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Mohammed Khairy

Derek Muir

See next page for additional authors

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Authors
Mohammed Khairy, Derek Muir, Camilla Teixeira, and Rainer Lohmann

Spatial Distribution, Air-Water Fugacity Ratios and Source Apportionment of Polychlorinated Biphenyls in the Lower Great Lakes Basin

Mohammed Khairy[†‡], **Derek Muir**[§], **Camilla Teixeira**[§], **Rainer Lohmann**[†]*

[†]Graduate School of Oceanography, University of Rhode Island, 215 South Ferry Road, Narragansett, Rhode Island 02882, United States

[‡]Department of Environmental Sciences, Faculty of Science, Alexandria University, 21511 Moharam Bek, Alexandria, Egypt

[§]Environment Canada, Aquatic Contaminants Research Division, Burlington, ON, Canada

[*]Corresponding author. E-mail address: rlohmann@mail.uri.edu

Phone: 401-874-6612; Fax 401-874-6811

Abstract

Polychlorinated biphenyls (PCBs) continue to be contaminants of concern across the Great Lakes. It is unclear whether current concentrations are driven by on-going primary emissions from their original uses, or whether ambient PCBs are dominated by their environmental cycling. Feely dissolved PCBs in air and water were measured using polyethylene passive samplers across Lakes Erie and Ontario during summer and fall, 2011 to investigate their spatial distribution, determine and apportion their sources and to asses the air-water exchange gradients. Average gaseous and freely dissolved $\sum_{29}$ PCB concentrations ranged from 5.0 to 160 pg/m^3 and 2.0 to 55 pg/L respectively. Gaseous concentrations were significantly correlated ($R^2 = 0.80$) with the urban area within a 20 km radius. Fugacity ratio calculations indicated that the majority of PCBs are volatilizing from the water thus acting as a secondary source for the atmosphere. Dissolved PCBs were probably linked to direct PCB emissions from areas of concern. Positive Matrix Factorization indicated that although volatilized Aroclors (gaseous PCBs) and unaltered

Aroclors (dissolved PCBs) dominate in some samples, on-going non-Aroclor sources such as paints/pigments (PCB 11) and coal/wood combustion showed significant contributions across the lower Great Lakes. Accordingly, control strategies should give further attention to PCBs emitted from current use sources.

Introduction

Polychlorinated biphenyls (PCBs) are a class of persistent, bioaccumulative toxic organic pollutants (PBTs) that were produced as complex mixtures, each containing more than 80 different congeners. In USA, mixtures were given the trade name Aroclor.[1] Their production was banned in 1977 due to their hazardous properties.[2] Nevertheless, PCBs are still detected in environmental samples worldwide.[2-7] PCBs are released to the environment from hazardous waste sites, improper disposal of industrial wastes and consumer products, leaks from old transformers, landfills[2], as byproducts formed during thermal combustion processes, in wastewater and from pigment manufacture.[8, 9] These activities occur in urban areas suggesting their importance as significant sources of PCBs.[10] In the atmosphere, volatilization of PCBs from on-going use, contaminated soil and aquatic ecosystems (affected by the above mentioned anthropogenic activities), and incineration processes have become the major sources. To establish effective control strategies, their atmospheric sources need to be understood first. The sampling campaign discussed here was set-up to determine and assess sources of PCBs across the lower Great Lakes.

The Great Lakes Basin is an example of a freshwater ecosystem heavily influenced by urban activities. PBTs have been widely detected in the Great Lakes ecosystem[11-20] during the last three decades. Previous studies have indicated that urban centers are the major emission sources of atmospheric PCBs at the Great Lakes.[6, 13, 21, 22] As a consequence, adverse effects were observed in aquatic life[23] and expected to affect humans through the ingestion (fish consumption and drinking water) exposure route.

Determination of PCB emissions depends on accurate determination of the spatial distribution, and variability of PCB congener concentrations. However, due to the limitations in the conventional sampling technique, only few sampling sites are included even in large sampling campaigns like the Integrated Atmospheric Deposition Network (IADN) binational project.[24] Accordingly, it is difficult to accurately measure the spatial distribution of PBT and the available datasets not enough to support current modeling and source apportionment methods.

To overcome these challenges, low density polyethylene (LDPE) passive samplers have proven to be an effective, simple and inexpensive tool for monitoring gaseous and truly dissolved PBTs.[25-28] As detailed elsewhere we utilized LDPE to investigate the spatial distribution, sources and air-water exchange of organic contaminant across the lower Great Lakes, including polycyclic aromatic hydrocarbons[27] (PAHs) and organochlorine pesticides[28].

Air quality management requires accurate source identification of PBTs. Due to the lack of PCB source profiles, apportionment of PCB sources using chemical mass balance models will not be easily applicable. In contrast, receptor models can determine contributions from all sources based on concentration measurements.[29] Although Factor Analysis and Positive Matrix Factorization (PMF) have been used successfully to identify the sources of PAHs, (see Khairy and Lohmann[30] and references therein), source apportionment of PCBs has been scarce.[3, 4, 29, 31] Here, we make use of the PCBs determined from passive samplers to assess sources of PCBs to air and water of the lower Great Lakes.

Although the temporal trends of atmospheric PCBs have been extensively investigated in the Great Lakes, limited information is available about the spatial distribution of atmospheric PCBs and the spatial and temporal trends of freely dissolved PCBs with a high geospatial resolution within each of the lower Great Lakes. One recent study investigated the spatial distribution of flame retardants and legacy pollutants in the Great Lakes water.[20] However, southern parts of Lake Erie and Lake Ontario along the US coast, which are highly influenced by urban activities, were not included.

In the current study, LDPEs were deployed in the air and water at Lake Ontario and Lake Erie during three major sampling campaigns in 2011 (April−June; June−August; August−October). The aims were to (i) investigate the spatial and temporal trends of the gaseous and freely dissolved PCBs (ii) examine the influence of the meteorological parameters and land use patterns on their spatial and temporal variations, (iii) apportion the sources of PCBs, and (iv) calculate temporally and spatially resolved air-water gaseous exchange fluxes of PCBs.

