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1 THE SIGNIFICANCE OF POPULATION CENTERS AS SOURCES OF GASEOUS AND  
2 DISSOLVED PAHS IN THE LOWER GREAT LAKES

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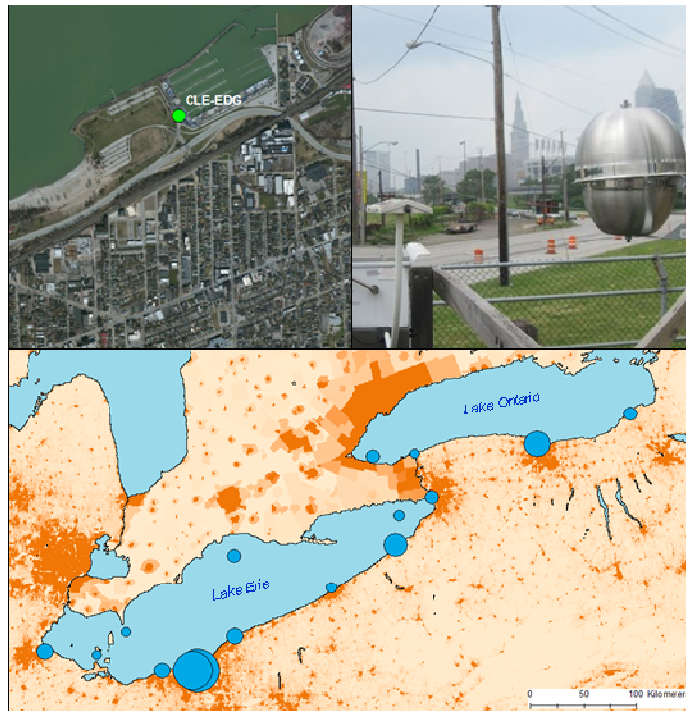
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9 **TOC ART**



11 **ABSTRACT**

12 Polyethylene passive samplers (PEs) were used to measure concentrations of gaseous and  
13 dissolved polycyclic aromatic hydrocarbons (PAHs) in the air and water throughout the lower  
14 Great Lakes during summer and fall of 2011. Atmospheric  $_{15\text{PAH}}$  concentrations ranged from 2.1  
15  $\text{ng/m}^3$  in Cape Vincent (NY) to 76.4  $\text{ng/m}^3$  in downtown Cleveland (OH). Aqueous  $_{18\text{PAH}}$   
16 concentrations ranged from 2.4  $\text{ng/L}$  at an offshore Lake Erie site to 30.4  $\text{ng/L}$  in Sheffield Lake  
17 (OH). Gaseous PAH concentrations correlated strongly with population within 3-40 km of the  
18 sampling site depending on the compound considered, suggesting that urban centers are a  
19 primary source of gaseous PAHs (except retene) in the lower Great Lakes region. The  
20 significance of distant population (within 20 km) versus local population (within 3 km) increased  
21 with sub-cooled liquid vapor pressure. Most dissolved aqueous PAHs did not correlate  
22 significantly with population, nor were they consistently related to river discharge, wastewater  
23 effluents, or precipitation. Air-water exchange calculations implied that diffusive exchange was a  
24 source of phenanthrene to surface waters, while acenaphthylene volatilized out of the lakes.  
25 Comparison of air-water fluxes with temperature suggested that the significance of urban centers  
26 as sources of dissolved PAHs via diffusive exchange may decrease in warmer months.

27

28

## 29 INTRODUCTION

30 Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants that originate from  
31 oil spills as well as anthropogenic and natural combustion processes. Major sources include  
32 fossil fuel combustion, metal production, waste incineration, residential and commercial biomass  
33 burning, and vehicular emissions.<sup>1-5</sup> PAHs are often associated with densely populated areas,  
34 especially in industrialized countries.<sup>3,4,6,7</sup> PAHs and their transformation products are a primary  
35 carcinogenic component of urban air pollution and health effects resulting from chronic exposure  
36 are a serious concern.<sup>8,9</sup>

37 Polyethylene passive samplers (PEs) are cost-effective, simple tools with lower detection  
38 limits than traditional active sampling techniques. Instead of pumping air or water through a  
39 filter, PEs accumulate hydrophobic organic contaminants (HOCs) over time via diffusion,  
40 accumulating only truly dissolved or gas-phase molecules.<sup>10</sup> Concentrations of truly dissolved  
41 HOCs are of interest because this fraction is available for direct diffusive exchange between  
42 water and other reservoirs such as air, biota, or sediment.

43 The use of PEs facilitates simultaneous spatially resolved measurements and calculations  
44 of air-water diffusive exchange rates. For most HOCs, concentrations measured by PEs reflect a  
45 time-integrated concentration representative of the entire deployment period. For compounds  
46 that equilibrate during deployment, concentrations reflect the most recent concentration the  
47 sampler was exposed to. PEs have previously been used to measure HOCs in water and air<sup>11-13</sup>  
48 and to calculate air-water gradients of HOCs, but this method has not been applied to the lower  
49 Great Lakes.<sup>14-16</sup>

50 Lake Erie and Lake Ontario are the smallest of the Great Lakes by volume and have  
51 estimated residence times of 2.7 and 7.5 years, respectively.<sup>17</sup> About 80% of Lake Erie's water is

52 supplied by the Detroit River, which is fed by Lake Huron via Lake St. Claire. Among the Great  
53 Lakes, Lake Erie is the shallowest (average depth 19 m), warmest, and most biologically  
54 productive.<sup>18,19</sup> Lake Ontario is much deeper (average depth 86 m) and primarily receives water  
55 from Lake Erie via the Niagara River.<sup>19</sup> Currents in the Great Lakes are weak (a few cm/s) with  
56 complex temporal variability that depends on recent atmospheric conditions. In the summertime,  
57 circulation is generally counterclockwise.<sup>20</sup> The lakes are stratified from May through October  
58 and well-mixed for the remainder of the year.<sup>20</sup>

59 Heavy urbanization and valuable ecosystems often coincide along the shores of the lower  
60 Great Lakes. Atmospheric deposition from urban sources has been identified as a major source  
61 of gaseous and particle-bound HOCs to the region's aquatic environment.<sup>2,7,21,22</sup> Concentrations of  
62 total atmospheric PAHs have been shown to correlate strongly with population in this region and  
63 urban centers have been linked to significantly increased loadings of contaminants to the  
64 lakes.<sup>23,24</sup> In some cases, however, the lakes have been found to act as a source of HOCs via  
65 revolatilization.<sup>25,26</sup> Much of the previous work describing sources of atmospheric pollution to the  
66 Great Lakes is based on a limited number of air monitoring sites as part of the Integrated  
67 Atmospheric Deposition Network (IADN). While this data is indispensable in determining  
68 baseline concentrations and temporal trends of POPs in the Great Lakes, more detailed  
69 knowledge of spatial trends is crucial to identify major sources and transport pathways.

70 The objectives of this study were to (1) provide baseline concentrations of gaseous and  
71 dissolved PAHs in Great Lakes air and water, (2) evaluate the importance of urban regions as  
72 sources of dissolved PAHs by investigating the relationship between population and PAH  
73 concentration, and (3) determine whether the lower Great Lakes are sources or sinks for  
74 dissolved PAHs.

