Seasonal trends of PCBs in air over Washington DC reveal localized urban sources and the influence of Anacostia River☆

Mandar Bokare [a], Nathalie Lombard [a], Samuel Magee [a], Dev Murali [b], Upal Ghosh [a,*]

[a] *Dept. of Chemical, Biochemical, and Environmental Engineering, University of Maryland Baltimore County, Baltimore, MD, 21250, USA*
[b] *Washington DC Department of Energy and Environment, 1200 First Street NE, Washington, DC, 20002, USA*

ARTICLE INFO

ABSTRACT

Semi-volatile organic compounds like polychlorinated biphenyls (PCBs) undergo diffusive exchange flux between a water body and the overlying air. The magnitude of this exchange can be a substantial component of the overall pollutant mass balance and needs to be determined accurately to identify major pollutant sources to the water body and to plan appropriate remedies. For the PCB-impacted Anacostia River in Washington DC (USA), quantification of air-water exchange has been a major data gap. In the present study, polyethylene passive samplers were used to measure PCB concentrations in air phase at six locations in DC over a period of one year to capture spatial and seasonal variations. Concurrent water phase PCB measurements were used to quantify the direction and magnitude of air-water exchange in the Anacostia River. Two locations had nearly an order of magnitude higher air phase PCB concentrations that could be related to localized sources. Remaining four locations provided similar air phase PCB concentrations that averaged from 270 ± 44 pg/m^3 (summer) to 32 ± 4.3 pg/m^3 (winter). $\sum$PCB water-air exchange fluxes were positive across all seasons, with net PCB volatilization of 180 ± 19 g/year from the surface water. Volatilization rate was an order of magnitude lower than previously estimated from a fate and transport model. PCB load from atmospheric deposition based on previous studies in this watershed was an order of magnitude lower than the volatilization rate. Results refuted a long-standing understanding of the air phase serving as a source of PCBs to the river as per the currently approved Total Maximum Daily Load assessment. The study demonstrates the utility of passive air phase measurements in delineating local terrestrial sources of pollution as well as providing estimates for air-water exchange to complete a robust mass balance for semi-volatile pollutants in an urban river.

1. Introduction

Widespread impairments have been documented for polychlorinated biphenyls (PCBs) in several locations within the Chesapeake Bay, driven by elevated concentrations in sediments and fish tissue (Chesapeake Bay Program, 2020; U.S. EPA, US Geological Survey, US Fish and Wildlife Service, 2012). Fish represent a major route of PCB exposure to humans, leading to consumption advisories for fish caught in the Bay and several of its tidal waters. One such tidal body, the Anacostia River in Washington DC, has been declared as a "region of concern" in the Bay due to PCB contamination (Chesapeake Bay Program, 2020; U.S. EPA, 2020). This river is currently under a fish-consumption advisory (DOEE, 2016) and recently underwent a Remedial Investigation – Feasibility Study (RI-FS) to determine the nature and extent of contamination from toxic pollutants (DOEE, 2019a, 2019b; 2019c).

For a water body, the dissolved concentration of hydrophobic pollutants represents the driving force for biological uptake into aquatic organisms, and controls transport processes such as air-water exchange, porewater-surface water exchange, and impact from point and non-point sources. Quantifying these processes can provide insights into which of these serve as sources and sinks for pollutants and help inform potential remedial actions. Diffusive exchange of pollutants across the air-water interface is an important component of environmental fate and transport of semi-volatile pollutants in river systems (Apell and Gschwend, 2017; Minick and Anderson, 2017; Tidwell et al., 2017). The atmosphere can act as a sink or source for pollutants in the water column depending on the chemical fugacity gradients. For site investigations, determining the direction and magnitude of air-water exchange of

---

pollutants can be critical in evaluating whether the water body is responsible for elevated levels of pollutants in the air. For example, volatilization of PCBs from the New Bedford Harbor (NBH) Superfund Site in Massachusetts was determined to be responsible for high levels of gas-phase PCBs ($\sum$ PCBs: 0.4–38 ng/m^3) in the vicinity (Martinez et al., 2017). Similarly, the Deepwater Horizon oil spill incident was at least partially responsible for elevated levels of PAHs and oxygenated PAHs (OPAHs) in air at coastal sites in Louisiana, Mississippi, Alabama, and Florida (Tidwell et al., 2017). Additionally, the direction and magnitude of air-water exchange can also be used to evaluate the impacts of atmospheric inputs of pollutants on current or potential remediation strategies. For example, concerns over recontamination of the Lower Duwamish Waterway in Seattle from ongoing atmospheric deposition of PCBs from the surrounding urban area are being investigated (Apell and Gschwend, 2017). Previous measurements in the Northern Chesapeake Bay and Baltimore Harbor showed the importance of volatilization as the dominant process for removal of PCBs from the Chesapeake Bay (Bamford et al., 2002, 1999; Nelson et al., 1998). However, there are no recent measurements quantifying the diffusive exchange of PCBs over the Anacostia River. In the PCB fate and transport model for the Anacostia and Potomac Rivers (LimnoTech, 2007), volatilization rate of PCBs from the Anacostia River to the atmosphere was estimated to be 2200 g/year and was two orders of magnitude higher than direct atmospheric deposition to the river (46 g/year). However, diffusive flux in this assessment was estimated from model calibration and was not based on direct measurements. Furthermore, $\sum$PCBs were modeled instead of individual congeners, while using air-phase PCB concentrations measured by Brunciak et al., in 2001 over the northern Chesapeake Bay, which is closer to Baltimore than to Washington DC. Crucially, PCB inputs from a major tributary (Lower Beaverdam Creek) were not included in this fate and transport model. This tributary has been found in several investigations to be an important ongoing source of PCBs to the Anacostia River (Ghosh et al., 2020; Lombard et al., 2022; Wilson, 2019). The true magnitude of the diffusive flux between air and water remains an important data gap for the Anacostia River PCB mass balance due to: a) lack of direct measurements of the air-phase PCB concentrations in Washington DC, b) lack of direct measurements of dissolved PCB concentrations in the Anacostia River, and c) omission of an important ongoing PCB source from the fate and transport model.