Material and Methods

Detailed description of the deployments of LDPE in air and water, meteorological data used, the chemical analysis methodologies and preparation of the LDPE passive samplers can be found elsewhere.[28] Details on the calculations of the gaseous and freely dissolved concentrations of PCBs based on LDPE, quality assurance, multiple linear regression, fugacity ratios calculations and positive matrix factorization are given in the Supporting Information; a brief description is given below.

Samplers were deployed in air and water by volunteers during three different sampling campaigns (Table S1) at 13 different locations along the southern coasts of Lakes Ontario and Erie and 7 on-lake locations (Supplementary Figure S1). Water and air passive samplers were placed in the same location whenever possible. Deployed air and water samplers at Niagara, Fairport and Dunkirk were less than 500 meters apart, whereas samplers at Cleveland and Gibraltar were 1-2 km apart from each other. Atmospheric samplers were deployed in two inverted bowls (acting as a shelter from direct sun light and precipitation) ~1–2 m above the ground and/or water surface, whereas water samplers were deployed in water ~1 m below the surface. A total of 45 air samplers (including duplicates) and 48 water samples were collected in the current study. 10 Air samplers and 15 water samplers were either lost during deployment or not deployed by the volunteers (Table S1).

After processing of the collected LDPE samplers[28], 29 PCB congeners (PCB 8, 11, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206, 209) were analyzed using an Agilent GC 6890N with a DB-5 MS fused silica capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific) equipped with a Quattro micro GC tandem MS (Waters) according to the method described in Khairy et al.[32].

Procedural blanks, field blanks, matrix spikes, and duplicate samples were included in the analysis. Most of the investigated PCBs were detected at very low concentrations in the procedural and field blanks (Supplementary Table S2). Accordingly, samples were blank corrected for PCBs. Limits of detection (LODs) were calculated as the mean plus three standard deviations of the detected PCBs in the field blanks. LOD ranged from 0.07 pg/m^3 (PCB 189) to 21 pg/m^3 (PCB 8) in the air samples and 0.020 pg/l to 3.0 pg/l in the water samples. Recoveries of the surrogate standards were 77.0 ± 21.0 % for $^{13}C_{12}$-PCB 8, 82.0 ± 19.0 % for $^{13}C_{12}$-PCB 28, 83.0 ± 18.0 % for $^{13}C_{12}$-PCB 52, 84.0 ± 14.0 % for $^{13}C_{12}$-PCB 118, 85.0 ± 14.0 % for $^{13}C_{12}$-PCB 138, 82.0 ± 20.0 % for $^{13}C_{12}$-PCB 180 and 86.0 ± 16.0 % for $^{13}C_{12}$-PCB 209. Recoveries of PCBs in the matrix spikes (94−102 %) are given in Supplementary Table S2.

Multiple Linear Regression (MLR). A MLR was performed stepwise using SPSS (V20) to investigate the influence of land use patterns and meteorology on the spatial distribution of atmospheric and freely dissolved PCBs. MLR was not performed for PCBs with detection frequency < 50 % of the total number of samples (PCB 126, 128, 156, 157, 167, 169, 170, 189, 195 in the air samples and PCB 189 in the water samples). Land use data for North America (NALC, 2005 Anderson Level II) was obtained from the National Park Service Database maintained by the United States (http://science.nature.nps.gov/im/monitor/npscape; see Supplementary data for more details).

Fugacity Ratios of PCBs. Water fugacity (f_w) and air fugacity (f_a) were calculated according to the following equations[33]:

$$f_w = C_{iw} \ . \ H \qquad (1)$$

$$f_a = C_{ia} \ . \ R \ . \ T_a \qquad (2)$$

where C_{iw} and C_{ia} are the freely dissolved and gaseous phase concentrations (pg/m^3) in water and air, respectively, R is the gas constant (J mol^{-1} K^{-1}), T_a is the atmospheric temperature (Kelvin), and H is Henry's law constant. H were calculated from the air-water partitioning coefficients (K_{AW} = H/RT). The internally consistent, finally adjusted K_{AW} values of Schenker et al.[34], which are recommended as the best available values[35] were used in the current study. Missing K_{AW} values for PCB congeners that were not included in Schenker's study were obtained by correlating the available values against those obtained from Mackay et al.[36]

A propagated error analysis was used to assess uncertainties in calculated fluxes (see Supporting Information for more details) Uncertainties ranged from 38 % (PCB 138) to 56 % (PCB 11).

Positive Matrix Factorization (PMF). To determine the sources of PCBs in the lower Great Lakes, the newest version of the U.S. EPA positive matrix factorization (V5.0) was used (see Supplementary data for more information on the model). PMF is a receptor model used for quantifying the contribution of sources to samples based on the composition or fingerprints of the sources assuming that a measured dataset conforms to a mass-balance of a number of constant source profiles contributing varying concentrations over the time of dataset.

Preparation of the Data. Measured concentrations of PCB congeners were entered separately for each deployment period at each site. PCB congeners that were below the limit of detection in > 50 % of the samples were excluded (see the MLR section above). Concentration values that were below the LOD were set to LOD/2. The uncertainty was calculated for each data point according to Aydin et al.[29], and entered into the model.

Diagnostic Tools for the PMF Model. To determine the optimal number of sources, two major rules were applied: First, the number of factors that provide clear, physically meaningful results while reducing matrix dimensionality as much as possible was selected. Second, the number of factors that caused the theoretical Q value to be equal to the true Q value (calculated by the model) was selected. To determine the PCB congeners that can be used for source profiles, the coefficient of determination (R^2) measuring the goodness of fit between the measured and modeled concentrations was used.

For gaseous PCBs, the initial matrix was composed of 38 samples x 20 species, whereas for the freely dissolved PCBs, the matrix contained 26 samples x 29 species. Calculated R^2 values for the gaseous PCB were all greater than 0.80 (Table S3) except for PCB 66 and 81. Accordingly, these two congeners were down-weighed to weak. In the water samples, PCB 123, 114 and 195 were down weighted to weak (Table S4) and PCB 169, 206 and 209 to bad ($R^2 < 0.40$). Thus, the last three congeners (bad) were excluded and the matrix was composed of 26 samples x 26 species.