## 75 **MATERIALS AND METHODS**

76 **Passive Sampling Procedures.** A map of all air and water sites and a table outlining temporal  
77 coverage and meteorology are provided in the Supporting Information (Figure S1, Table S1 &  
78 S2) along with information on sampler preparation and deployment. PEs were spiked with  
79 performance reference compounds (PRCs) via a method adapted from Booij et al.<sup>27</sup> and sent to  
80 trained volunteers throughout the Great Lakes region with the aim of completing three 8-week  
81 deployments at each site. After deployment, volunteers returned samplers via overnight delivery.

82 Four sites formed an east-west transect along Lake Ontario's southern shore. The  
83 westernmost site, Grimsby (ON), was an offshore buoy monitored by Environment Canada. On  
84 Lake Erie, samplers were deployed at nine US shoreline sites and six offshore sites monitored by  
85 Environment Canada. Samplers were deployed at the offshore sites once, during late summer.  
86 Samplers at Gibraltar Island (OH) and Toledo (OH) were deployed once during late spring/early  
87 summer.

88 **Meteorological Information & Site Characteristics.** Monthly wind speed averages during the  
89 sampling campaign ranged from 3.8 m/s in July to 6.1 m/s in November, with the greatest  
90 average wind speeds offshore of Toledo. Average air temperatures ranged from 7.7°C in April to  
91 24.3°C in July and the mean deployment temperature for all sampling periods was 18.6±1.8 °C.  
92 Surface water temperatures were generally very similar to air temperatures and ranged from  
93 3.7°C (Lake Ontario in May) to 25.1°C (Lake Erie in July).<sup>28</sup> There were westerly prevailing  
94 winds during the sampling campaign for most of the study region (Figure S2).<sup>29</sup> Precipitation and  
95 river discharge were lowest during June and July while flows in late spring and early fall were  
96 similar.<sup>30</sup> Locations near major rivers are listed in Table S4.

97 **Sample Analysis.** All PEs were spiked with deuterated PAHs and extracted twice, each time for  
98 18 hours. Air PEs were extracted with ethyl acetate followed by hexane. Aqueous PEs were  
99 extracted with dichloromethane followed by hexane. Extracts were concentrated to

100 approximately 100  $\mu\text{L}$  and p-terphenyl- $\text{d}_{14}$  was added as an injection standard. Extracts were  
101 analyzed using an Agilent 6890 GC coupled to an Agilent 5973 MSD in EI+ selected ion  
102 monitoring (SIM) mode. PAH analysis and quality control procedures are further outlined by  
103 Khairy et al.<sup>11</sup>

104 PAH concentrations were corrected for internal standard recoveries (Table S5) and blank-  
105 subtracted using the field blank relevant to the sampling site. If no field blank for the site was  
106 available, the average concentration from all available field blanks was used. More information  
107 on quality assurance and quality control is in the Supporting Information.

108  
109 **Determination of Sampling Rate and Ambient Concentration.** The uptake of HOCs by PEs is  
110 described in detail by Lohmann<sup>31</sup> and PE-air partitioning is detailed by Khairy et al.<sup>11</sup> To  
111 determine ambient PAH concentrations from concentrations in polyethylene, site-specific  
112 sampling rates were estimated via a method adapted from Booij et al.<sup>32</sup> Further details are  
113 provided in the Supporting Information. The average air sampling rate was  $28 \pm 17 \text{ m}^3/\text{day}$  and the  
114 average aqueous sampling rate was  $112 \pm 57 \text{ L/day}$  (for more details, see SI and Tables S1 and  
115 S2).

116 **Physico-chemical Parameters.** Sampler-matrix partition coefficients ( $T=25^\circ\text{C}$ ) used to calculate  
117 ambient concentrations for each PAH are listed in Table S7, along with other physico-chemical  
118 properties. Temperature-adjusted partition coefficients were obtained using mean temperature  
119 during the deployment period for the nearest meteorological buoy or weather station and the  
120 modified van't Hoff equation, as in Khairy et al.<sup>11</sup> The enthalpy of vaporization ( $H_{\text{vap}}$ ) was used  
121 to account for  $K_{\text{PEA}}$ -temperature sensitivity and internal energy of dissolution ( $U_{\text{w}}$ ) for  $K_{\text{PEW}}$ -  
122 temperature sensitivity.



123 **Population Analysis.** Population data for each sampling site are presented in Table S8. Total  
124 population within a circular area with a 1-cell (about 1 km) radius was calculated using the Focal  
125 Statistics tool in ArcMap. The process was repeated for larger radii to create a dataset of the total  
126 population within 1, 2, 3, 5, 10, 15, 20, 25, 30, 40, and 50 km of each of the sampling locations.  
127 More information about the population dataset used is available in the Supporting Information.

128 **Air-Water Exchange Rates.** The difference in equilibrium concentrations of an HOC in two  
129 PEs deployed in different matrices is proportional to the difference in the compound's chemical  
130 activity between those two matrices.<sup>14,15</sup> Air-water exchange gradients can therefore be  
131 determined from the ratio of PAH concentrations in PEs deployed simultaneously in air and  
132 water, corrected to equilibrium concentrations using PRC loss data. Details of air-water  
133 exchange calculations are shown in the Supporting Information.

## 134 **RESULTS AND DISCUSSION**

135 **PAHs in Air.** Average atmospheric  $\Sigma_{15\text{PAH}}$  ranged from 2.1 ng/m<sup>3</sup> in Cape Vincent (NY) to 76.4  
136 ng/m<sup>3</sup> at George T. Craig air sampling station in downtown Cleveland (OH). The spatial  
137 distribution of  $\Sigma_{15\text{PAH}}$  is shown in Figure 1A. Concentrations of all PAHs during each deployment  
138 are detailed in Table S9. Gaseous PAHs were dominated by phenanthrene (28 – 60%) and  
139 fluorene (6 – 48%) (Figure S4). Typical concentrations ranged from below the detection limit to  
140 40.3 ng/m<sup>3</sup> and 14.6 ng/m<sup>3</sup> for phenanthrene and fluorene, respectively. Methylphenanthrenes  
141 accounted for 3 - 5% of  $\Sigma_{15\text{PAH}}$  at the offshore sites and 6 - 10% of  $\Sigma_{15\text{PAH}}$  at shoreline sites. 4-5-ring  
142 PAHs made up no more than 10% of total PAHs, with PAHs of greater molecular weight than  
143 chrysene (high molecular weight (HMW) PAHs) accounting for <1% of  $\Sigma_{15\text{PAH}}$ . Ratios of gaseous  
144 Flra/Flra+Pyr were • 0.6 and Phn/ MPhns > 1 at all sites, suggesting that gaseous PAHs were  
145 primarily combustion-derived.<sup>33</sup>

146 The two sites in Cleveland consistently displayed the greatest concentrations of gaseous  
147 PAHs except retene throughout the deployment season. Retene is often considered to be  
148 indicative of wood smoke or pulp/paper mill effluent, as opposed to fossil fuel combustion.<sup>34,35</sup>  
149 Retene was greatest west of Cleveland in Sheffield Lake, but even here accounted for less than  
150 0.7% of total gaseous PAHs. In contrast, Ruge found retene to be a significant component of  
151 gaseous PAH profiles at many sites on Lake Superior.<sup>36</sup>

