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

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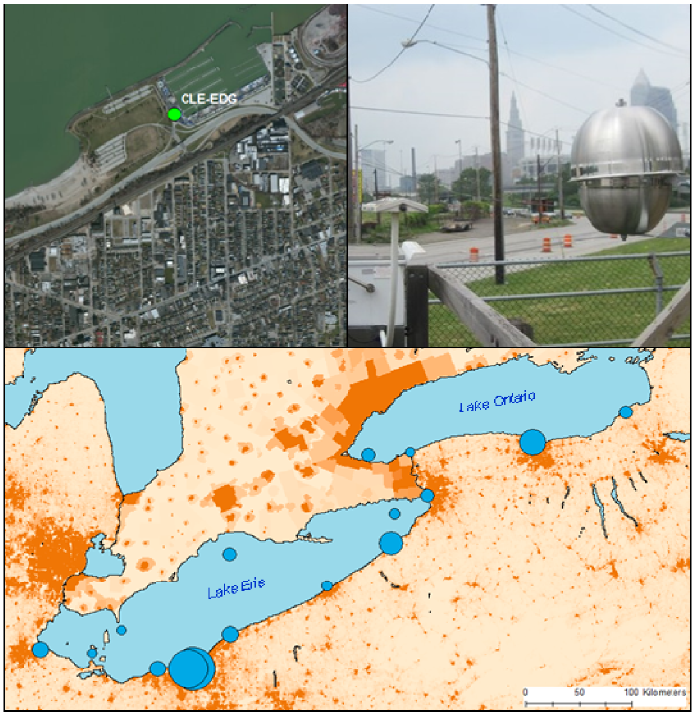

ABSTRACT

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

INTRODUCTION

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

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

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

Lake Erie and Lake Ontario are the smallest of the Great Lakes by volume and have estimated residence times of 2.7 and 7.5 years, respectively.[17] About 80% of Lake Erie's water is supplied by the Detroit River, which is fed by Lake Huron via Lake St. Claire. Among the Great Lakes, Lake Erie is the shallowest (average depth 19 m), warmest, and most biologically productive.[18,19] Lake Ontario is much deeper (average depth 86 m) and primarily receives water from Lake Erie via the Niagara River.[19] Currents in the Great Lakes are weak (a few cm/s) with complex temporal variability that depends on recent atmospheric conditions. In the summertime, circulation is generally counterclockwise.[20] The lakes are stratified from May through October and well-mixed for the remainder of the year.[20]

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

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

MATERIALS AND METHODS

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

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

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

Sample Analysis. All PEs were spiked with deuterated PAHs and extracted twice, each time for 18 hours. Air PEs were extracted with ethyl acetate followed by hexane. Aqueous PEs were extracted with dichloromethane followed by hexane. Extracts were concentrated to approximately 100 μL and p-terphenyl-d_{14} was added as an injection standard. Extracts were analyzed using an Agilent 6890 GC coupled to an Agilent 5973 MSD in EI+ selected ion monitoring (SIM) mode. PAH analysis and quality control procedures are further outlined by Khairy et al.[11]

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

Determination of Sampling Rate and Ambient Concentration. The uptake of HOCs by PEs is described in detail by Lohmann[31] and PE-air partitioning is detailed by Khairy et al.[11] To determine ambient PAH concentrations from concentrations in polyethylene, site-specific sampling rates were estimated via a method adapted from Booij et al.[32] Further details are provided in the Supporting Information. The average air sampling rate was 28±17 m^3/day and the average aqueous sampling rate was 112±57 L/day (for more details, see SI and Tables S1 and S2).

Physico-chemical Parameters. Sampler-matrix partition coefficients (T=25°C) used to calculate ambient concentrations for each PAH are listed in Table S7, along with other physico-chemical properties. Temperature-adjusted partition coefficients were obtained using mean temperature during the deployment period for the nearest meteorological buoy or weather station and the modified van't Hoff equation, as in Khairy et al.[11] The enthalpy of vaporization (H_{vap}) was used to account for K_{PEA}-temperature sensitivity and internal energy of dissolution (U_w) for K_{PEW}-temperature sensitivity.