While much of the past efforts at quantifying air and water phase concentrations of semi-volatile compounds have relied on high volume sampling over short periods (hours), recent developments in passive sampling have allowed a time-integrated measurement in both the air and water phases thereby providing more useful data to determine annual fluxes. Passive sampling using low-density polyethylene (PE) is being increasingly used to provide time-integrated measurements of the dissolved and air phase concentrations of PCBs, OCPs, and PAHs (Adams et al., 2007; Apell and Gschwend, 2017; Khairy and Lohmann, 2013, 2012; 2014; Liu et al., 2016a). In the present study, PE passive samplers were used for the measurement of air-phase PCB concentrations over the Anacostia River and concurrently for measuring freely-dissolved concentrations in surface water of the Anacostia River in Washington DC. The magnitude of air-water exchange flux of PCBs was determined from the concentration gradients in the air and water phase to quantify an important component of the environmental fate of PCBs in this watershed.

2. Material and methods

2.1. Sampling locations

Air sampling was conducted at five air monitoring stations around Washington DC while water column PCBs in the river were measured at 4 to 5 sampling locations along the length of the river, depending upon the sampling period (Fig. A1 and Table A1). Overall, water and air concentrations were simultaneously measured across 4 consecutive

deployment periods from March 2017 to May 2018. Additional air sampling was carried out at the University of Maryland Baltimore County (UMBC) campus for comparison. The same passive samplers used for water sampling were used for air sampling. For air samplers, a set of metal bowls were used to house and protect the air samplers from direct deposition, while still allowing air exchange (Khairy and Lohmann, 2014; Liu et al., 2016a; Lohmann et al., 2011). For water sampling, 1 g PE was used while 2 g of PE was used for air sampling. All measurements were performed in duplicate.

2.2. Preparation of passive samplers

Passive samplers were prepared using 50 μm thickness PE sheets (Husky, Bolton, Ontario). The PE sheets were cut into 6 in. by 6 in. strips, each weighing about 1 g. The strips were cleaned by immersing them in acetone/hexane mixture (50/50 v/v) for 24 h on an orbital shaker to remove residual monomers and any target and non-target contaminants, as described in U.S. EPA user manual for passive sampling (SERDP/ESTCP/U.S. EPA, 2016). After drying, PE strips were loaded with four performance reference compounds (PCB 29, PCB 69, PCB 155 and PCB 192) in a 80%–20% v/v methanol-deionized (DI) water solution, as per Booij et al. (2002). A day before transporting them to the field, a small of piece from each PE strip was removed, the pieces were separated into 3 sets and used for obtaining the initial mass of PRCs in the PE. PE strips were then enclosed in a stainless-steel mesh, wrapped in food-grade aluminum foil, stored in freezer to minimize PRC loss and transported to the field in coolers.

2.3. Sample processing, extraction, and analysis

After retrieval, passive samplers were cleaned on-site by using deionized water to remove any particles adhering to the surface, placed in labeled glass vials, and transported back to the lab in a cooler. Each sample was extracted in 40 mL amber vials using pesticide-grade hexane. A total of 119 PCB congeners were measured either as individual congeners or as groups of congeners. Method detection limits ranged from 2.58E-05 pg/L (PCB 209) to 97 pg/L (PCB 1) for water, and from 3.5E-04 pg/m^3 (PCB 209) to 280 pg/m^3 (PCB 1) for air. PCB 14 and 65 were used as surrogates. Recoveries for PCB 14 ranged from 70% to 319% across all water samplers (including those deployed in the river and in the tributaries, with complete sampling sites provided in Ghosh et al. (2020)), with average recovery of 104%. Recoveries for PCB 65 across water samplers ranged from 72 to 147% (105% average recovery. High recoveries (>140%) for PCB 14 and PCB 65 observed in 13% and 3.2% of the samples, respectively, were linked to interferents eluting close to the surrogate peaks in the chromatograms. Excluding samples with surrogate recoveries >140% resulted in average recoveries of 98% (PCB 14) and 104% (PCB 65) for water samplers. For air samplers, recoveries for PCB 14 ranged from 67 to 119% (94% average recovery), while those for PCB 65 ranged from 70 to 112% (93% average recovery). Samples with recoveries <70% for both surrogates were excluded from analysis. Further description of the extraction and analytical methods, along with Quality Assurance and Quality Control (QA/QC) procedures adopted, including concentrations detected in procedure and PE blanks are provided are provided in the Supporting Information (SI).

2.4. Freely-dissolved PCBs in surface water

Freely-dissolved concentrations in the water column were estimated as per Equation (1) (Perron et al., 2013), where C_W is the water column concentration (ng/L), $C_{PE-W,t}$ is the target compound concentration in the passive sampler at time t (ng/kg), K_{PE-W} is the partition coefficient of the target compound between water phase and passive sampler (L/kg), k_e is a first-order dynamic coefficient (day^{-1}), and t is the deployment time (days). For PCBs, K_{PE-W} values were based on published consensus values in Ghosh et al. (2014). Target analytes with non-equilibrium

correction factor, f_{eq} (= $1 - \exp(-k_e*t)$), below 0.1 were not reported due to uncertainty linked with low uptake and high non-equilibrium correction factor (Joyce et al., 2020). Estimated uncertainties in f_{eq} are provided in the SI.

$$C_W = \frac{C_{PE-W,t}}{(1 - e^{-k_e*t}) \times K_{PE-W}} \tag{1}$$

2.5. PCB concentrations in air

Concentrations of PCBs in air were calculated as per Equation (2), where C_A is the concentration of the compound in air (ng/L), $C_{PE-A,t}$ target compound concentration in the passive sampler at time t (ng/kg), K_{PE-A} is the partition coefficient of the target compound between air phase and passive sampler (L/kg), while f_{eq} is the non-equilibrium correction factor calculated based on the concentration of PRCs in the PE before and after deployment (Liu et al., 2016a). Additional details, including estimated uncertainties in f_{eq} are provided in the SI.

$$C_A = \frac{C_{PE-A,t}}{K_{PE-A} \times f_{eq}} \tag{2}$$

For PCBs, K_{PE-A} values for all measured congeners were calculated from correlation between K_{PE-A} and subcooled liquid vapor pressure (p_L, Pa) (Khairy and Lohmann, 2014), using p_L values obtained from Mackay et al. (2006).

$$\log K_{PE-A} \left(\frac{L}{kg} \right) = -0.82 \log p_L + 6.22 \tag{3}$$

2.6. Temperature correction for partitioning coefficients

PE-air and PE-water partitioning coefficients were corrected for temperature using the Van't Hoff equation as per Lohmann (2012). Further details are provided in the SI.