152 Principal component analysis (PCA) using the FactoMineR package<sup>37</sup> in the statistical  
153 programming language R<sup>38</sup> was employed to visualize similarities and differences between PAH  
154 profiles (Figure S5). Profiles were similar at all sites with the exception of Sheffield Lake,  
155 Rochester, and the Cleveland sites, which were clustered separately. The clustering of most sites  
156 in the same region of the plot suggests that sources of PAHs were similar across the study region.  
157 Profiles in Cleveland may have been distinct due to nearby point sources. In addition to impacts  
158 from vehicular emissions associated with heavy traffic in downtown areas, these sites were  
159 within 5 km of a greater number of industrial point sources (primarily chemical manufacturing,  
160 petroleum industry, and metalworking facilities) when compared to the other sites using the EPA  
161 Toxic Release Inventory (TRI).<sup>39</sup>

162 ***Comparison with Literature Values.*** Sun et al. reported mean gaseous concentrations for  
163 the 1990s to 2003 of 16 PAHs, 13 of which were measured here.<sup>23</sup> They reported 7.2 ng/m<sup>3</sup> at  
164 Sturgeon Point, a semi-urban site south of Buffalo, 1.2 ng/m<sup>3</sup> at Point Petre, a northern Lake  
165 Ontario site representative of background, and 73.4 ng/m<sup>3</sup> in Chicago (IL).<sup>23</sup> Concentrations of  
166 individual PAHs in Cleveland reported here were comparable to those reported by IADN for  
167 Chicago. Gaseous PAH profiles showed dominance of phenanthrene and fluorene, as reported  
168 here.

169 PAH concentrations in this study were comparable to those measured by Ruge at urban  
170 locations along the shore of Lake Superior.<sup>36</sup> Melymuk et al. measured a total gaseous PAH  
171 concentration of 51 ng/m<sup>3</sup> in downtown Toronto (ON), comparable to Cleveland and Rochester  
172 concentrations in this study.<sup>6</sup> Concentrations in this study were lower than those reported for  
173 Alexandria, Madrid, or Lake Chaohu, China and greater than concentrations on the Taiwan  
174 coast.<sup>11,40-42</sup> Total (aerosol and dissolved) 2-3-ring PAHs near Lake Victoria, East Africa were  
175 lower than 2-3-ring gaseous PAHs in Cleveland, but greater than the remainder of the  
176 deployment sites.<sup>43</sup>

177 ***Gaseous PAHs and Population.*** Sampling sites were classified as urban, semi-urban,  
178 rural, or remote based on population within 3 km (Table S8). Mean  $\Sigma_{15\text{PAH}}$  for each type of site are  
179 summarized in Table 1. For both lakes, the greatest concentrations of gaseous PAHs were  
180 observed at urban sites. However,  $\Sigma_{15\text{PAH}}$  was not significantly different based on site classification  
181 using a one-way ANOVA ( $p > 0.05$ ). There were no obvious changes in PAH profile  
182 composition based on whether the site was urban, semi-urban, rural, or remote (Figure S4).

183 To explore relationships with population in more detail, population within discrete radii  
184 of 1 to 40 km from each site were compared to average atmospheric PAH concentrations to  
185 determine the importance of local versus distant contributions in determining PAH  
186 concentrations. Total gaseous PAHs correlated most strongly with population within a 20 km  
187 radius around each site ( $r^2_{20\text{ km}} = 0.73$ ,  $p < 0.001$ ,  $n = 17$ ,  $\text{SE}=11.3$ ) (Figure 2). Significant  
188 correlations ( $0.58 < r^2 < 0.77$ ,  $p < 0.001$ ) were observed for all measured PAHs at some radius,  
189 with retene exhibiting the weakest correlation ( $r^2_{1\text{ km}} = 0.30$  at a radius of 1 km,  $p = 0.02$ ,  
190  $\text{SE}=0.02$ ). This is most likely due to retene's association with wood smoke, as opposed to fossil  
191 fuel combustion.<sup>34, 35</sup> Strong correlations suggest that urban centers are a primary source of  
192 gaseous PAHs (except retene) in the lower Great Lakes region.

193 For each PAH, the strength of the correlation between population and concentration  
194 varied as we changed the radius used to characterize population at the site (Figure 3). All  
195 compounds except retene displayed a bimodal relationship, with two radii of maximum  
196 correlation. This relationship was less pronounced for the low molecular weight (LMW) PAHs  
197 than HMW PAHs. Strong similarities between correlation profiles (e.g., the 5-ring PAHs)  
198 suggest similar sources and affinities for transport.

199 Hafner and Hites suggested that the significance of local sources in determining Great  
200 Lakes HOC concentrations varies based on a compound's atmospheric lifetime.<sup>7</sup> The  
201 atmospheric lifetimes of gaseous PAHs is determined primarily by susceptibility to hydroxyl  
202 degradation and gas-particle partitioning.<sup>7</sup> Anthracene exhibited a distinctly shaped correlation  
203 curve with two maxima at radii 25 km ( $r_{25\text{ km}}^2 = 0.77$ ) and 5 km ( $r_{5\text{ km}}^2 = 0.77$ ). Anthracene has a  
204 shorter lifetime (1.5 hrs) with respect to hydroxyl radical degradation relative to other PAHs,  
205 which may explain why stronger correlation is observed at short distances than for other 3-ring  
206 PAHs.<sup>44,45</sup> However this does not explain the comparable correlation at 25 km. Acenaphthylene is  
207 expected to have a similar lifetime to anthracene (1.6 hrs)<sup>44</sup> and exhibited stronger correlations  
208 with more local population than fluorene (Figure 3).

209 Fluorene is often observed to be more stable with respect to photochemical oxidation  
210 than similarly-sized PAHs (average lifetime 22 - 26 hrs),<sup>44,46</sup> but more distant sources did not  
211 become more significant for this compound due to its longer lifetime. Fluorene correlated less  
212 strongly with population than acenaphthylene at all radii, but the divergence was largest at  
213 shorter distances. Gaseous HMW PAHs are expected to have short atmospheric residence times  
214 due to reaction with hydroxyl radicals, which may contribute to the increased relevance of local  
215 versus long-range sources that was observed for these compounds.<sup>7</sup> These results suggest that  
216 reaction with hydroxyl radicals limited the importance of sources distant from sampling sites.