Identification of Resolved Factors. To identify the resolved factors, spatial variation of the factor scores, comparison of congener patterns with known sources, and presence of the non-Aroclor congener PCB 11 were considered. The cosine theta similarity metric, which is a measure of similarities between two vectors by measuring cosine the angle between them, was used for the congener pattern matching.[4] Profiles of unaltered Aroclor mixtures (1221, 1232, 1016, 1242, 1248, 1254, 1260 and 1262) were obtained from Frame et al.[1]. Profile of Aroclor 1268 was obtained from Wyrzykowska et al.[37]. Profiles of PCBs in different combustion sources, municipal solid waste incineration, cement plant emissions (35 PCB congeners measured), coke oven, landfill sites and electric arc furnaces were all obtained from Ishikawa et al.[38]. Profiles of PCBs emitted from wood and coal combustion (48 congeners) were obtained from Lee et al.[39] and Conolly[40] (23 – 58 measured PCB congeners). Profiles were rescaled to match the congeners measured in the current study. Profiles of volatilized Aroclor mixtures were also included considering the phase- out of PCB production long time ago. Volatilized Aroclor mixtures were obtained by multiplying the concentration of each congener in the mixture by its corresponding subcooled liquid vapour pressure obtained from Schenker et al.[34]. Missing values were obtained by regressing available values from Schenker et al.[34] against those from Falconer and Bidleman.[41]. Activity coefficients were set to 1.0 as proposed by Schwarzenbach et al.[42].

Results and Discussion

Atmospheric Concentrations of PCBs. Average gaseous $\sum_{29}$PCB concentrations of all deployment periods per site ranged from 5.0-160 pg/m^3 (Figure 1a). Concentrations of PCBs were significantly greater (Mann−Whitney rank sum test, $p < 0.05$) for Lake Erie (5.0−160 pg/m^3) compared to Lake Ontario (13−46 pg/m^3). This difference is attributed to the higher detected gaseous PCB concentrations at the urban and rural sites. PCB concentrations at the urban sites on Lake Erie (Buffalo and Cleveland; average: 122

pg/m^3) were significantly higher (Mann−Whitney rank sum test, p = 0.001) than concentrations at Lake Ontario's urban sites (Oswego and Rochester; average: 31 pg/m^3). Average PCB concentration (28 pg/m^3) at the rural sites on Lake Erie (ERI at the southern coast and Gibraltar at the southwestern part) was 2 folds higher than PCB concentration (13 pg/m^3) at Cape Vincent (rural site on Lake Ontario). All the other suburban and offshore sites showed comparable concentrations in both lakes.

The highest detected gaseous PCB concentrations were observed at Cleveland on the southern coast of Lake Erie (Figure 1a) which was 2.0-35 folds higher than concentrations observed at all other locations. Elevated gaseous PCB concentrations were also observed at other urban sites, including Toledo, Buffalo (Lake Erie) and Rochester (Lake Ontario) (Figure 1a). Gaseous PCB concentrations observed in the Lower Great Lakes during each deployment period were comparable with no statistical significant difference (ANOVA, p = 0.079) probably due to the long deployment periods (2 months each) of the LDPE and the minor variations in the calculated average ambient temperatures for each deployment period. (See Supplementary data and Table S5 and Figure S2 for more details on the spatial distribution of gaseous PCBs and comparison with gaseous concentrations previously detected in the region).

Freely Dissolved Concentrations of PCBs. $\sum_{29}$ PCB concentrations (average of all deployments at each site) ranged from 2.0 - 55 pg/L (Table S5). The maximum detected PCB concentration was observed at Toledo at the western part of Lake Erie. Relatively high PCB concentrations (23-37 pg/L) were also observed at the southern (Sheffield, Cleveland, Fairport, Erie and Dunkirk) and eastern (Buffalo) coasts of Lake Erie and at the southern coast of Lake Ontario (Niagara and Oswego) (Figure 1b). No statistical significance difference was observed between measured freely dissolved PCB concentrations in both lakes. Similar to atmospheric PCBs, no statistical significant difference (ANOVA, p = 0.772) was observed when detected concentrations of freely dissolved PCBs during each deployment period were compared. (See Supplementary data and Figure S3 for more details on the spatial distribution of freely dissolved PCBs and comparison with previously reported concentrations).

Correlations of Atmospheric and Freely Dissolved Concentrations. Multiple Linear Regression was performed separately for the gaseous and freely dissolved PCBs. $\sum_{29}$ PCBs in the gas-phase were significantly correlated with the urban area within a 20 km radius of each sampling site, which explained 80 % of the total variability in gaseous concentrations (Table S6). This indicates that urban activities continue to be the major source of PCBs to the atmosphere across the lower Great Lakes. As for PCB congeners, the strength of the correlation between urban area and concentration varied as we changed the radius used to characterize urban area at the site (Table S6), which was previously observed by other researchers.[43-45] As shown in Figure (S4), di-, tri- and tetra-chlorinated biphenyls were released from longer range sources (15-25 km radius), possibly due to the higher volatility of these lower chlorinated biphenyls. In contrast, penta- (except PCB 105), hexa-, hepta-, nona- and deca-chlorinated biphenyls were released from more local sources (3-5 km radius) owing to their lower volatility.

No significant correlations were observed for the majority of the freely dissolved PCB congeners (Table S7). For congeners that showed significant correlations with urban area, less than 50 % of the total variability in concentrations was explained by this relation, and the standard error value for the regression parameter was high (Table S7). Clearly, PCBs in air and water stem from different sources. This likely implies that knowing atmospheric concentrations and sources of PCBs is not sufficient to understand or predict concentrations in the lakes.