2.7. Water-air exchange flux

The water-air exchange flux for PCBs ($Flux_{W \to A}$, ng/m^2/day) was calculated as per Equation (4) (Liu et al., 2016a), where $\nu_{A/W}$ is the overall mass transfer velocity (m/day), C_W is the freely-dissolved concentration of compound in water (ng/m^3), C_A is the air concentration of compound (ng/m^3) and K_{AW} is the temperature-corrected air-water partitioning coefficient. K_{AW} values for each congener were calculated from the ratio of respective K_{PE-W} and K_{PE-A} values (Apell and Gschwend, 2017), as shown in Equation (5). The water-air exchange flux was also calculated based on use of Henry's Law constant for calculating K_{AW}. Additional details on this approach and the comparison of fluxes calculated using these two approaches are provided in the SI. Flux values preceded by "+" indicate "volatilization" from surface water to the atmosphere, while values preceded by "−" indicates "absorption" from atmosphere into surface water. All PCB concentration and flux calculations were performed at the congener level and then added to provide homolog and total PCB concentrations.

$$Flux_{W \to A} = \nu_{A/W} \times \left(C_W - \frac{C_A}{K_{AW}} \right) \tag{4}$$

$$K_{AW} = \frac{K_{PE-W}}{K_{PE-A}} \tag{5}$$

Water-air fugacity ratios were also calculated for each homolog group to delineate volatilization/absorption from equilibrium (Supporting Information). Calculations were performed for each deployment period using respective surface water and air concentration data. For flux calculations, the average concentration in the surface water was calculated by averaging the dissolved PCB levels measured at the various monitoring sites along the river. The air PCB concentration in the watershed was represented by the average of concentrations measured at American University (AU), River Terrace (RT), McMillan Reservoir (MMR) and Earth Conservation Center (ECC). For sites in the Anacostia watershed in Washington DC, average ambient temperature and wind speed during the deployment periods were calculated using data from the National Data Buoy Center (NDBC) Station WASD2 - 8594900 - Washington, DC (National Data Buoy Center, 2020a). Temperature data for UMBC was obtained from Station BLTM2 - 8574680 - Baltimore, MD (National Data Buoy Center, 2020b).

2.8. Error propagation analysis

Propagated error in fugacity ratios was calculated considering the uncertainties in the measured concentrations for PCBs in both water and air. The absolute uncertainty in the flux was calculated based on relative uncertainty of 30% for $\nu_{A/W}$ (Rowe and Perlinger, 2012), a relative uncertainty of 50% for all K_{PE-W} values, a relative uncertainty of 50% for all K_{PE-A} values (Liu et al., 2016b), in addition to the uncertainties in the measured concentrations, and in non-equilibrium correction factors. Additional details are provided in the SI.

2.9. Water-air exchange rate

The net annual transfer rate ($M_{W/A}$, g/year) of PCBs exchanged across the air-water interface of the Anacostia River was quantified as shown in Equation (6) where $Flux_{W \to A,N}$ (ng/m^2/day) and t_N are the flux and air sampler deployment time for a season N, where $\sum t_N$ is total deployment time (days) for all four periods of air sampler deployment, while 365 and 10^{-9} are the conversion factors for extrapolation over a year and for converting between ng and g, respectively. The surface area of the tidal region of the Anacostia River is estimated to be 850 acres or 3,440,000 m^2 (Anacostia Watershed Restoration Partnership, 2009).

$$M_{W \to A} = 10^{-9} \times \text{Surface Area} \times \frac{365}{\sum t_N} \times \sum_{N=Spring\ 2017}^{Winter2017/18} \left[Flux_{W \to A,N} \times t_N \right] \tag{6}$$