217 The degree to which a given PAH partitions from gaseous to particulate phase, and thus  
218 is not detected by PEs, depends on the composition and concentration of ambient aerosol as well  
219 as temperature and vapor pressure.<sup>47-49</sup> Sub-cooled liquid vapor pressures ( $p_L$ /Pa) for all PAHs  
220 (except methylphenanthrenes and retene, for which data was not available) were determined for  
221 average deployment temperature (18.6°C) using empirical regressions from Paasivirta et al.<sup>50</sup> Log  
222 ( $p_L$ /Pa) was plotted against the radius where maximum population-concentration correlation was  
223 seen for each compound in Figure S6. Excluding anthracene, PAHs with  $p_L > 10^{-4}$  Pa were most  
224 highly correlated with population within a 20 km radius, while PAHs with  $p_L < 10^{-4}$  Pa were most  
225 highly correlated with population within 3 km. Other studies have observed similar values for  
226  $\log(p_L)$  at which PAHs transition from being primarily gaseous to particle-bound.<sup>26,51,52</sup>

227 While Figure S6 highlights maximum correlation, many PAHs exhibited significant  
228 correlation with population at both 20 km and 3 km. As shown in Figure 4, the relative  
229 significance of correlation at 20 km versus 3 km ( $r_{20\text{ km}}^2/r_{3\text{ km}}^2$ ) was significantly correlated with  
230  $\log(p_L)$  ( $r^2 = 0.62$ ,  $p < 0.005$ ,  $n = 13$ ,  $\text{STE} = 0.1$ ), suggesting the existence of two sources of  
231 varying importance depending on PAH volatility. The relatively greater importance of local  
232 sources in determining concentrations of gaseous HMW PAHs could be due to the partitioning of  
233 these compounds to relatively cleaner background aerosols at remote sites as described by  
234 Gustafson et al.<sup>53</sup> Due to their lower vapor pressure, gaseous HMW PAHs are more likely than 2-  
235 3-ring PAHs to partition into the particulate phase where they will not be measured by PEs and  
236 may be deposited more readily via wet or dry deposition.<sup>42,54,55</sup>

237 Previous studies have reported that coastal areas receiving cleaner air from over water  
238 bodies exhibit lower atmospheric PAH concentrations than would be predicted based on  
239 surrounding population.<sup>56</sup> Concentrations of total atmospheric PAHs were lower in Buffalo and  
240 Oswego than Cleveland or Rochester, though these sites were classified similarly in terms of

241 population. One explanation is that prevailing westerly winds brought over-lake air towards  
242 Buffalo and Oswego, diluting the urban plume. Offshore measurements confirmed that air  
243 masses over Lake Erie had relatively lower PAH concentrations than shoreline sites (Table 1).  
244 Likewise, the offshore site near Grimsby was closer to the shoreline and more likely to be  
245 impacted by westerly air masses arriving over land from Hamilton (ON).

246 To further explore this hypothesis, 6-hour HYSPLIT back trajectories were calculated  
247 every 24 hours during the entire deployment period at Cleveland, Buffalo, Rochester, and  
248 Oswego using EDAS 40km archived meteorology . The number of trajectories arriving from  
249 over water versus over land was counted (Table S3). This analysis supports the idea that  
250 Oswego's urban plume could be diluted by over-water air masses, but shows that Buffalo and  
251 Cleveland received similar amounts of air traveling from over water and over land.

252 Another explanation for lower concentrations at Oswego and Buffalo could be the  
253 amount or type of industry nearby. EPA TRI<sup>39</sup> reported 109, 54, and 37 regulated facilities within  
254 20 km of Cleveland Edgewater, Buffalo, and Rochester, respectively, but there were only 4  
255 within 20 km of Oswego. However, this does not explain lower PAH concentrations at Buffalo  
256 and it is difficult to use the TRI data to accurately gauge the volume of relevant emissions near  
257 each site.

258 **PAHs in Water.** Average concentrations of  $_{18\text{PAH}}$  ranged from 2.38 ng/L off Long Point (Stn  
259 452) to 30.4 ng/L in Sheffield Lake, directly west of Cleveland (Figure 1B, Table S10). Average  
260 dissolved  $_{18\text{PAH}}$ s, shown in Table 1, were somewhat greater in Lake Erie than in Lake Ontario  
261 when similar sites were compared, but not significantly (one-way ANOVA,  $p > 0.05$ ). Dissolved  
262  $_{18\text{PAH}}$  exhibited less spatial variation (STDEV = 6.3 ng/L) than gaseous  $_{15\text{PAH}}$  (STDEV = 19.6  
263 ng/m<sup>3</sup>).

264 Aqueous PAHs were dominated by phenanthrene (8 – 41%; <DL - 2.4 ng/L),  
265 fluoranthene (9 – 37%; <DL - 8.7 ng/L), and pyrene (8 – 31%; <DL - 8.5 ng/L) (Figure S4B).  
266 Methylphenanthrenes accounted for 7 – 11% of  $_{18\text{PAH}}$  at the offshore sites and 11 – 35% of  $_{18\text{PAH}}$   
267 at shoreline sites. HMW PAHs accounted for <2% of  $_{18\text{PAH}}$  at all sites. Retene accounted for 0.1 –  
268 2%  $_{18\text{PAH}}$  and was greatest in Oswego (NY). The diagnostic ratio Phn/ MPhn ranged from 0.6 at  
269 Fairport Harbor and Sheffield Lake to 3.7 at the central and eastern Lake Erie buoy sites. Ratios  
270 of Flra/Flra+Pyr were > 0.5 at all sites except Gibraltar Island (Flra/Flra+Pyr = 0.3, Phn/ MPhn =  
271 1.2) suggesting that dissolved PAHs originated primarily from combustion, with possible  
272 contributions from petroleum spills at Gibraltar.<sup>14,33</sup>

273 PCA results for dissolved PAHs showed locations clustered differently than for gaseous  
274 PAH composition, suggesting that source profiles differed for atmospheric and aqueous PAHs.  
275 This may be because in addition to atmospheric deposition, runoff and sediment-water exchange  
276 contributed to dissolved concentrations. The dissolved PAH profile was most distinct at  
277 Sheffield Lake, while Toledo and Buffalo, both expected to be impacted by river discharge, were  
278 clustered together (Figure S5).

279 ***Comparison with Literature Values.*** Dissolved PAH concentrations were similar to  
280 those reported by Ruge for heavily impacted sites on Lake Superior.<sup>36</sup> Previous work in Lake  
281 Michigan reported average total dissolved aqueous PAH concentrations of 9 ng/L from  
282 shipboard measurements, which was similar to the mean dissolved  $_{18\text{PAH}}$  concentration of all sites  
283 in this study (9.1 ng/L).<sup>2</sup> Concentrations reported here were generally greater than surface waters  
284 of Narragansett Bay (RI)<sup>14</sup> or the Patapsco River (MD),<sup>57</sup> though maximum concentrations  
285 measured on the Patapsco exceeded maximum concentrations measured here. Concentrations  
286 were lower than dissolved PAHs in a freshwater lake in China.<sup>42</sup> PAH profiles were similar to  
287 those reported for Narragansett Bay.<sup>14</sup>

288 *Potential Sources of Dissolved PAHs.* Linear correlation with population was not  
289 significant ( $r^2 < 0.3$ ,  $p > 0.05$ ) for dissolved PAHs, with the exception fluorene ( $r^2_{15km} = 0.36$ ,  $p <$   
290  $0.05$ ), perylene ( $r^2_{1km} = 0.38$ ,  $p < 0.01$ ), and retene ( $r^2_{1km} = 0.59$ ,  $p < 0.001$ ). The explanation for  
291 correlations observed for these three compounds is unknown. One possible reason for the weak  
292 correlation for most aqueous PAHs is that the two most populated sites in downtown Cleveland  
293 were absent from the aqueous dataset. Aqueous sampling near Cleveland was not done at the  
294 same sites as air sampling, rather PEs were deployed further from shore.

295 The lack of strong correlations also suggests that sources other than atmospheric  
296 deposition, such as river discharge and WWTP effluent, could have been significant in  
297 determining dissolved PAH concentrations in surface waters. In addition, longer-term reservoirs  
298 that are not representative of current emissions, such as PAHs from sediments or from deeper in  
299 the water column, could be contributing to surface concentrations so that aqueous concentrations  
300 reflect longer term deposition while atmospheric concentrations reflect recent emissions.  
301 However, summertime stratification occurring throughout most of the sampling period is  
302 expected to reduce the importance of these contributions.