The observed spatial distribution pattern could be related to loadings from the numerous areas of concern (Supplementary Figure S5) such as the Maumee River, Black River, Cuyahoga River, Ashtabula River, Buffalo River, Hamilton Harbour and Niagara River (all of which are contaminated with PCBs)[46-50] and the water circulation patterns. Basin-wide average concentrations of freely dissolved PCBs (Supplementary Figure S6) in Lake Erie indicated no specific trends and that comparable PCB concentrations were observed at the western, central and eastern basins. This implies that similar PCB loadings occur at the three basins of Lake Erie, or that circulation and inventory outweigh point sources.

Accordingly, PCBs are expected to be discharged with loadings from areas of concern occurring at the three basins, which may explain the comparable basin-wide average concentrations of PCBs, and the elevated PCB concentrations observed at the sampling sites affected by loadings of AOCs (Toledo, Sheffield, Cleveland, Fairport and Buffalo). Similarly, elevated concentrations of PCBs at Niagara and Oswego could be attributed to loadings from the Niagara and Oswego Rivers at the southern coast of Lake Ontario.[51, 52] Niagara could also be influenced by the urban activities occurring at Toronto and Hamilton given the counterclockwise circulation of water at the western part of Lake

Ontario. Sediment resuspension and atmospheric deposition could act as secondary sources contributing to the enrichment of the water with PCBs.

Water Quality Concerns. To assess the water quality in both lakes, concentrations of PCBs were compared with different water quality standards. Freely dissolved PCB concentrations from the current study were below the NYSDEC water consumption standard (90 ng/l), and below the U.S. EPA National recommended water quality criteria for the protection of human health from the consumption of fish and water (64 pg/l)[54] which is based on 10^{-6} cancer risk criterion. Yet freely dissolved PCB concentrations were much greater than the NYSDEC standards for the consumption of water and fish (1.0 pg/l)[53], which were previously applied by Marvin et al.[49] for monitoring water quality in the lower Great Lakes. Accordingly, PCBs could be considered contaminants of concern in Lake Erie and Lake Ontario although a decline in the freely dissolved PCB concentrations (compared to previous measurements) was observed in the current study. However, difference in the analytical methodologies and measured concentrations (freely dissolved in the current study versus whole concentration in the guidelines) should be considered when this comparison is used.

Source Factors of PCBs. Seven sources were identified for each of the gaseous and freely dissolved PCBs (Figure 2). The relationship between the measured and modeled concentrations for the gaseous and freely dissolved PCBs was significant ($p < 0.001$) and the slope of the regression line was close to unity in the majority of the congeners indicating a close agreement (Supplementary Tables S2 and S3).

For gaseous PCBs, the first factor (Figure 2a) was responsible for 20 % of the mass of PCBs with high loadings on PCB 11 (66 % of the species) and PCB 28 (18 %). PCB 11 is a non-Aroclor congener and is present in paints/pigments.[55] Accordingly, we selected factor 1 to represent volatilization from paints (painted surfaces and/or wastewater effluents containing paints). PCB 11 represented on average 16 % of the total concentrations of atmospheric PCBs in the current study, which is in good agreement with the output obtained from the PMF model (20 %). However, the PMF model could have overestimated the contribution of PCB 11 as only 29 out of 209 PCB congeners were measured in the current study, biasing it towards PCB 11 and paint/pigments as sources of PCBs. To investigate this, total PCB concentrations were calculated according to the German DIN Norm 12766-2[56]. If the total PCB concentration is used, average contribution of PCB 11 decreases from 16 % (using the congeners measured in the current study) to 8.0 % indicating that this source could be overestimated by as much as a factor of 2.0.

The second factor (Figure 2b) was responsible for 11 % of PCB mass. This factor showed the highest similarity with the profiles of domestic wood combustion[39, 40] (Cos $\theta = 0.92 – 0.93$) and coal combustion[40] (Cos $\theta = 0.91 – 0.92$) and thus this factor probably represents coal/wood combustion. [39, 40]. In the eight states surrounding the five Great Lakes, there are more than 144 coal-fired power plants[57] and domestic burning of wood is a common activity in North America especially in more rural areas.[58]

Factor 3 (Figure 2c) explained 6.0 % of the variability in the dataset; it showed the highest similarity with volatilized Aroclor 1248[1] (Cos θ = 0.92). Aroclor 1248 comprised 7.0 % of US Aroclor production between 1957 and 1977.[59]

Factor 4 was heavily loaded on PCB 123 and the lower chlorinated PCBs (Figure 2d). This factor identified 22 % of the total mass of PCB and had the highest similarity with unaltered Aroclor 1242[1] (Cos θ = 0.91) and Aroclor 1016[1] (Cos θ = 0.90). Aroclor 1016 is so similar in the congener pattern to Aroclor 1242[4] and accordingly, this factor may represent contribution from unaltered lower chlorinated mixtures. Aroclor 1242 comprised 51 % of US Aroclor production between 1957 and 1977[59] and was commonly used in paper industries.[60] This factor had also some loading on PCB 11, which may indicate that this factor is associated with treated wastewater or stormwater input into the area.

Factor 5 (Figure 2e) was similar to volatilized Aroclor 1260[1] (Cos θ = 0.91), and explained 12 % of the total variability in the dataset. Aroclor 1260 represented 11% of US production of PCBs[59] and its use was limited to transformers, hydraulic fluids, as a plasticizer in synthetic resins, and dedusting agents.[4]

Factor 6 (Figure 2f) identified 25 % of the total variability in the data. Its profile is similar to volatilized Aroclor 1254[1] (Cos θ = 0.89). This technical mixture represented 16% of U.S. PCB production of Aroclors and was used in the widest variety of applications.[59]

Factor 7 explained 4.0 % of the variability in the gaseous concentrations and was heavily loaded on the higher chlorinated PCBs (Figure 2g) and moderately loaded on PCB 18, 28, 77 and 101. The profile of this source factor did not show any similarity with the investigated source profiles from literature and thus we assume that this factor either represents volatilization of several Aroclor mixtures (including 1268) or a signature of particulate PCBs. This factor was named “other”.