3. Results and discussion

3.1. Spatial and seasonal variations in air PCB concentrations

Total PCB concentrations ($\sum$PCB) in air along with homolog distribution for the four deployment periods are shown in Fig. 1 A-D, and also provided in Table A9. PCB concentrations showed a seasonal influence with higher concentrations measured during the Summer 2017 (average ambient temperature: 297 K) and lowest concentrations during Winter 2017/18 (average ambient temperature: 282 K). $\sum$PCB concentrations ranged from 28 pg/m^3 to 5400 pg/m^3 across the four sampling campaigns. With the exception of Spring 2017, the highest concentrations in air were measured at LBC1, which is close to the Lower Beaverdam Creek that has been shown to have high levels of dissolved PCBs in surface water in our recent work comparing PCBs in surface waters of major tributaries of the Anacostia River (Ghosh et al., 2020; Lombard et al., 2022). The elevated localized PCB concentrations in both the air and water phases in the LBC1 area indicates an ongoing source in the adjacent industrial areas comprising metal recycling facilities and rail yards which are now (as a consequence of the present study) the subject of additional ongoing investigations (Maryland Department of the Environment, 2021a; 2021b). For Spring 2017, the HP site exhibited concentration of 3400 ± 440 pg/m^3, an order of magnitude higher than those measured at other sites, indicating a possible localized source. However, use of this site for subsequent sampling campaigns and confirmation was not possible due to ongoing construction at the site and a subsequent lack of access, and sampling was moved to a nearby Lower Anacostia River location at ECC (see Fig. 2A), which did not show similar high air phase concentrations. For the other three sampling
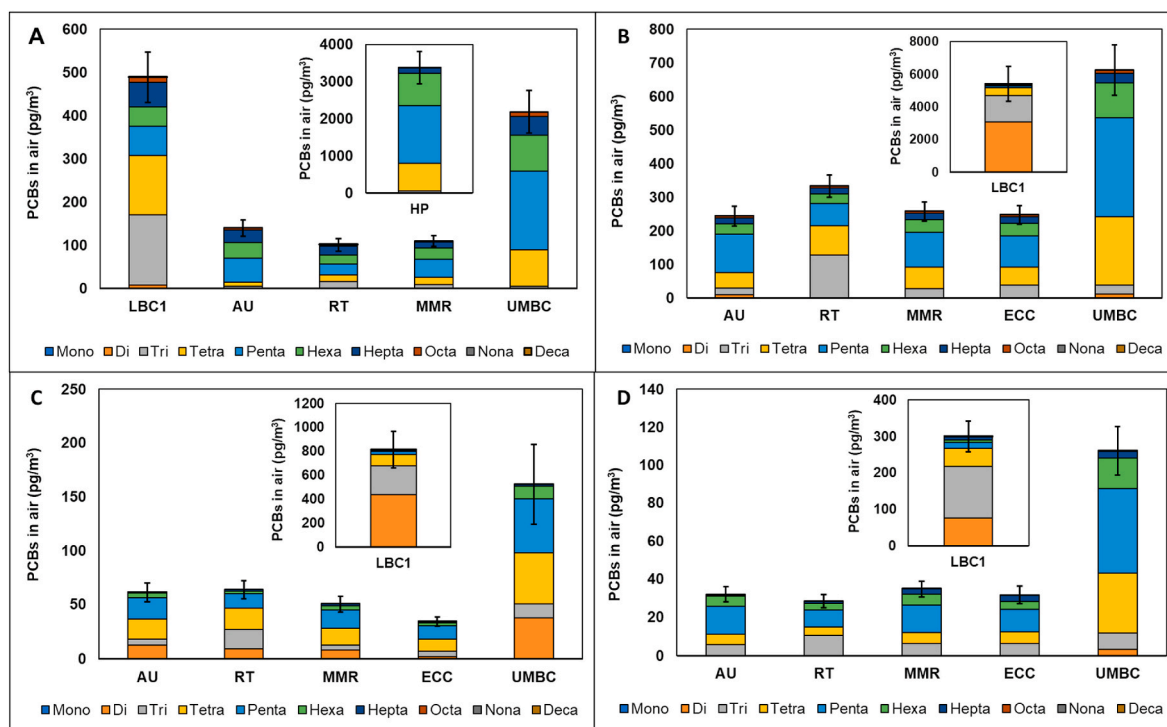
Fig. 1. PCB concentrations by homolog in air over Washington DC and at UMBC. **A:** Spring 2017; **B:** Summer 2017; **C:** Fall 2017, and **D:** Winter 2017/18. Error bars represent propagated uncertainty in $\sum$PCB concentrations based on uncertainty in concentration of individual PCB congeners in replicate samplers, non-equilibrium correction factors, and PE-air partitioning coefficients.

campaigns, LBC1 continued to exhibit concentrations an order of magnitude greater than those at other sites, ranging from 300 ± 41 pg/m³ (Winter, 2017/18) to 5400 ± 1100 pg/m³ (Summer, 2017) likely reflecting the local sources of PCBs (Fig. 1B–D). The homolog distribution at LBC1 was different from those observed at other sites with di-, tri-, and tetra-chlorobiphenyls comprising the majority of air $\sum$PCBs (ranging from 63 to 96% across the different deployment periods) whereas at the other sites, tetra-, penta- hexa- and hepta-chlorobiphenyls generally dominated with their relative contribution to ΣPCBs ranging from 63% to 98% over the four deployment periods. Congener pattern at LBC1 for air-phase PCBs reflects that in the surface water of the LBC tributary with higher proportion of di- and tri-chlorinated PCB congeners (Ghosh et al., 2020; Lombard et al., 2022) (Fig. A7). RT was also an exception where the concentrations were dominated by tetra-to hepta-chlorobiphenyls for Spring 2017 but were mainly comprised of tri-to penta-chlorobiphenyls for the other deployment periods (Fig. A3-A6). RT is located close to the surface water sampling location ARP101 (Fig. A1), where the homolog pattern fall, spring, and winter surface water deployments shows tri-to penta--chlorinated PCBs to be the most dominant homolog groups (Fig. A8). Although surface water data at ARP101 for Spring 2017 are not available, volatilization of PCBs from surface water or a common terrestrial source could explain the homolog pattern observed for the air-phase PCBs at RT.

3.2. Comparison with regional measurements

Air PCB concentrations measured at the UMBC campus showed seasonal trends similar to those observed for Washington DC sites but were 2.5–3.5 times higher than the average air PCB concentrations over Washington DC. Average concentrations measured at UMBC were 410 ± 49 pg/m³ (Spring 2017), 680 ± 74 pg/m³ (Summer, 2017), 160 ± 37 pg/m³ (Fall, 2017) and 110 ± 13 pg/m³ (Winter, 2017/18).

For each deployment period, ΣPCB concentrations at AU, RT, MMR and ECC sites were similar and were used to calculate the average air

ΣPCB concentration. Similarity of the concentrations across these sites suggests that PCBs in the air primarily originate from diffuse volatilization from soils and surface water in the area, and that localized sources are likely not present at these sampling sites, unlike those identified at LBC and HP. The average air concentrations over Washington DC, calculated by excluding LBC1 and HP, were 120 ± 17 pg/m³ (Spring 2017), 270 ± 35 pg/m³ (Summer, 2017), 52 ± 8.0 pg/m³ (Fall, 2017) and 32 ± 4.3 pg/m³ (Winter, 2017/18) (Fig. 2B). No prior measurements of PCBs in air are available over DC for a direct comparison. The most relevant air PCB concentrations for comparison are those reported by Brunciak et al. (2001) and Bamford et al. (2002) for Baltimore Harbor and Northern Chesapeake Bay, due to their proximity to the current study area. Concentrations were lower than those reported by Brunciak et al. (2001) over the Chesapeake Bay ($\sum_{26}$PCB: 550 ± 220 pg/m³), indicating a possible decrease in the air ΣPCB levels in the watershed over time. However, the range of concentrations in DC are closer to the range of 5.1–370 pg/m³ ($\sum_{45}$PCB) reported by Bamford et al. (2002) over the Northern Chesapeake Bay. Concentrations measured at UMBC were lower than those reported in the above studies at Baltimore Harbor, approximately 6 miles away from UMBC campus. Brunciak et al. (2001) reported average PCB concentrations of 1180 ± 420 pg/m³ near Baltimore Harbor, while Bamford et al. (2002) reported concentrations in the range of 67–1400 pg/m³, with a geometric mean concentration of 330 pg/m³.