303 Concentrations at offshore Lake Erie sites were greatest in the western basin where the  
304 lake is shallowest and inputs from the Detroit and Maumee watersheds, both AOCs, were  
305 expected to be significant (Figure S3A). Due to the central Erie basin's counterclockwise  
306 circulation during the study season,<sup>20</sup> it is unlikely that elevated dissolved PAHs in Sheffield  
307 Lake resulted from aqueous transport from Cleveland. Black River, a historically polluted AOC,  
308 discharges 8 km west of the Sheffield Lake site and may have contributed to dissolved PAH  
309 concentrations there. More measurements over time are needed to determine whether elevated  
310 dissolved PAHs at Sheffield Lake were episodic or chronic. Unexpectedly, concentrations near  
311 Cleveland were lower than at Sheffield Lake. This may be because of sampler placement, as PEs



312 at Cleveland were farther offshore where water was deeper and currents carrying more highly  
313 impacted water may have been entrained closer to the shore.

314 Besides Sheffield Lake, the greatest dissolved PAHs were measured in Toledo, Buffalo,  
315 and Erie. Average dissolved PAH concentrations in Erie sampled from early June to early  
316 September were greater ( $\Sigma_{18\text{PAH}} = 11.4 \text{ ng/L}$ ) and showed a lower percent contribution from LMW  
317 PAHs (Figure S5) than other rural sites, possibly due to contributions from contaminated  
318 sediments or WWTP effluent. The Erie site was within the recently delisted Presque Isle Bay  
319 AOC, which was dredged for the first time in 20 years during summer of 2011, possibly  
320 releasing elevated concentrations of PAHs into the water column.<sup>15,58,59</sup> The greatest  
321 concentrations were seen during the second deployment, which took place in early fall ( $\Sigma_{18\text{PAH}} =$   
322  $15.6 \text{ ng/L}$ ), perhaps due to the weakening of summertime stratification. The site was also within  
323 5 km of a major (~ 150 million liters/day) WWTP (Figure S3A).

324 **Air-Water Exchange.** Mass transfer coefficients and flux gradients are listed in Tables S11 and  
325 S12 and flux gradients for select PAHs are presented in Figure S9. Mass transfer velocity ranged  
326 from 0.2 cm/day to 73 cm/day and values decreased with decreasing volatility. Uncertainty in  
327 flux gradients was <30% for all compounds of lower molecular weight than benz(a)anthracene  
328 except retene. Flux gradients for HMW PAHs were not different from equilibrium within the  
329 95% confidence level.

330 Net flux rates ( $\text{ng/m}^2/\text{day}$ ) are provided in Table S13. Patterns in flux direction were  
331 similar to those reported by Bamford et al. in that LMW PAHs were volatilizing and  
332 phenanthrene was being absorbed but less volatilization was seen here than in Patapsco River  
333 and depositional fluxes of phenanthrene in our study were greater on average.<sup>57</sup> Fluxes for

334 acenaphthylene, phenanthrene, methylphenanthrenes, and pyrene at each site were summarized  
335 in Figure 5 over three time periods: April – June, June – August, and August – November.

336 Acenaphthylene volatilized from surface waters during most deployments, with  
337 volatilization fluxes ranging from 19.3 ng/m<sup>2</sup>/day in Niagara to 363 ng/m<sup>2</sup>/day in Erie.  
338 Phenanthrene was absorbed at all sites with the exception of Niagara during the second  
339 deployment, where a volatilization flux of 236 ng/m<sup>2</sup>/day was measured. Phenanthrene  
340 deposition fluxes ranged from 237 ng/m<sup>2</sup>/day at Cape Vincent in early fall to 3271 ng/m<sup>2</sup>/day at  
341 Dunkirk in summer. This suggests that during the study period the lakes were primarily a source  
342 of acenaphthylene to the overlying atmosphere, while the atmosphere was a source of dissolved  
343 phenanthrene to the lakes. However, dissolved phenanthrene concentrations in air and water  
344 were not significantly correlated, suggesting that diffusive exchange was not the only mechanism  
345 influencing aqueous phenanthrene concentrations. Blanchard et al. estimated annual net  
346 absorption of phenanthrene for Lake Erie and Lake Ontario to be 1020 ng/m<sup>2</sup>/day and 310  
347 ng/m<sup>2</sup>/day, respectively, in 2005.<sup>24</sup>

348 The greatest depositional fluxes were measured at Dunkirk and Grimsby, particularly  
349 during June – August. Though average temperatures during deployment were warm (17 – 21.4  
350 °C), all PAHs except acenaphthylene were absorbed at these sites. Deposition at Grimsby  
351 suggests that the Toronto/Hamilton conurbation acted as a source of dissolved PAHs to the open  
352 water. Deposition at Dunkirk was likely driven by the greater gaseous PAH concentrations at this  
353 site and clean surface waters.

354 At Erie, Niagara, Sheffield, and Buffalo (second deployment only), the majority of PAHs  
355 were volatilizing. Erie and Sheffield exhibited the strongest volatilization, driven by elevated

356 aqueous concentrations. The greatest volatilization fluxes measured at the two sites were for  
357 fluoranthene (927 ng/m<sup>2</sup>/day at Erie, 879 ng/m<sup>2</sup>/day at Sheffield Lake) and pyrene (591  
358 ng/m<sup>2</sup>/day at Erie, 857 ng/m<sup>2</sup>/day at Sheffield Lake). Volatilization was comparable at the two  
359 sites, though anthracene and benz(a)anthracene volatilized more strongly at Sheffield Lake.  
360 Lohmann et al. observed volatilization of PAHs in an urbanized portion of Narragansett Bay (RI)  
361 and suggested that river input and runoff were more significant sources of dissolved PAHs than  
362 atmospheric deposition.<sup>14</sup> Volatilization at Niagara may indicate that river discharge was a  
363 significant source of PAHs at these sites.

364 Air-water exchange is strongly influenced by air temperature, wind speed, and wind  
365 direction and large daily variations in fluxes have been observed.<sup>57</sup> During deployments where  
366 mean temperature was greater than 19°C, phenanthrene and anthracene were the only PAHs  
367 being absorbed into surface waters, with the exception of measurements from Oswego (3<sup>rd</sup>  
368 deployment) as well as Dunkirk. In Buffalo, most PAH fluxes changed from net deposition  
369 during the first deployment (mean temperature of 11 °C) to net volatilization during the second  
370 deployment (mean temperature 19 – 20.5 °C). During the third deployment, most fluxes were not  
371 significantly different from equilibrium. In Oswego, the temperature dependency observed in  
372 Buffalo was not evident.

### 373 **IMPLICATIONS**

374 Strong correlation with population suggests that urban centers played an important role in  
375 determining spatial distributions of gaseous PAHs. However, air-water fluxes and distributions  
376 of dissolved PAHs implied that additional sources beyond diffusive exchange influenced  
377 aqueous distributions, especially in urban areas. In some cases surface waters acted as a source  
378 of PAHs to the atmosphere. Enhanced spatial coverage near AOCs and major urban areas like

379 Toronto, as well as consistent temporal coverage, could help explain how river discharge,  
380 sediment-water exchange, WWTP effluent, and other sources influence dissolved PAH  
381 concentrations in the lower Great Lakes.