We indicated that the PMF model in the current study may have overestimated the contribution from the paint/pigment source by a factor of two. This implies that the contributions of each of the other extracted sources may have been underestimated by a factor up to a factor of two, but likely less for the dominant sources. For sources other paints/pigments, the congeners measured in this study typically accounted for 30-40% of total PCBs.

PMF source profiles of the freely dissolved PCBs are shown in Figure 2h-n. The first factor (Figure 2h) explained 15 % of the total PCBs and showed high loadings on PCB 11 (64 % of the species), 81, 105 and 157 and moderately loaded on PCB 128, 138, 153 and 153. PCB 11 is known to be a non-Aroclor congener. Du et al.[61] indicated that PCB 11 is produced as a by-product from the manufacture of the yellow pigment which is used in ink, paint and textile printing. They used this congener as a tracer of contamination from wastewater/stormwater in Delware River. Similarly, Rodenburg et al.[62] indicated that concentrations of PCB 11 in NY/NJ Harbour varied as a function of the flow of wastewater effluents. Accordingly, the factor was selected to represent wastewater/stormwater inputs. PCB 11 represented on average 8.0 % of the $\sum_{29}$ freely dissolved PCBs in the Lower Great Lakes, which may indicate that the PMF model overestimated the contribution from this source possibly due to the contributions from the other PCB congeners. Additionally, the limited number of congeners measured in the current study could result in overestimating this source by up to a factor of 3.0 if all PCB congeners had been measured.

The second factor (Figure 2i) explained 13 % of the total variability in the data and was heavily loaded on PCB 28, 81, 156 and 157 and moderately loaded on PCB 8, 18, 52, 44, 66, 118 and 128. This pattern was close to the profile of PCBs in wood/coal combustion (Cos θ = 0.93). The similarity is based only on the resolved PCB congeners in this profile, which represented 16-27 % by weight of the total PCB congeners reported for this source.

The other five resolved factors (Figure 2j-n) represented unaltered Aroclor 1260 (Figure 2j; Cos θ = 0.90), unaltered Aroclor 1242 (Figure 2k; Cos θ = 0.96), volatilized Aroclor 1260 (Figure 2l; Cos θ = 0.91), volatilized Aroclor 1254 (Figure 2m; Cos θ = 0.89) and unaltered Aroclor 1254 (Figure 2n; Cos θ = 0.89) comprising 15 %, 12 %, 11%, 16 % and 18 % respectively of the total mass of PCBs in the dataset.

As for the gaseous PCBs, we assume that the limited number of the freely dissolved PCB congeners measured in the current study together with the overestimated contribution of the wastewater/stormwater source have resulted in an underestimated contributions for each of the other extracted sources by a factor < 3.0.

Source Apportionment of PCBs across the Lower Great Lakes. Average normalized contributions of the PMF source factors for the three deployment periods are shown in Figure 3. For simplicity, all unaltered Aroclor mixtures were summed together and presented as one figure each for the gaseous (Figures 3c) and freely dissolved PCBs (Figure 3g). Volatilized Aroclors were treated in the same manner (Figure 3d, h). The source representing volatilization from paints/pigments is presented as normalized concentrations of PCB 11. For gaseous PCBs, volatilized Aroclors (mainly Aroclor 1254) were the major contributors in all the locations at Lake Ontario (Figure 3d) comprising 59 – 79 % of the total gaseous PCB concentrations. Coal/wood combustion (Figure 3b) showed significant contribution at Cape Vincent, Oswego and Niagara (10 – 20 % of the total gaseous PCB concentrations), which are influenced by emissions from the coal-fired power plants close to these sampling locations (Figure S7), and the prevailing southwesterly wind. Volatilization from paints/pigments source factor showed significant contributions at all the sites on the southern and northern coasts of Lake Erie (12-34 %) and at Niagara on Lake Ontario (15 %). Unaltered Aroclor 1242 showed significant contribution only at the urban site Oswego.

Lake-wide average percent contributions at Lake Erie indicated that volatilized Aroclors were the major contributors to the total gaseous PCB concentrations comprising 44 % of the total concentration followed by, Aroclor 1242 (28 %), coal/wood combustion and volatilization from paints/pigments (17 % each). This supports the observation made above that urbanization, which is linked to volatilization of PCBs from current and former use, is the main source of PCBs.

However, different patterns were observed at the sampling sites (Figure 3a-d). Volatilized Aroclors (mainly 1254 and 1260) dominated (72 – 100 % of the total PCB concentration) at Buffalo and ERI-2 (onlake site at the northern part). Comparable contributions from the four sources (paints/pigments, coal/wood combustion, Aroclor 1242 and volatilized Aroclors) were observed at Dunkirk, Fairport, Sheffield and Toledo comprising 15 - 25 %, 13 – 19 %, 22 – 32 % and 21 – 36 % respectively of the total gaseous PCB concentrations. A similar pattern was observed at Gibraltar at the southwestern part of Lake Erie except that paints/pigments source showed only a minor contribution (5.0 %) of the total PCB concentration. At Erie and ERI-3 (onlake site on the northwestern part of Lake Erie), volatilized Aroclors and paints/pigments sources comprised 84 – 100 % of the total gaseous PCB concentrations. Additionally, volatilization from paints/pigments was the main source of gaseous PCBs at the on-lake site ERI-2. This supports the results from the PMF, as the open lake sites will receive PCB from long-range transport only.

The two sites at Cleveland showed a different pattern, where Aroclor 1242 was the major source comprising 36 – 62 % of the total concentrations. (Figure 3c). All the other sources showed comparable contributions (Figure 3a,b,d).