The observed seasonal variation is likely caused by greater volatilization of PCBs from the water, land surface, and buildings during summer due to higher temperatures (See Claysius-Clapeyron plots in *SI* Fig. A10). Bamford et al. (2002) noted similar trends in Baltimore, with highest air PCB concentrations measured during June (corresponding to Summer, 2017 deployment period in the present study) and lowest during February (corresponding to Winter, 2017/18 deployment in the present study). High concentrations in June were partly attributed to an increase in ambient temperature in the study by Bamford et al. (2002). Nelson et al. (1998) also observed a similar trend for air-phase PCBs over the Chesapeake Bay, with higher concentrations in June and September
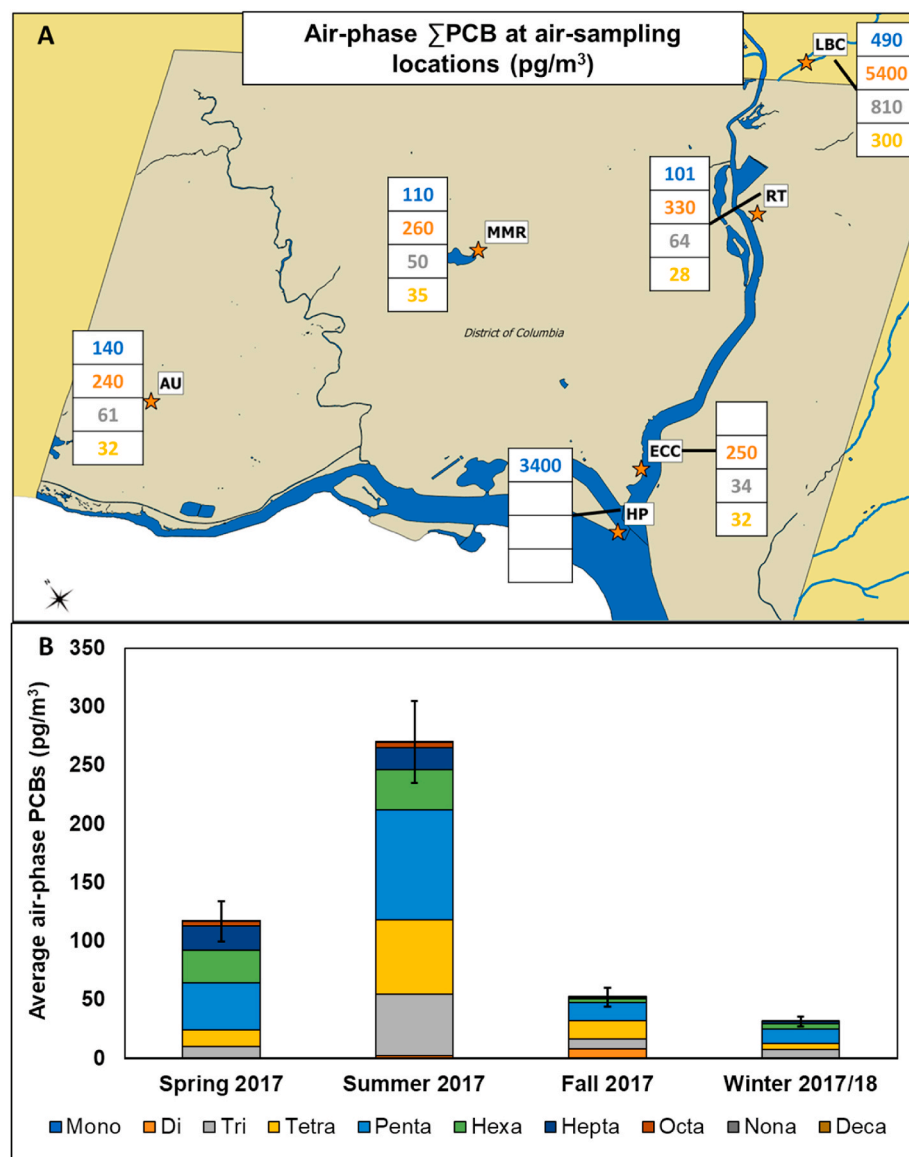
Fig. 2. A: Average Air-phase PCB concentrations in Washington DC across the seasons (**Blue:** Spring 2017; **Orange:** Summer, 2017; **Grey:** Fall, 2017; **Yellow:** Winter, 2017/18). **B:** Homolog-wise average air-phase PCB concentrations in Washington DC across the seasons. Error bars represent propagated uncertainty in $\sum$PCB concentrations based on uncertainty in concentration of individual PCB congeners in replicate samplers, non-equilibrium correction factors, and PE-air partitioning coefficients. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

than in March. Similar temperature-driven seasonal variation in atmospheric PCB concentrations has been observed in several locations in North America such as Lake Superior (Hornbuckle et al., 1994), Hudson River (Yan et al., 2008), Indiana Harbor (Martinez et al., 2019), Toronto (Motelay-Massei et al., 2005), and Chicago (Hu et al., 2010).

The average air concentrations in DC during Spring and Summer 2017 are similar to those reported in previous studies at urban locations in North America such as San Francisco Estuary ($\sum_{40}$PCB: 170–320 pg/m^3, Tsai et al., 2002), Toronto (($\sum_{48}$PCB: 196 pg/m^3, Pozo et al., 2006), Lower Duwamish Waterway ($\sum_{27}$PCB: 220 pg/m^3, (Apell and Gschwend, 2017). These concentrations are also comparable to those reported for Lower Great Lakes ($\sum_{29}$PCB: 7.7–634 pg/m^3 (Liu et al., 2016a), and Lake Michigan ($\sum_{85}$PCB: 36–282 pg/m^3, Guo et al., 2017) (Fig. A11). However, the average concentrations for DC are much lower than those reported for contaminated sites such as Raritan Bay ($\sum_{15}$PCB: 472–1865 pg/m^3, Totten et al., 2001), New York Harbor ($\sum_{15}$PCB: 2789–3502 pg/m^3, Totten et al., 2001), Hudson River ($\sum_{140}$PCB: 620–2200 pg/m^3, Sandy et al., 2012), New Bedford Harbor ($\sum_{209}$PCB: 400–38,000 pg/m^3, Martinez et al., 2017) and Indiana Harbor and Ship Canal ($\sum_{209}$PCB: 1600–5900 pg/m^3, Martinez et al., 2019).