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

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

RESULTS AND DISCUSSION

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

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

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

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

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

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

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

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

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

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

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

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

Previous studies have reported that coastal areas receiving cleaner air from over water bodies exhibit lower atmospheric PAH concentrations than would be predicted based on surrounding population.[56] Concentrations of total atmospheric PAHs were lower in Buffalo and Oswego than Cleveland or Rochester, though these sites were classified similarly in terms of population. One explanation is that prevailing westerly winds brought over-lake air towards Buffalo and Oswego, diluting the urban plume. Offshore measurements confirmed that air masses over Lake Erie had relatively lower PAH concentrations than shoreline sites (Table 1). Likewise, the offshore site near Grimsby was closer to the shoreline and more likely to be impacted by westerly air masses arriving over land from Hamilton (ON).

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

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

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

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

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

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

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

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

Concentrations at offshore Lake Erie sites were greatest in the western basin where the lake is shallowest and inputs from the Detroit and Maumee watersheds, both AOCs, were expected to be significant (Figure S3A). Due to the central Erie basin's counterclockwise circulation during the study season,[20] it is unlikely that elevated dissolved PAHs in Sheffield Lake resulted from aqueous transport from Cleveland. Black River, a historically polluted AOC, discharges 8 km west of the Sheffield Lake site and may have contributed to dissolved PAH concentrations there. More measurements over time are needed to determine whether elevated dissolved PAHs at Sheffield Lake were episodic or chronic. Unexpectedly, concentrations near Cleveland were lower than at Sheffield Lake. This may be because of sampler placement, as PEs at Cleveland were farther offshore where water was deeper and currents carrying more highly impacted water may have been entrained closer to the shore.

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

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

Net flux rates (ng/m^2/day) are provided in Table S13. Patterns in flux direction were similar to those reported by Bamford et al. in that LMW PAHs were volatilizing and phenanthrene was being absorbed but less volatilization was seen here than in Patapsco River and depositional fluxes of phenanthrene in our study were greater on average.[57] Fluxes for acenaphthylene, phenanthrene, methylphenanthrenes, and pyrene at each site were summarized in Figure 5 over three time periods: April – June, June – August, and August – November.

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

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

At Erie, Niagara, Sheffield, and Buffalo (second deployment only), the majority of PAHs were volatilizing. Erie and Sheffield exhibited the strongest volatilization, driven by elevated aqueous concentrations. The greatest volatilization fluxes measured at the two sites were for fluoranthene (927 ng/m^2/day at Erie, 879 ng/m^2/day at Sheffield Lake) and pyrene (591 ng/m^2/day at Erie, 857 ng/m^2/day at Sheffield Lake). Volatilization was comparable at the two sites, though anthracene and benz(a)anthracene volatilized more strongly at Sheffield Lake. Lohmann et al. observed volatilization of PAHs in an urbanized portion of Narragansett Bay (RI) and suggested that river input and runoff were more significant sources of dissolved PAHs than atmospheric deposition.[14] Volatilization at Niagara may indicate that river discharge was a significant source of PAHs at these sites.