Output of the PMF model for the freely dissolved PCBs indicated that volatilized Aroclors (mainly 1260) and unaltered Aroclors (mainly 1254) were the major sources of freely dissolved PCBs at all the sites on Lake Ontario and at Buffalo on Lake Erie (Figure 3g-h) comprising 71 – 81 % of the total PCBs. This shows the importance of direct emissions of PCBs into Lake Erie, likely from the areas of concern. Particularly at Grimsby (Ontario) and Buffalo, contributions from unaltered Aroclors (53 – 60 %) were ~ 2 – 3 folds higher than volatilized Aroclors (18 – 27 %). PCBs associated with coal/wood combustion and volatilized Aroclors were the major sources at Cleveland, and Toledo on Lake Erie comprising 50 – 68 % of the total freely dissolved PCB concentrations (Figure 3e-f). These results are in-line with expectations due to the heavy industrialization and urbanization for these sampling locations. At the onlake sites (ERI-4 and ERI-6), coal/wood combustion was the dominant source comprising 42 – 45 % of the total freely dissolved PCB concentrations followed by comparable contributions from the other three sources. This likely represents atmospheric deposition of (particle-bound) PCBs. Similar to gaseous PCBs, comparable contributions from all the sources were observed at Fairport and Dunkirk on Lake Eire (Figure 3e-h). At Erie, 57 % of the freely dissolved originate from unaltered Aroclors, and comparable contributions from the other three sources were observed.

Based on the spatial distribution of the source contributions for gaseous and freely dissolved PCBs, we can easily observe that sources related to urban activities (combustion, wastewater and unaltered Aroclors) showed higher contributions at Lake Erie compared to Lake Ontario especially at the southern and southwestern coasts (Figure 3a-h). The relatively significant contribution from wastewater/stormwater in the freely dissolved PCBs at the southern part of Lake Erie could be attributed to effluents discharged from areas of concern close to those sites and the existence of several wastewater treatment plants.[27] In Contrast, volatilized Aroclors showed higher contributions at Lake Ontario. This implies that there is a still ongoing significant influence of urban activities on the levels of PCBs in Lake Erie. Additionally, significant contributions from non-Aroclor sources were observed at the majority of the sites indicating that contamination with PCBs in the lower Great Lakes is shifting from the legacy Aroclor-like signature to the current use (non-Aroclor) sources.

Gaseous Exchange of PCBs. Water-air fugacity ratios (*f*w/*f*a) are presented in Supplementary Figure S8. Calculated fugacity ratios were outside the uncertainty range for the majority of the samples indicating a non-equilibrium situation (either volatilization or deposition) between air and water concentrations (*f*w/*f*a ≠ 1). However, some chlorinated biphenyls (PCB 8, 11, 18, 28, 52, 44, 66, 101, 118) were within the uncertainty range at several sampling sites (Grimsby during the third deployment period, Buffalo, Dunkirk during the first deployment period, Cleveland, Fairport during the third deployment period and Sheffield). Accordingly, PCB fugacity ratio within the uncertainty range was considered at equilibrium.

Fugacity ratio was higher than one for the tetra- through hepta-chlorinated biphenyls in 62 – 100 % of the samples indicating net volatilization from the water to the air. Net deposition (*f*w/*f*a < 1) was observed for PCB 206 in the majority of the samples (67 %) and for PCB 11, 18 and 206 in 32 – 38 % of the samples. Calculated fugacity ratios were within the equilibrium (uncertainty) range for PCB 8, 11, 18, 28, 52 and 118 in 23 – 33 % of the samples. Net deposition and equilibrium was mainly observed at Buffalo, Cleveland, Dunkirk and Gibraltar (Lake Erie) and Grimsby (Lake Ontario).

Implications

Over 40 years after their production ceased in the US, PCBs across Lakes Erie and Ontario continue to exceed threshold values meant to protect the public from adverse effects. The Great Lakes Restoration Initiative is meant to change this. Our results indicate the on-going emissions of atmospheric PCBs from urban areas, and the release of freely dissolved PCBs from the numerous areas of concern along both lakes. Although the legacy Aroclor-like signature is still observed, other non-Aroclor signatures such as PCB 11, PCB 209 and PCBs emitted from coal/wood combustion were observed and showed significant contributions at the urban, suburban, rural and on-lake sites. The historical trend of PCB 11 is unknown and little is known about its toxicity. However, it is produced as a byproduct in the current paint manufacturing. We thus conclude that sources of PCB contamination in the Lower Great Lakes is shifting towards current use sources. This could be a challenge for political actions as sources of PCB 11 and 209 differ from Aroclor sources and therefore control strategies designed to lower the loads of most other PCB congeners are not likely to be successful in lowering PCB 11 and 209 loads. Albeit, measuring only a limited number of PCB congeners may overestimate contributions from the non-Aroclor congeners and underestimated contributions from Aroclor congeners in the source apportionment studies. In the current study, the relative percent differences between the contributions of the paint/pigment source based on 29 versus total PCB concentrations were 44 % and 67 % respectively for the gaseous and freely dissolved PCBs. We therefore support the recommendation of Rodenburg et al.[62] that monitoring programs (including IADN) should measure all possible PCB congeners in at least a subset of samples and should measure PCB 11 in all samples. As PCBs are regulated in USA as the sum of all 209 congeners, further attention should be given to non-Aroclor congeners.

Supporting Information

Details on spatial distribution of PCBs, air-water fugacity ratios, PMF and MLR can be found in the supplementary data. This material is available free of charge via the Internet at http://pubs.acs.org.