3.3. Spatial and seasonal variations in freely-dissolved PCB concentrations

Depending upon the sampling campaign and recovery of passive samplers, a minimum of 4 and maximum of 5 locations within the Anacostia River were monitored. Temperature-corrected $\sum$PCB concentrations across these sites ranged from 0.38 ± 0.01 to 1.90 ± 0.082 ng/L over the entire sampling campaign. A detailed assessment of the spatial and temporal trends of dissolved PCBs in the Anacostia River and its tributaries can be found in Lombard et al. (2022). Loading estimates indicate that inputs from LBC tributary and from contaminated sediments in the river bed to be important sources of PCBs to the Anacostia River (DOEE, 2019c; Ghosh et al., 2020; Wilson, 2019). The dissolved PCB levels in the river, obtained by averaging the PCB concentrations measured at the various sampling locations, were 0.92 ± 0.15 ng/L (Spring 2017), 0.83 ± 0.13 ng/L (Summer, 2017), 0.75 ± 0.18 ng/L (Fall, 2017) and 0.46 ± 0.11 ng/L (Winter, 2017/18) (Fig. 3). A seasonal influence was observed in the dissolved concentrations across most sites, with higher concentrations measured during the warmer Spring and Summer 2017 sampling campaigns (average water temperature: 291 K and 297 K, respectively) than the colder Fall 2017 and Winter 2017/18 campaigns (average water temperature: 288 K and 279 K, respectively).
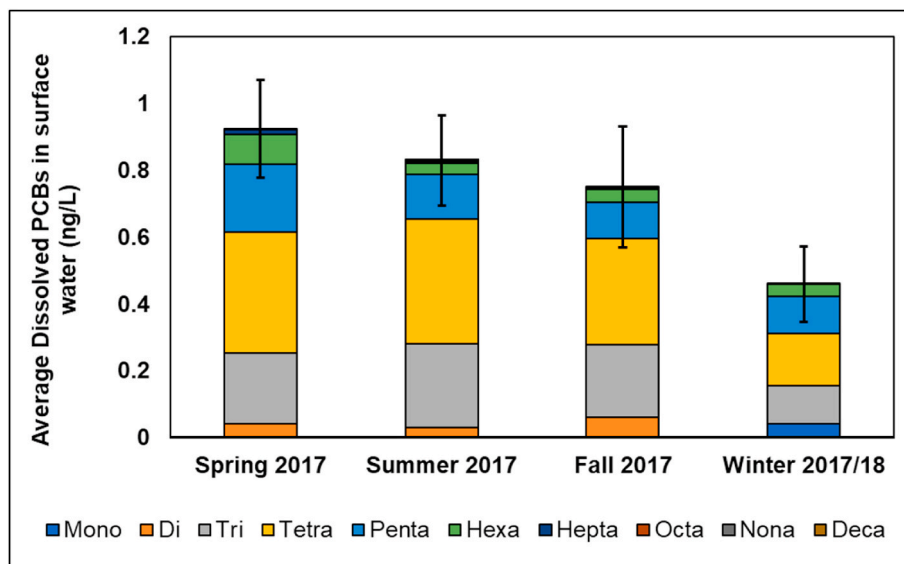
Fig. 3. Average dissolved PCB concentration in surface water of the Anacostia River across four deployment periods. Error bars represent propagated uncertainty in ∑PCB concentrations based on uncertainty in concentration of individual PCB congeners in replicate samplers, non-equilibrium correction factors, and PE-water partitioning coefficients.

For 8 out of the 18 measurements in the river across these sites, the temperature-corrected dissolved ∑PCB concentrations exceeded the 0.64 ng/L U.S. EPA Water Quality Criterion for Human Health from fish consumption (U.S. EPA, 2018), associated with an incremental cancer risk of 10^{-5}, while all measurements exceeded the Water Quality Criterion of 0.064 ng/L for ∑PCBs, associated with an incremental cancer risk of 10^{-6}.

3.4. Water-air exchange flux

Water-air exchange flux was calculated for each deployment period as per Equation (4). The overall mass transfer velocity for the congeners, calculated using the two-film air-water exchange model (Liu et al., 2016a), ranged from 8.9 cm/day to 26 cm/day over the duration of the study, which were in the lower range of values that Nelson et al. (1998) and Bamford et al. (2002) reported for the Chesapeake Bay (2–79 cm/day and 10–204 cm/day, respectively). The studies by Nelson et al. (1998) and Bamford et al. (2002) were based on a number of short sampling events, where higher wind speeds on certain days led to higher mass transfer velocities, whereas the present study is based on the average wind speed over each deployment period with little seasonal variation. For example, wind speeds varied from 1.8 m/s to 8.2 m/s in the study by Nelson et al. (1998), while Bamford et al. (2002) reported a 40-fold increase in mass transfer velocity for total PCBs due to an increase in wind speed from an average of 1 m/s on February 20, 1997 to 11 m/s on February 22, 1997. In comparison, the average seasonal wind speed in the present study varied from 1.98 m/s (Summer, 2017) to 2.98 m/s (Winter, 2017/18), which could explain the relatively low value of the calculated mass transfer velocity across seasons in the present study. It should also be noted that both the studies by Nelson et al. (1998) and Bamford et al. (2002) were performed on open waters of the Chesapeake Bay, where wind speeds are expected to be higher as compared to those
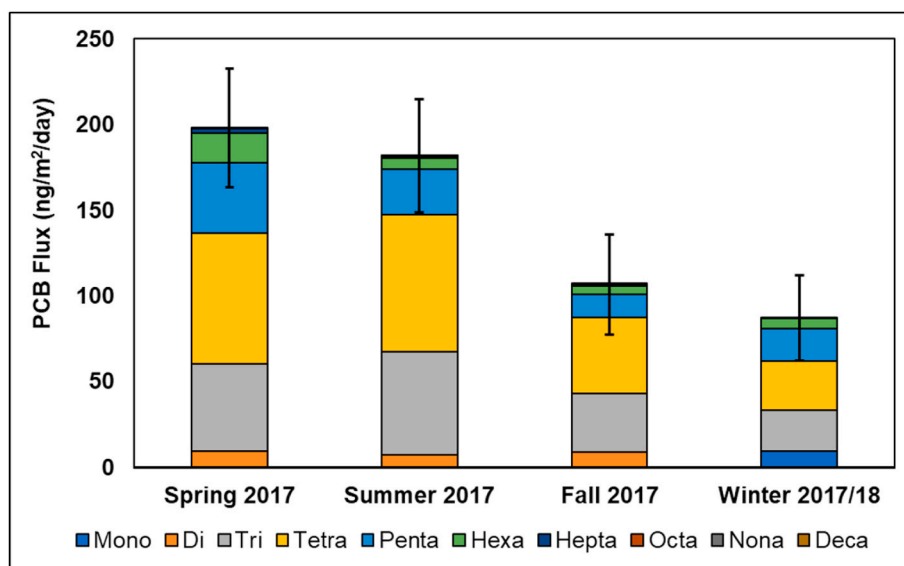