## 382 **ASSOCIATED CONTENT**

383 **Supporting Information.** Detailed information on sampler deployments, site characteristics, and  
384 compound properties can be found along with calculated sampling rates, table of concentrations,  
385 and plots describing the results of principal component analysis. This material is available free of  
386 charge via the Internet at <http://pubs.acs.org>.

## 387 **AUTHOR INFORMATION**

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389 **Author Contributions.** The manuscript was written through contributions of all authors. All  
390 authors have given approval to the final version of the manuscript.

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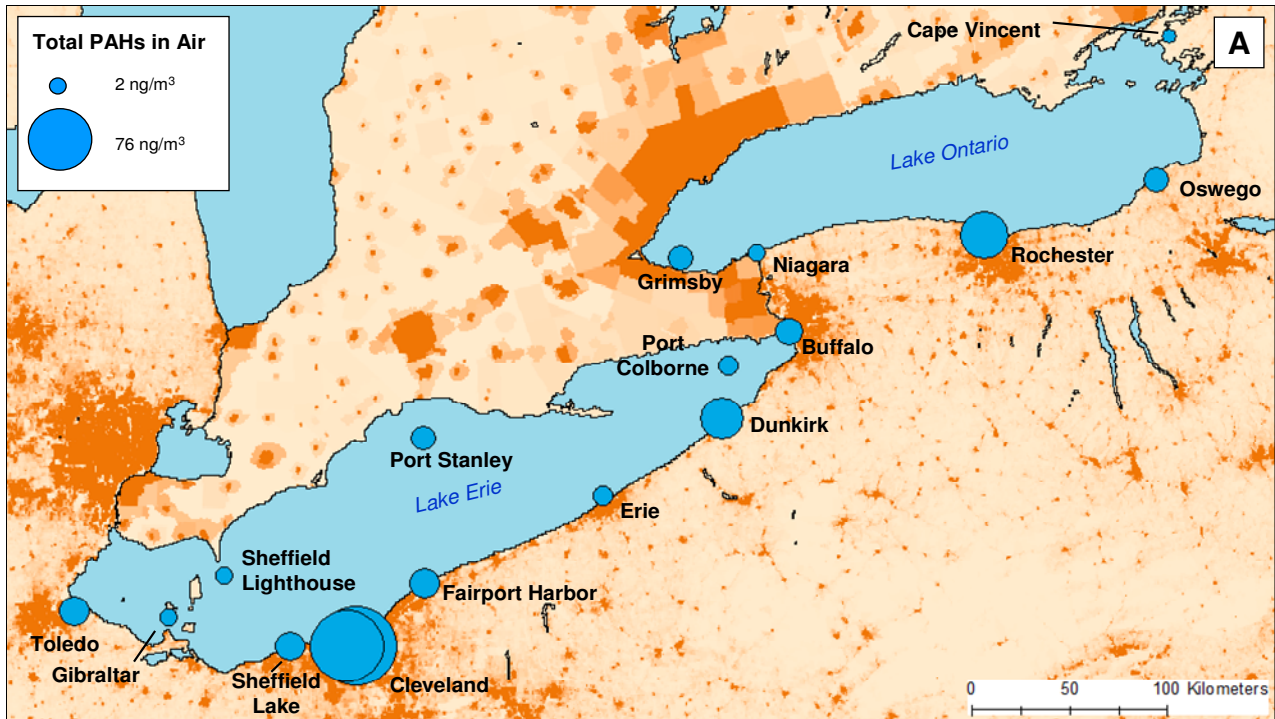


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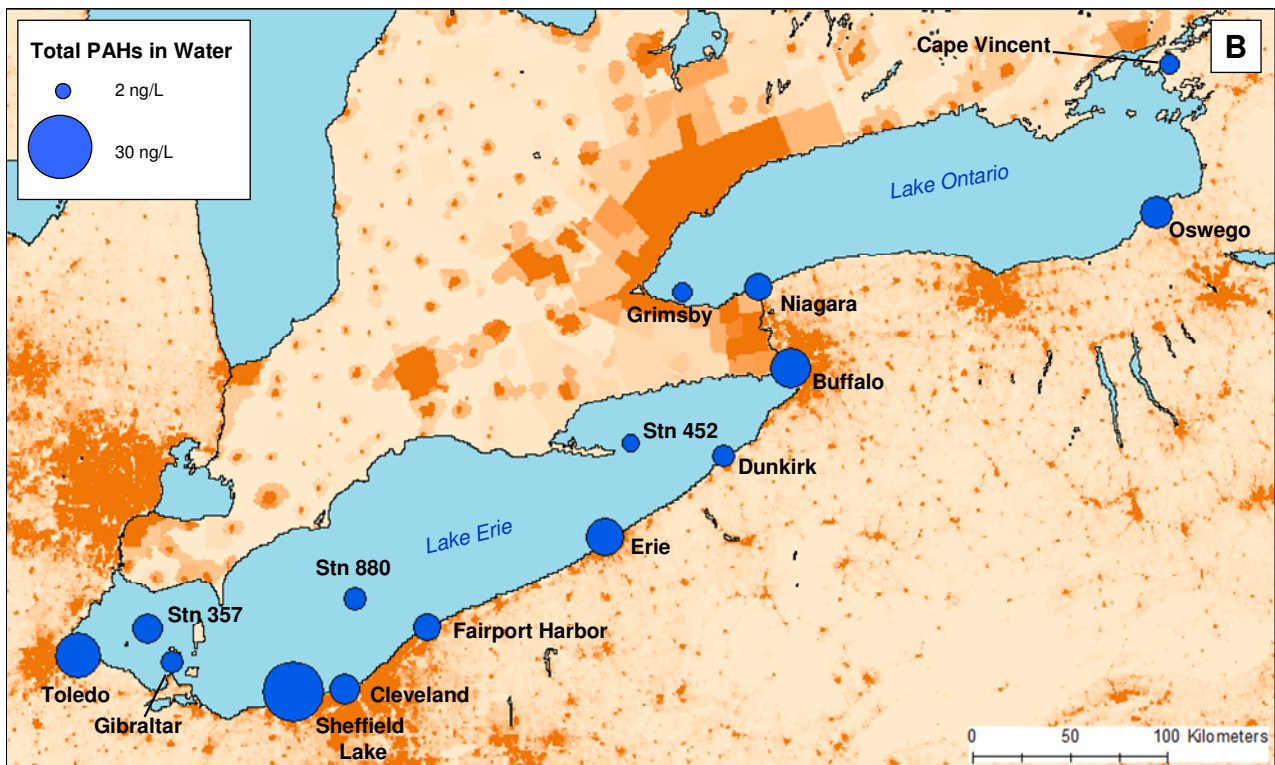
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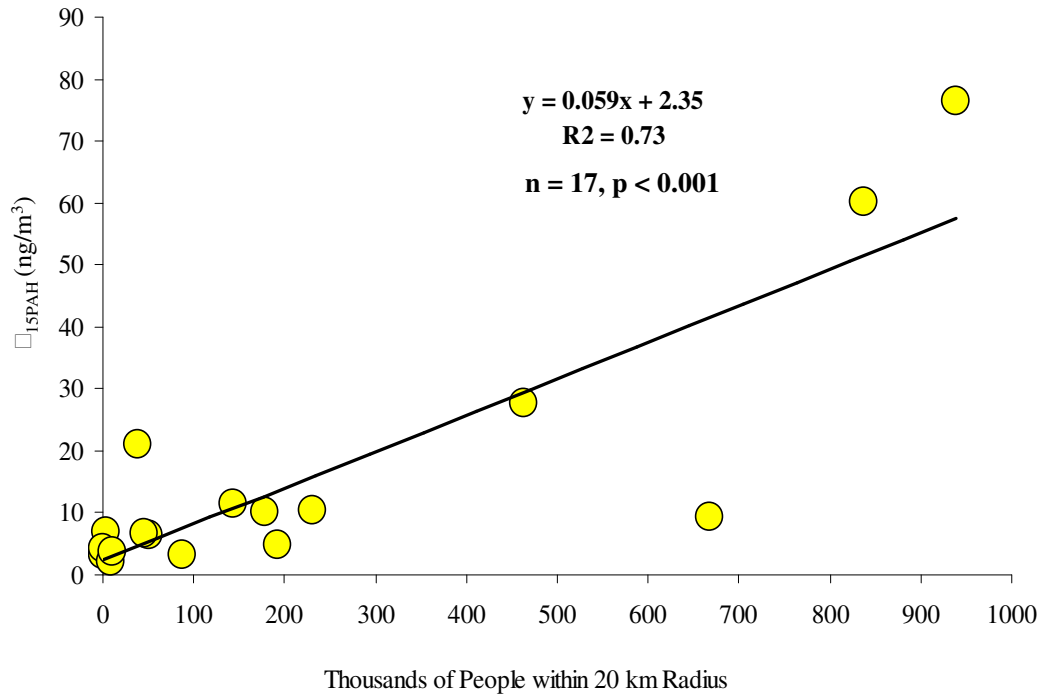