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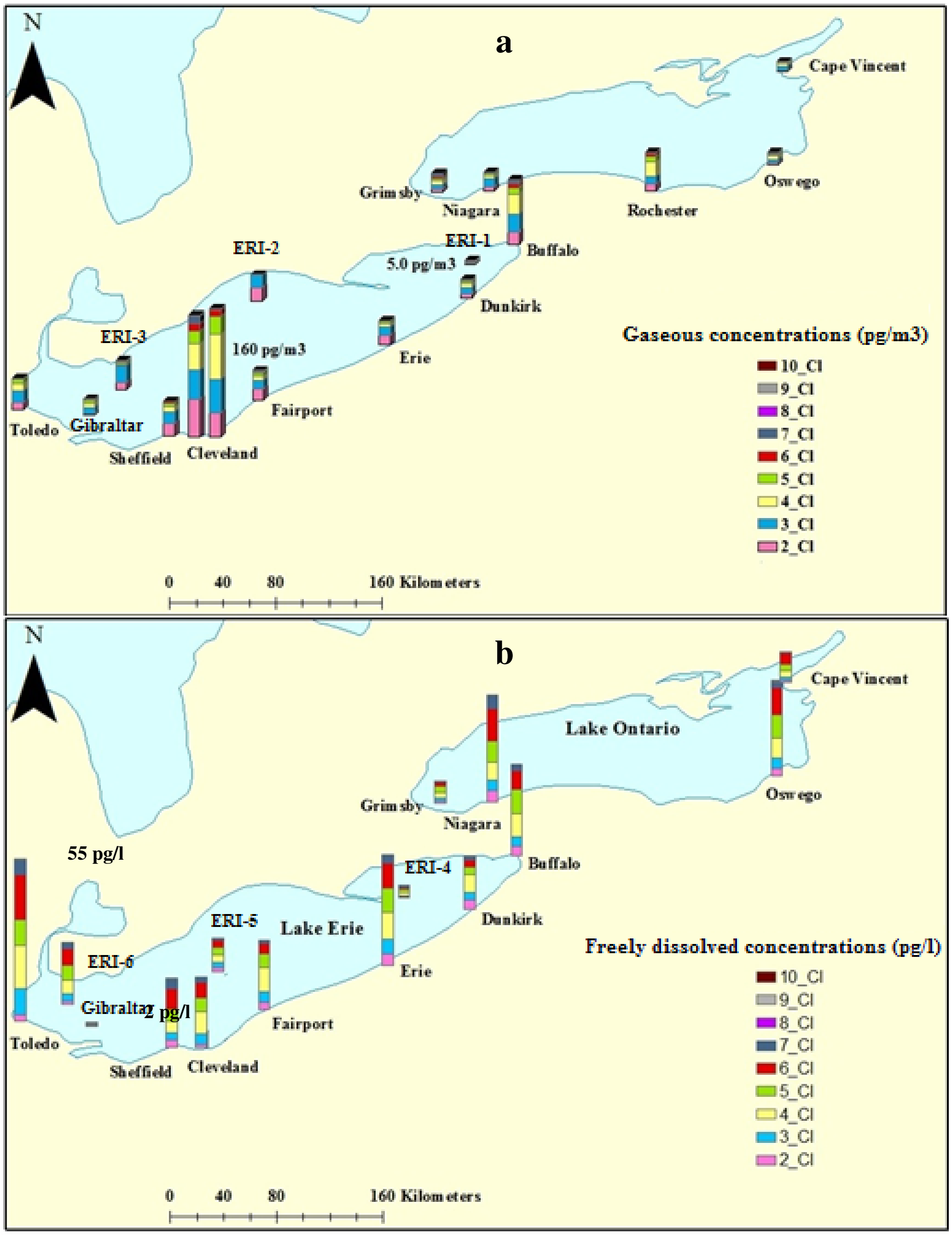


Figure 1: Spatial distribution of gaseous (a) and freely dissolved (b) concentrations of the $\sum_{29}$ PCBs at the lower Great Lakes.