Fig. 4. Seasonal air-water exchange flux for the Anacostia River across the seasons. Error bars represent propagated uncertainty in ∑PCB flux, based on propagated uncertainty in flux of individual PCB congeners.

in the Washington DC urban area.

The flux for each deployment period was $+200 \pm 35$ (Spring 2017), $+180 \pm 33$ (Summer, 2017), $+110 \pm 29$ (Fall, 2017) and $+87 \pm 25$ ng/m^2/day (Winter, 2017/18) (Fig. 4), showing that PCBs primarily volatilize from the surface water into the atmosphere. This trend in the diffusive flux across the seasons reflects the trend in the dissolved PCB concentrations in the surface water of the Anacostia River (Fig. 3), with a gradual decrease in concentrations from spring to winter, supporting the hypothesis that the PCBs measured in the air primarily originate from volatilization from surface water and landscape. Bamford et al. (2002) noted similar trends for the waters of Baltimore Harbor, with volatilization fluxes strongly driven by the dissolved phase PCBs. The range of calculated flux shows good agreement with mean PCB flux reported by Bamford et al. (2002) for the Northern Chesapeake Bay (geometric mean: $+330$ ng/m^2/day; range: $+90$ to $+1150$ ng/m^2/day) but is about an order of magnitude higher than the mean flux reported by Nelson et al. (1998) for Chesapeake Bay (mean: $+96$ ng/m^2/day; range: -63 to $+800$ ng/m^2/day). For each season, the net flux was dominated by tri-to hexa-chlorinated PCBs, with the contribution of these homolog groups to the net flux ranging from 89% (Winter, 2017/18) to 95% (Summer, 2017), which reflects the homolog distribution observed for freely-dissolved PCBs (Figs. A9 and A13). These observations are in line with those made by Bamford et al. (2002) for Baltimore Harbor where tri-to hexa-homolog groups accounted for nearly 90% of the total flux. Volatilization was also confirmed by calculating air-water fugacity ratios for the mono-to deca-homolog groups. Log-transformed fugacity ratios ranged from 0.2 (hepta-homolog group, Winter, 2017/18) to 4.7 (tri- and tetra-groups, Spring 2017) across the study period (Fig. A12). For all deployment periods, log of fugacity ratios for tri-to hexa-homolog groups were greater than zero (based on the propagated uncertainty), indicating volatilization of these homolog groups from the river.

The calculated flux was significantly lower than those reported in the past for other PCB contaminated sites such as Delaware River ($+360$ to $+3000$ ng/m^2/day, Rowe et al., 2007); Raritan Bay and New York Harbor ($+835$ to $+1898$ ng/m^2/day, Totten et al., 2001) and Green Bay ($+170$ to $+5300$ ng/m^2/day, Totten et al., 2003). A comparison of previously reported fluxes with those measured in the present study is shown in Fig. A14. The calculated flux was at least 3 orders of magnitude lower than that reported in recent studies at highly contaminated river sites such as the Indiana Harbor and Ship Canal ($+1.4$ to $+2.8$ μg/m^2/day, Martinez et al., 2019), Hudson River ($+0.5$ to $+13$ μg/m^2/day, Sandy et al., 2012) and New Bedford Harbor ($+160$ to $+1200$ μg/m^2/day, Martinez et al., 2017). Several of the above sites reported significantly higher dissolved PCB concentrations (0.35–18 ng/L) than those measured in the present study. The flux was up to two orders of magnitude higher than that reported for less contaminated waters such as the Great Lakes (-2.4 to $+9$ ng/m^2/day, Liu et al., 2016a) and Lake Superior (-2.3 to 3.9 ng/m^2/day, Ruge et al., 2018) and an order of magnitude greater than that reported for the Lower Duwamish Waterway ($+68$ ng/m^2/day) by (Apell and Gschwend, 2017). Lower PCB fluxes for Great Lakes, Lake Superior, and Lower Duwamish Waterway could also be attributed to smaller number of congeners measured (29 for Great Lakes, 18 for Lake Superior, 27 for Lower Duwamish), as compared to 119 congeners measured in the present study.

3.5. Net water-air transfer rate

The seasonal volatilization rates of PCBs between surface water and air were quantified at 0.68 ± 0.12 g/day (Spring 2017), 0.63 ± 0.11 g/day (Summer, 2017), 0.37 ± 0.10 g/day (Fall, 2017) and 0.30 ± 0.09 g/day (Winter, 2017/18). The net volatilization rate from water across 1.33 square miles of the Anacostia River was estimated to be $+180 \pm 19$ g/year and is comparable to the volatilization rate of 518 g/year estimated by the surface water model for the Anacostia River (DOEE,