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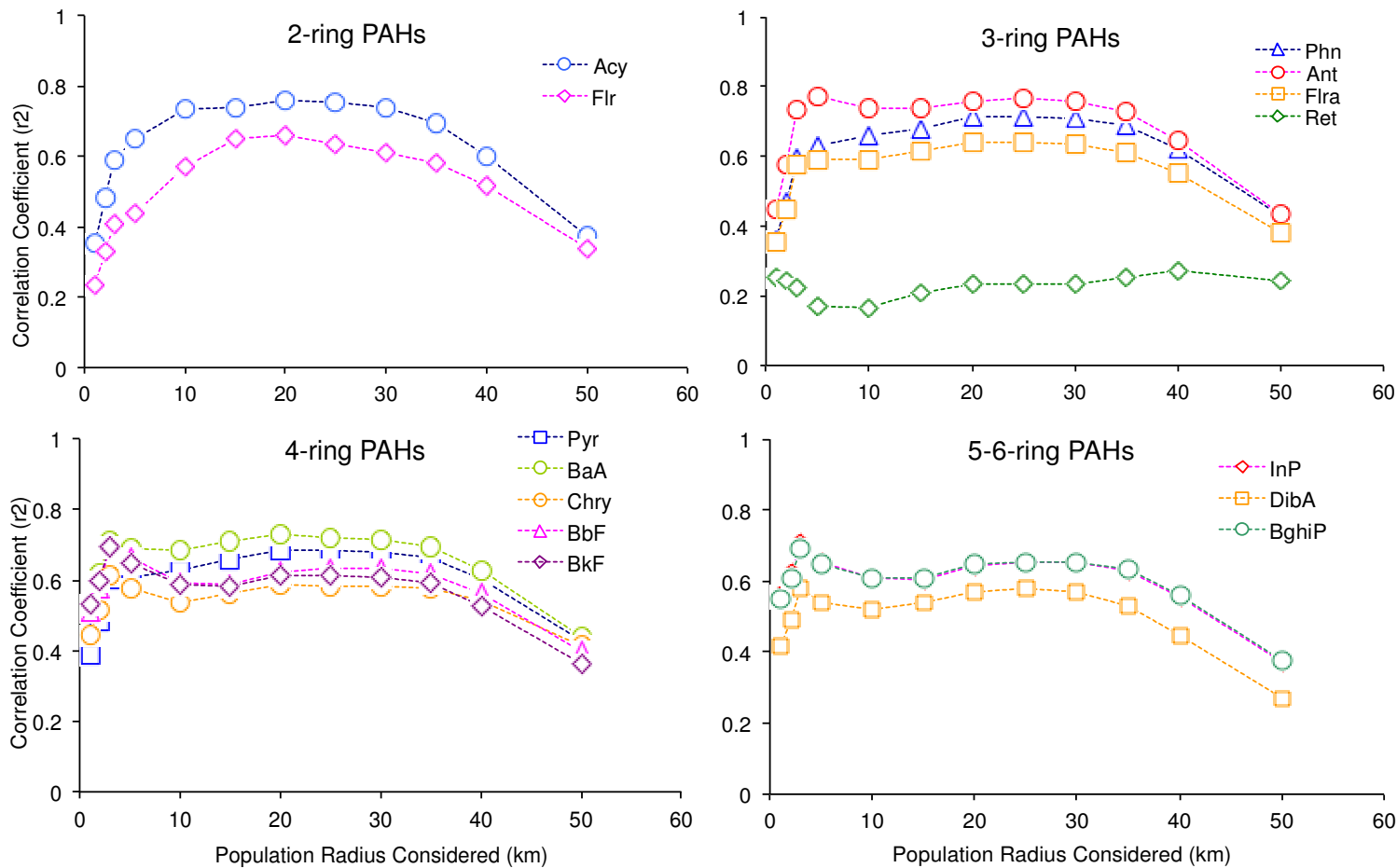


577

578 **Figure 1. PAH Concentrations in Air (A) and Water (B).** Average gaseous  $_{15\text{PAH}}$  (A) and  
579 dissolved  $_{18\text{PAH}}$  (B) in Lake Erie and Lake Ontario. Orange shading delineates population centers.