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

IMPLICATIONS

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

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

ASSOCIATED CONTENT

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

AUTHOR INFORMATION

Corresponding Author. Rainer Lohmann

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

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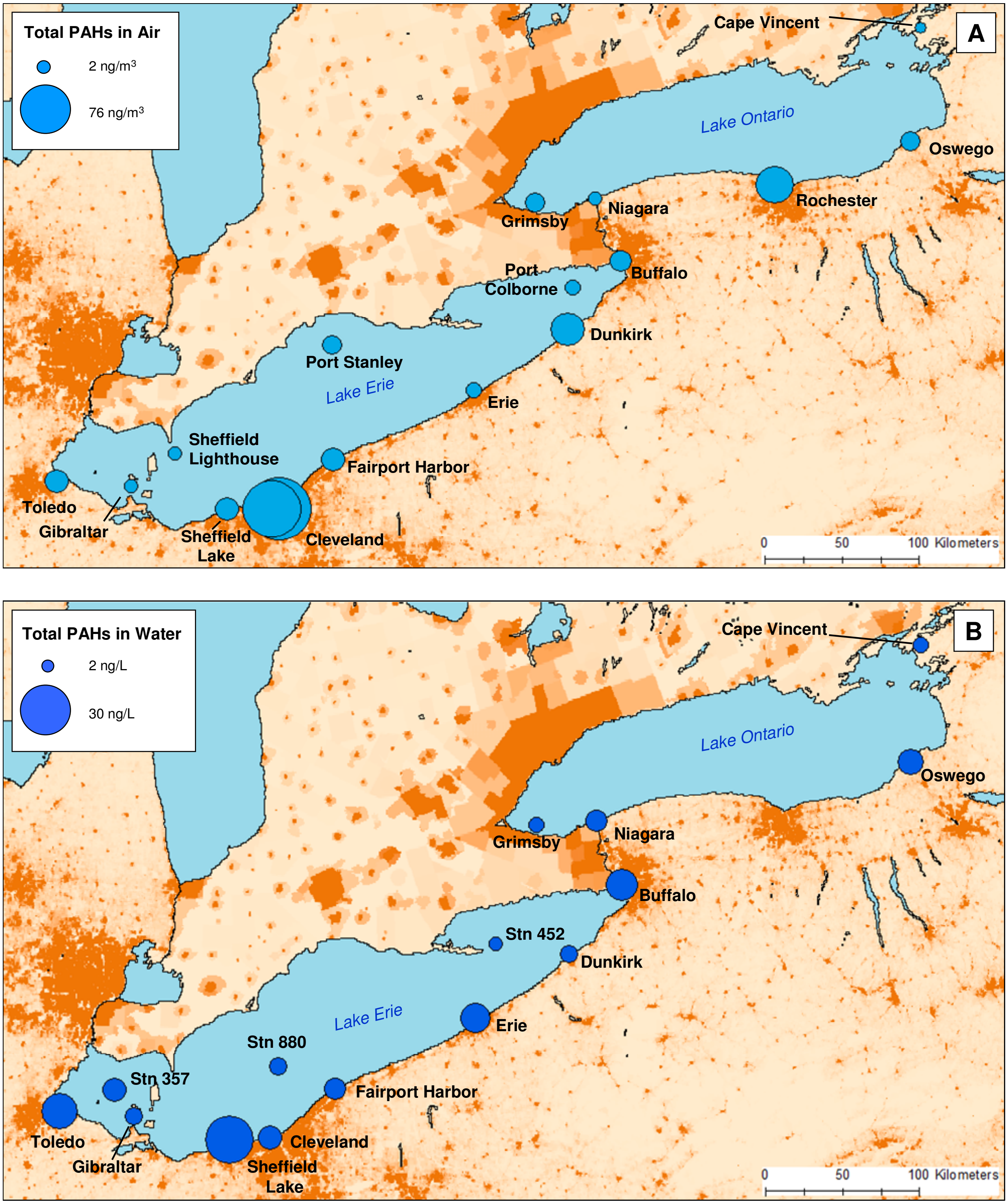
Total PAHs in Air
2 ng/m³
76 ng/m³
A
Cape Vincent
Lake Ontario
Oswego
Rochester
Niagara
Grimsby
Buffalo
Port Colborne
Dunkirk
Port Stanley
Lake Erie
Erie
Sheffield Lighthouse
Fairport Harbor
Toledo
Gibraltar
Sheffield Lake
Cleveland
0 50 100 Kilometers
Total PAHs in Water
2 ng/L
30 ng/L
B
Cape Vincent
Lake Ontario
Oswego
Niagara
Grimsby
Buffalo
Stn 452
Dunkirk
Lake Erie
Erie
Stn 880
Stn 357
Fairport Harbor
Toledo
Gibraltar
Cleveland
Sheffield Lake
0 50 100 Kilometers

