air-water exchange flux of Σ₇PCBs.

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