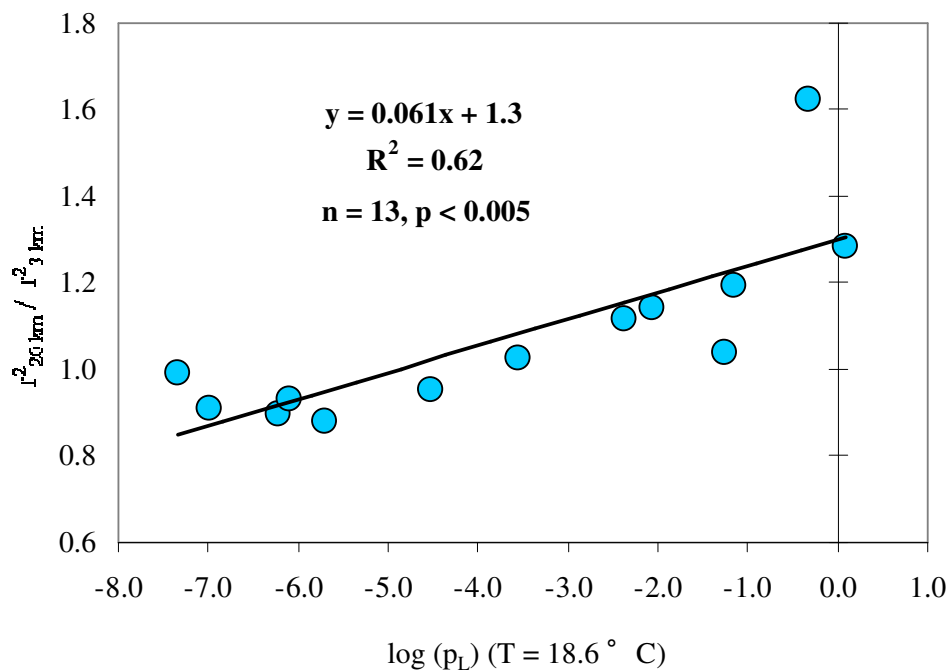


580  
581 **Figure 2. Atmospheric  $_{15\text{PAH}}$  and Population within 20 km.** Average atmospheric  
582 concentrations of gaseous PAHs at each site correlated well with population within 20 km. The  
583 two sites in downtown Cleveland exhibited the greatest  $_{15\text{PAH}}$  concentrations while concentrations  
584 in Buffalo were lower than would be predicted by the regression.

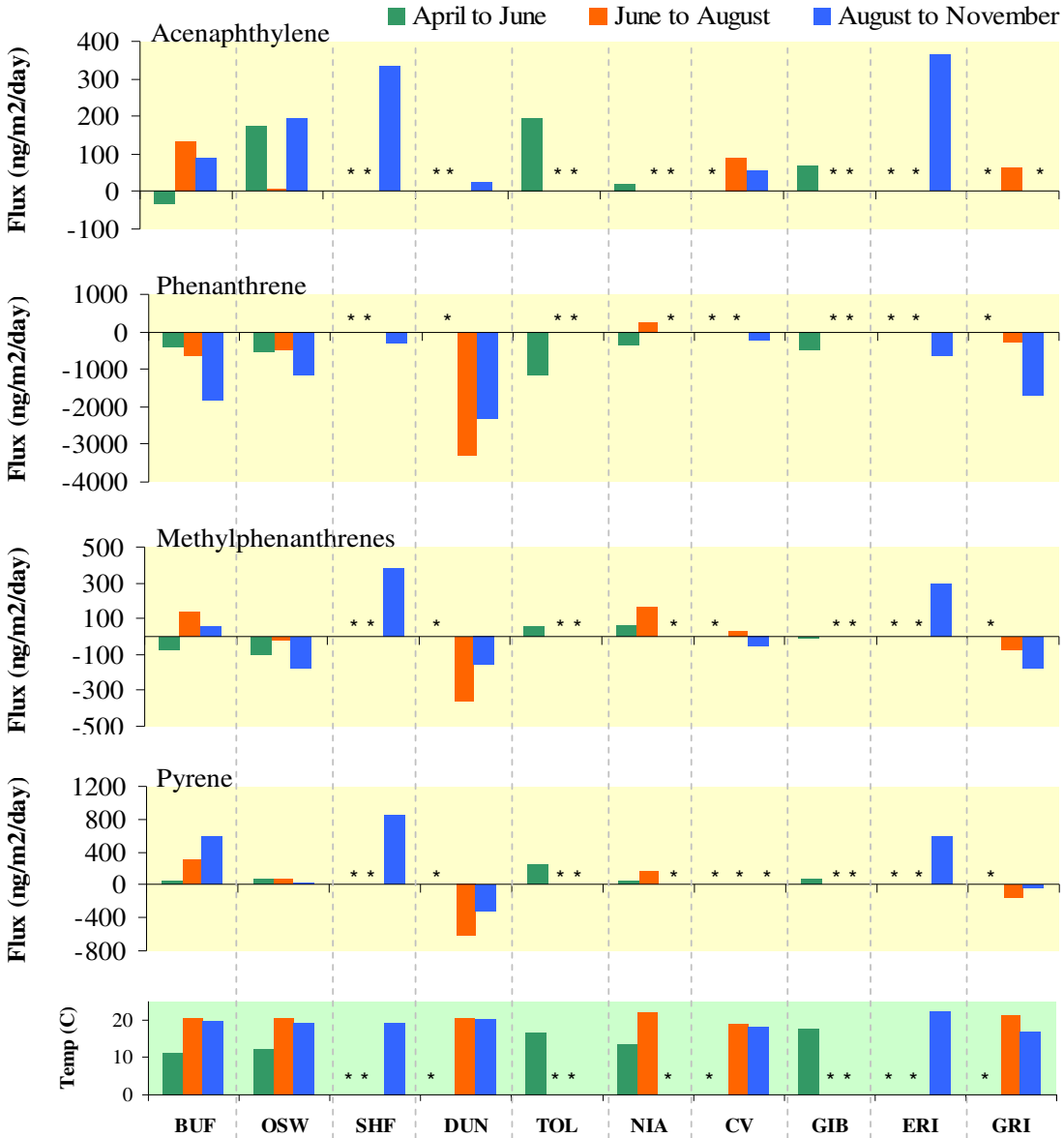


**Figure 3. Correlation Strength Varies with Population Radius Considered.** Depending on the radius used to calculate population at each site, the strength of correlation (depicted using the coefficient of determination,  $r^2$ ) between gaseous PAH concentration and

population varied, displaying a bimodal relationship. The radius of maximum correlation was similar for PAH molecules of similar size.



**Figure 4. Relative significance of population within 20 km and 3 km.** The ratio of  $r^2_{20\text{km}}$  to  $r^2_{3\text{km}}$  correlated well with sub-cooled liquid vapor pressure at mean deployment temperature, suggesting that distant sources were more significant for volatile PAHs.



1  
 2 **Figure 5. Net Air-Water Flux of Four PAHs.** Air-water fluxes (ng/m<sup>2</sup>/day) for four PAHs  
 3 during three deployment periods with mean air temperature at the bottom. Negative values  
 4 indicate absorption into surface waters while positive values indicate volatilization. Sites where  
 5 no data was available or air and water concentrations were both <DL are marked with \*.

6  
 7

ATMOSPHERIC PAHs (ng/m <sup>3</sup> )	AQUEOUS PAHs (ng/L)
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	Lake Erie			Lake Ontario			Lake Erie			Lake Ontario		
	n	PAH	STDEV	n	PAH	STDEV	n	PAH	STDEV	n	PAH	STDEV
<b>Offshore</b>	3	4.7	1.7	1	6.0	-	3	4.2	2.3	1	3.1	-
<b>Rural</b>	2	3.9	0.7	1	2.0	-	2	6.7	4.4	1	2.7	-
<b>Semi-Urban</b>	4	12.2	5.0	1	2.8	-	4	12.7	10.4	1	5.9	-
<b>Urban</b>	3	45.4	32.6	2	15.8	13.8	2	9.1	4.2	1	7.9	-

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9 **Table 1. Average Gaseous and Dissolved  $\Sigma_{\text{PAH}}$  Concentrations in Lake Erie and Lake**

10 **Ontario.** The number of sites within each category (n) is listed along with mean PAH

11 concentrations and standard deviation. Sites were classified based on population within 3 km to

12 facilitate comparison between lakes: 0-100 people: Offshore; 100-1000: Rural; 1000-10,000:

13 Semi-urban; >10,000: Urban.

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