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

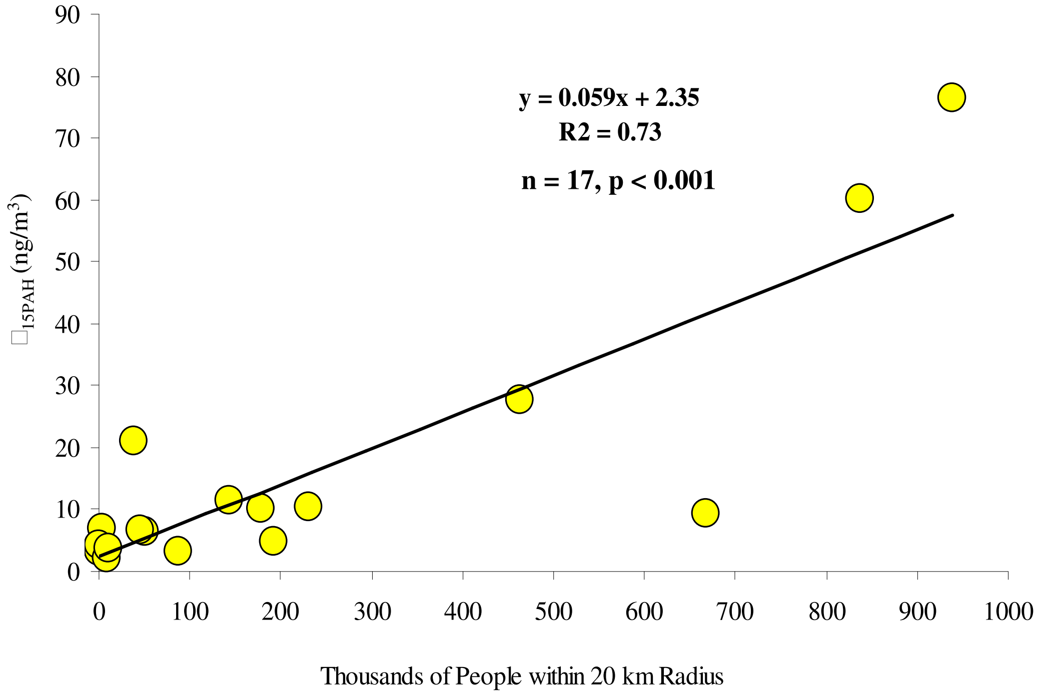

Figure 2. Atmospheric $_{15PAH}$ and Population within 20 km. Average atmospheric concentrations of gaseous PAHs at each site correlated well with population within 20 km. The two sites in downtown Cleveland exhibited the greatest $_{15PAH}$ concentrations while concentrations in Buffalo were lower than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