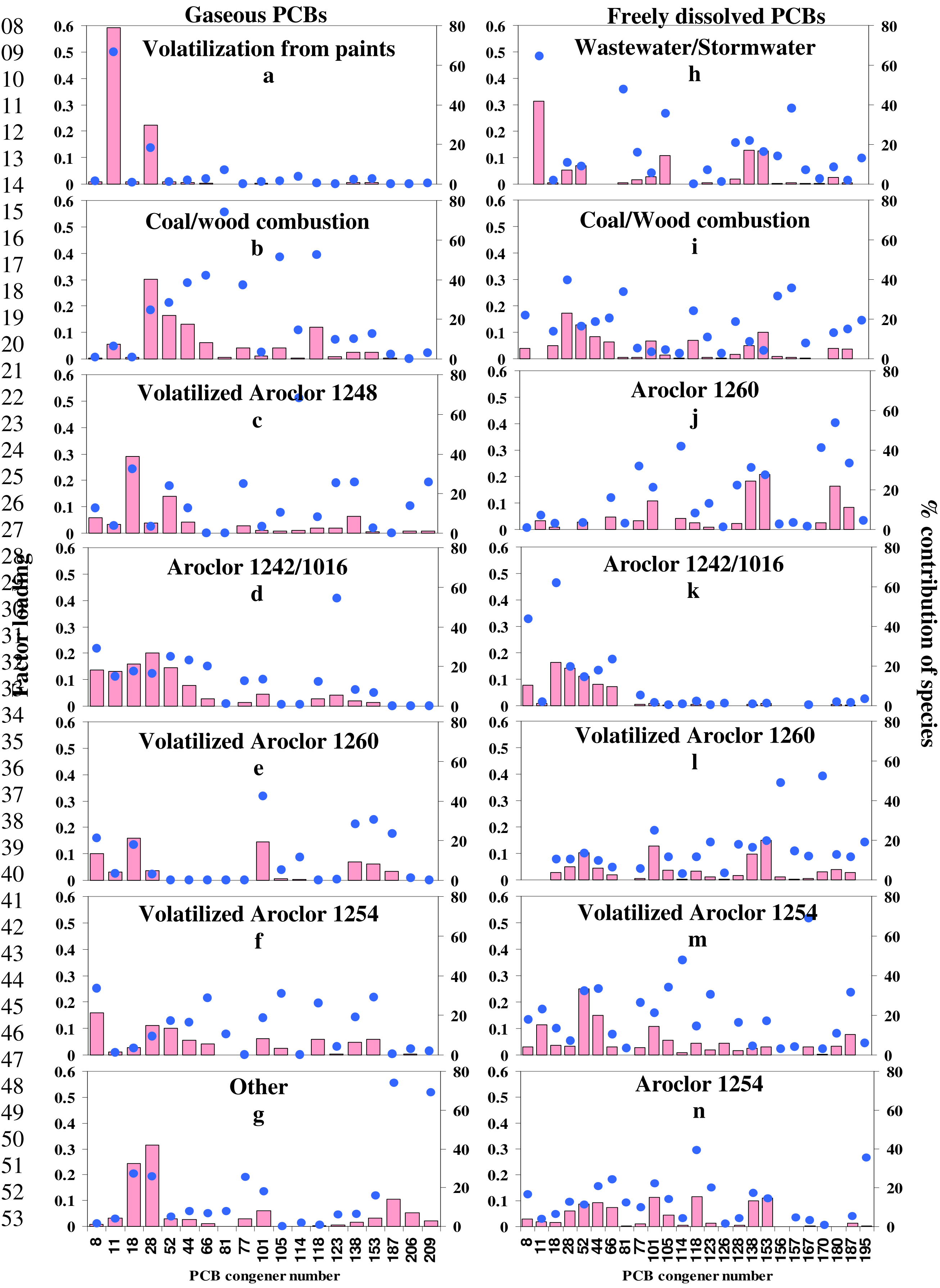


Figure 2: Positive matrix factorization source profiles of gaseous (a-g) and freely dissolved (h-n) PCBs. Bars represent factor loading and dots represent % contribution of each congener on each source factor.

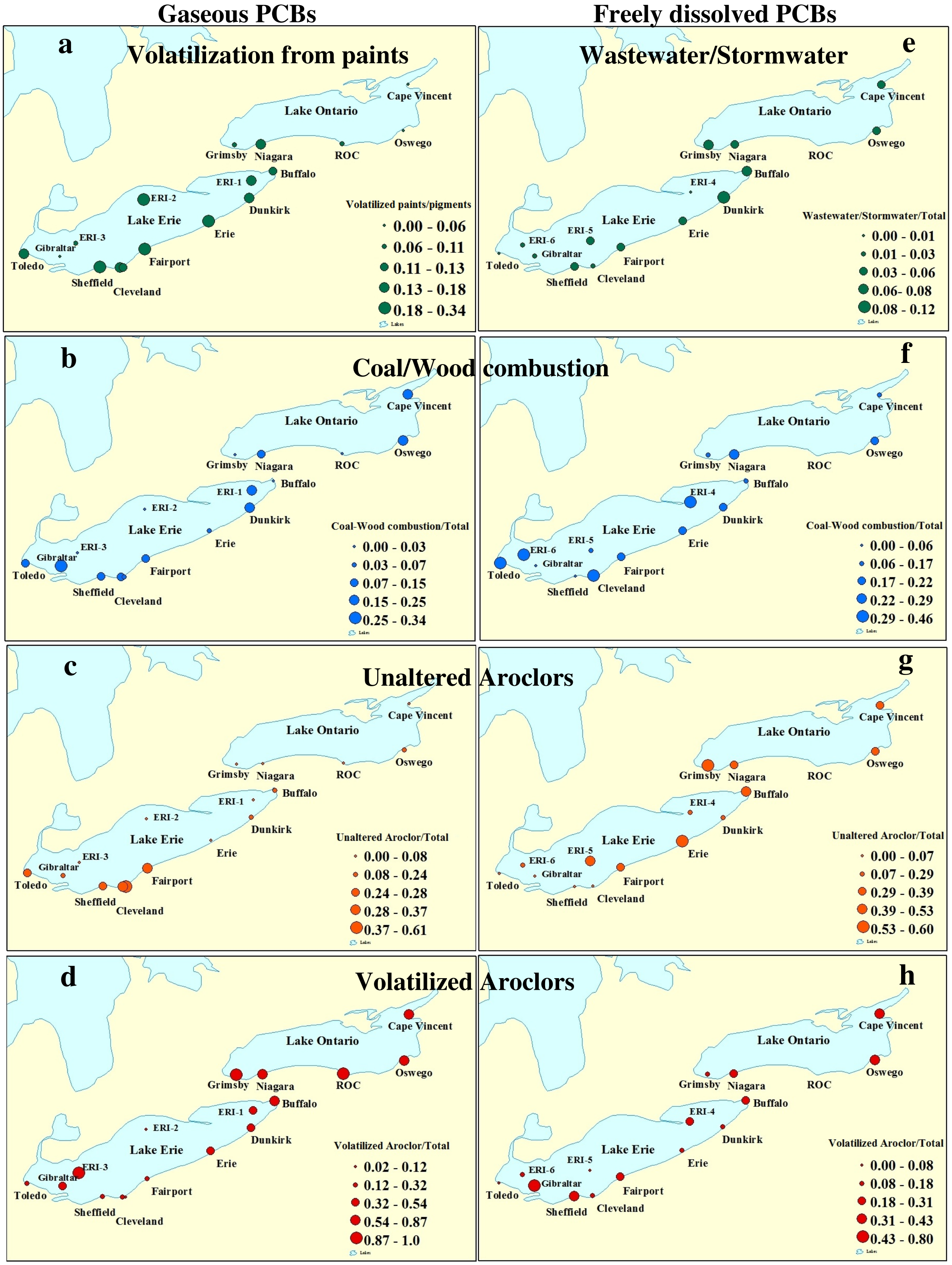
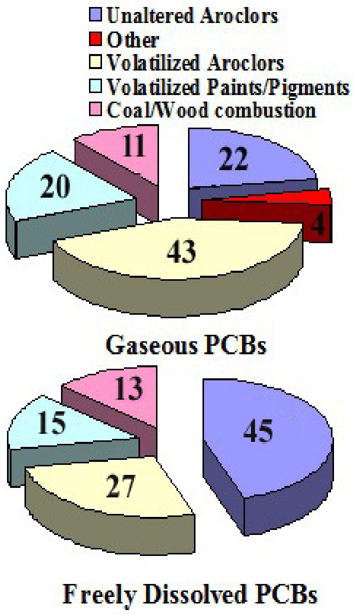


Figure 3: Average normalized contributions of the PMF source factors for the three deployment periods from total gaseous (a-d) and freely dissolved (e-h) PCBs at each sampling location. Figure 3a and 3e were presented based on the concentrations of PCB 11 in the samples rather than the output of the PMF model.


Unaltered Aroclors
Other
Volatilized Aroclors
Volatilized Paints/Pigments
Coal/Wood combustion
11
22
20
4
43
Gaseous PCBs
13
15
45
27
Freely Dissolved PCBs

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