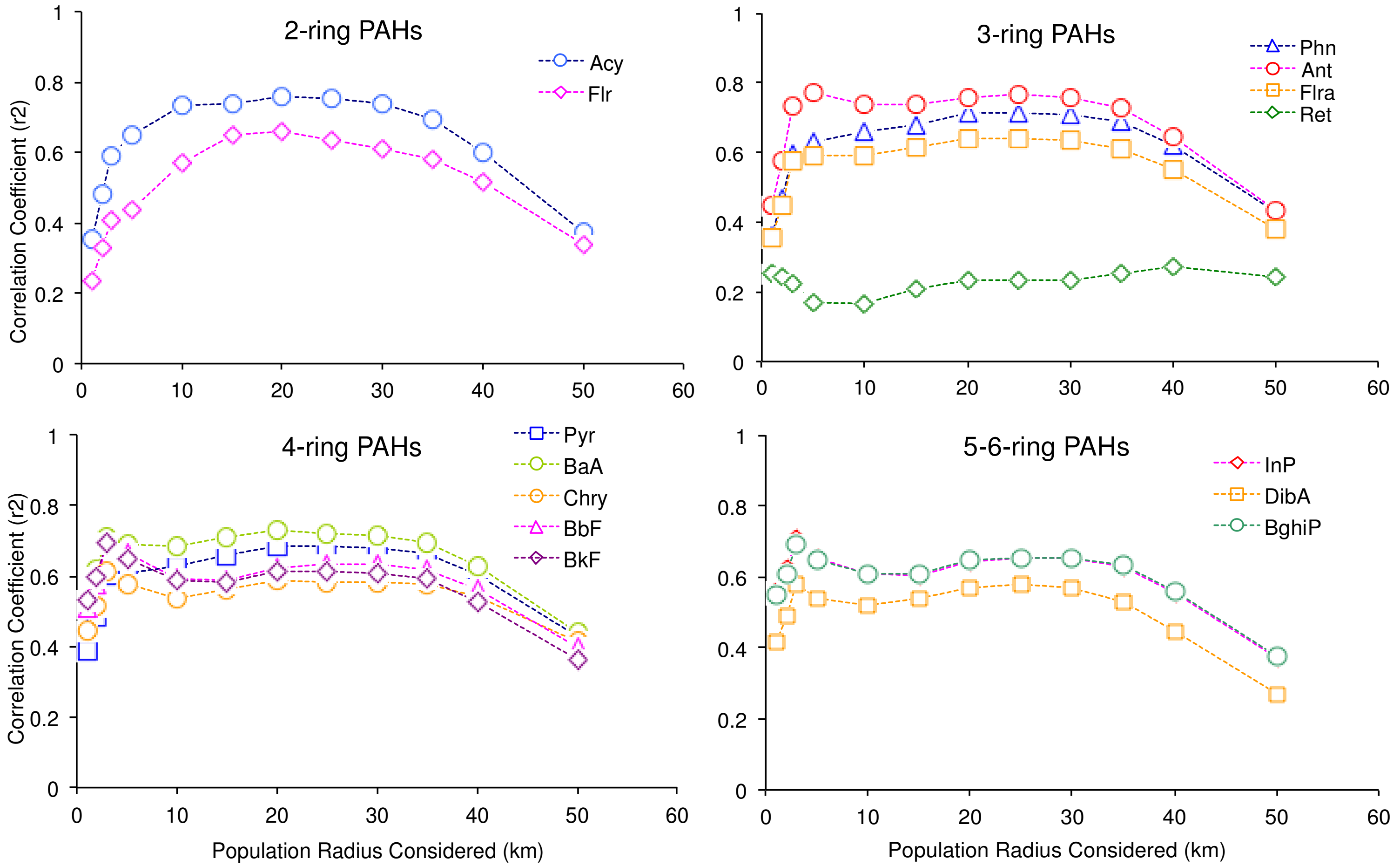

Figure 3. Correlation Strength Varies with Population Radius Considered. Depending on the radius used to calculate population at each site, the strength of correlation (depicted using the coefficient of determination, r^2) between gaseous PAH concentration and

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

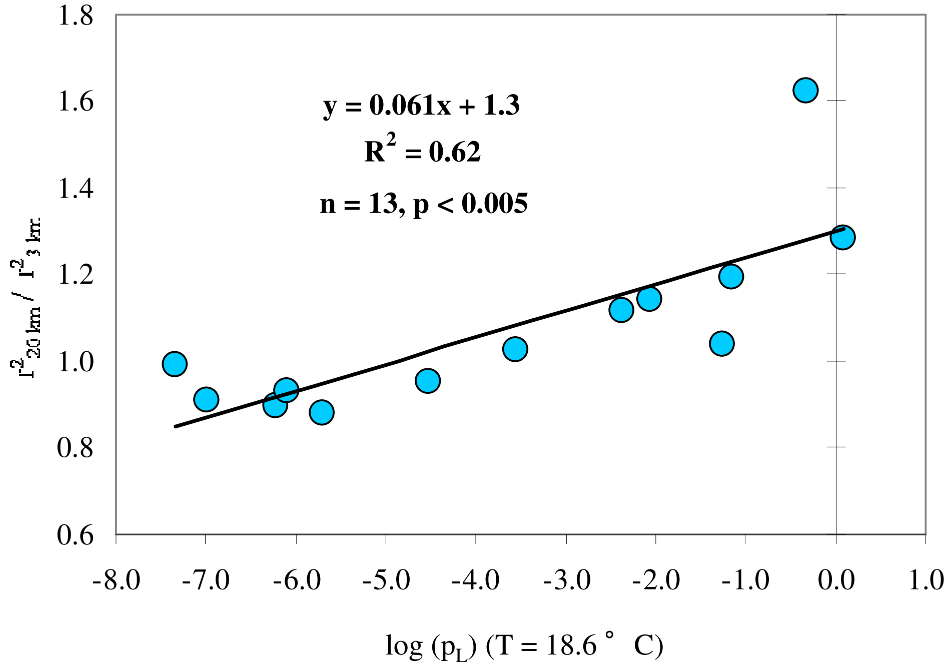

Figure 4. Relative significance of population within 20 km and 3 km. The ratio of $r^2_{20\ km}$ to $r^2_{10\ km}$ correlated well with sub-cooled liquid vapor pressure at mean deployment temperature, suggesting that distant sources were more significant for volatile PAHs.

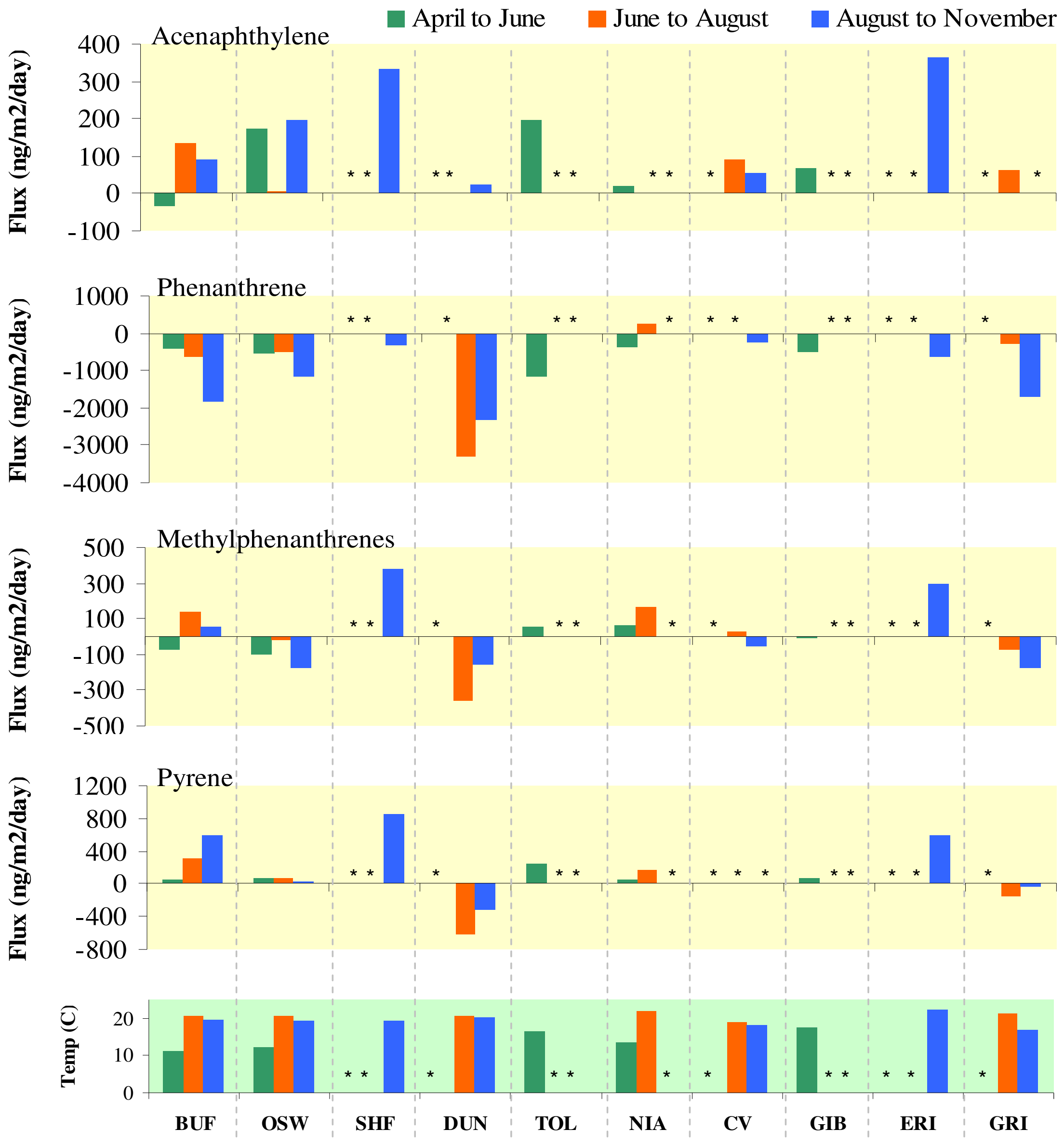

Figure 5. Net Air-Water Flux of Four PAHs. Air-water fluxes (ng/m^2/day) for four PAHs during three deployment periods with mean air temperature at the bottom. Negative values indicate absorption into surface waters while positive values indicate volatilization. Sites where no data was available or air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

ATMOSPHERIC PAHs (ng/m^3)	AQUEOUS PAHS (ng/L)

	Lake Erie			Lake Ontario			Lake Erie			Lake Ontario		
	n	**PAH**	**STDEV**	**n**	**PAH**	**STDEV**	**n**	**PAH**	**STDEV**	**n**	**PAH**	**STDEV**
Offshore	3	4.7	1.7	1	6.0	-	3	4.2	2.3	1	3.1	-
Rural	2	3.9	0.7	1	2.0	-	2	6.7	4.4	1	2.7	-
Semi-Urban	4	12.2	5.0	1	2.8	-	4	12.7	10.4	1	5.9	-
Urban	3	45.4	32.6	2	15.8	13.8	2	9.1	4.2	1	7.9	-

Table 1. Average Gaseous and Dissolved Σ_{PAH} Concentrations in Lake Erie and Lake Ontario. The number of sites within each category (n) is listed along with mean PAH concentrations and standard deviation. Sites were classified based on population within 3 km to facilitate comparison between lakes: 0-100 people: Offshore; 100-1000: Rural; 1000-10,000: Semi-urban; >10,000: Urban.