2019d). Differences in volatilization rates from the present study and the DOEE surface water model (DOEE, 2019d) could be attributed to methods used for estimating these rates. The surface water model results are based on $\sum$PCBs and not at the level of individual congeners as performed in the present study. Additionally, freely-dissolved PCBs in surface water and air-phase PCB concentrations were not directly measured as part of the Remedial Investigation (DOEE, 2019c). Results from the present study and the latest DOEE surface water model, however, are both an order of magnitude lower than the volatilization rate of 2200 g/year estimated by the older PCB fate and transport model for Anacostia River (LimnoTech, 2007). These stark differences in results from the fate and transport model and the present study might be related to differences in the methods used in this study and those in the fate and transport model (calculations at the level of individual congeners vs $\sum$PCBs, and use of more representative measured air-phase concentrations in the present study). The surface water concentrations (dissolved + particulate) predicted by the LimnoTech fate and transport model ranged from 2 to 19 ng/L and were in some instances up to 5 times higher than those measured by the Academy of Natural Sciences in 2002 (estimated from Figs. 120 and 121 in LimnoTech, 2007). Predicted freely dissolved concentrations from the model were not specified. A median value of 29.2% for the fraction of PCBs in dissolved form in the Anacostia River was calculated in the TMDL (Haywood and Buchanan, 2007) based on the above fate and transport model. Applying this dissolved fraction % to the fate and transport model results leads to predicted freely dissolved concentrations in the range of 0.58–5.5 ng/L in the Anacostia River. These predicted freely dissolved concentrations are up to an order of magnitude higher than those measured in the present work (Fig. 3) and could be responsible for the differences in the volatilization rates estimated in the fate and transport model and those calculated in this work.

3.6. Implications for management options

The volatilization rate of 2200 g/year in the PCB fate and transport model (LimnoTech, 2007) was nearly three times higher than total PCB inputs from the two largest tributaries of the Anacostia River (the Northeast and Northwest Branches). As discussed previously, PCB inputs from the Lower Beaverdam Creek tributary, an important ongoing source, were also not incorporated in this model. However, the results from this fate and transport model were used to develop load reductions for PCB sources to the Anacostia and Potomac Rivers through the Total Maximum Daily Load (TMDL) approach. Achieving these load reductions was projected to result in surface water and sediment targets that would in turn achieve a threshold $\sum$PCB concentration in fish protective of human health. The order of magnitude difference in the volatilization rate between the fate and transport model and the present study can thus have important implications for management options to reduce PCB contamination in the Anacostia River. Furthermore, the TMDL model (Haywood and Buchanan, 2007) based on the above fate and transport model assumes net flux across the water-air interface to be zero as part of the TMDL design conditions. Iterative model runs based on this "no net flux" assumption determined that PCB load from direct atmospheric deposition to the surface area of the Anacostia River and Potomac Rivers must be reduced by 93%. The inconsistent handling of water-air exchange in the TMDL has thus led to the perception that atmospheric deposition is currently a major source of PCBs to these rivers. The results from the present study thereby have important management implications with regards to possible remedial options for reducing PCB levels, not only for the Anacostia River, but also for the larger Potomac-Anacostia tidal water body. The inconsistency in the treatment of water-air exchange of PCBs in the fate and transport model and in the present TMDL needs to be addressed in light of the findings from direct measurements in the present study.

3.7. *Comparison with dry and wet deposition rates*

Although wet and dry deposition PCB fluxes were not measured in the present study, previous estimates of total deposition fluxes (wet + dry deposition) for urban areas in the Chesapeake Bay range from 5 μg/m^2/year (Baker et al., 1994) to 16 μg/m^2/year (Chesapeake Bay Program, 1999)). Extrapolation of these fluxes to the Anacostia River results in deposition rates of 17 g/year and 56 g/year, respectively. The upper end estimates for the deposition rates, based on uncertainties in the measured wet and dry deposition fluxes, are estimated to be 34 and 110 g/year, respectively (Supporting Information). Both the average and upper end estimates are lower than the volatilization rate of 180 ± 19 g/year reported in the present study, indicating that there is a net loss of PCBs from the surface water to the atmosphere. These findings are similar to those reported by Nelson et al. (1998) for the Chesapeake Bay, wherein the estimated PCB volatilization rate (400 kg/year) was more than 10 times larger than the inputs via dry and wet deposition (37 kg/year). The findings of the present study indicate that the atmosphere acts as a net sink for PCBs in the Anacostia River.

4. Conclusions

A quantitative understanding of whether the atmosphere acts as a sink or source for PCBs in the Anacostia River has been limited due to lack of recent data on air and water phase concentrations. By integrating air- and water-phase passive sampling data from field measurement campaigns over a period of two-years, this study shows that the atmosphere acts as a net sink for PCBs in the river, and that the volatilization rate is an order of magnitude lower than previously estimated. These results demonstrate the utility of passive sampling for accurately measuring air phase concentrations and freely dissolved concentrations in surface water for fate and transport assessment of PCBs and provide a compelling argument for incorporating time-integrated passive sampling in the development of PCB TMDLs. Additionally, results from air passive sampling indicated two potential landscape sources that resulted in high localized concentrations in air and corroborated findings at one of the locations where other studies identified a major tributary as an important source of PCBs (Ghosh et al., 2020; Lombard et al., 2022; Wilson, 2019).

Author statement

M. Bokare: investigation, methodology, data curation, original draft, validation; N. Lombard: investigation, methodology, editing; S. Magee: methodology, investigation; D. Murali: funding acquisition, project administration, editing; U. Ghosh: conceptualization, supervision, reviewing, editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

We have provided the primary congener data in tables in the Supplemental Infomation

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.120490.

References

Adams, R.G., Lohmann, R., Fernandez, L.A., MacFarlane, J.K., Gschwend, P.M., 2007. Polyethylene devices: passive samplers for measuring dissolved hydrophobic organic compounds in aquatic environments. Environ. Sci. Technol. 41, 1317–1323. https://doi.org/10.1021/es0621593.

Anacostia Watershed Restoration Partnership, 2009, 5.5.17 Anacostia River Hydrography [WWW Document]. URL. https://web.archive.org/web/20161224181818/http://www.anacostia.net/history/hydrology.html. accessed.

Apell, J.N., Gschwend, P.M., 2017. The atmosphere as a source/sink of polychlorinated biphenyls to/from the Lower Duwamish Waterway Superfund site. Environ. Pollut. 227, 263–270. https://doi.org/10.1016/j.envpol.2017.04.070.

Baker, J.E., Church, T.M., Ondov, J.M., Scudlark, J.R., 1994. Chesapeake Bay Atmospheric Deposition Study Phase 1: July 1990 - June 1991. Annapolis, MD.

Bamford, H.A., Offenberg, J.H., Larsen, R.K., Ko, F., Baker, J.E., 1999. Diffusive exchange of polycyclic aromatic hydrocarbons across the air - water interface of the Patapsco river , an urbanized subestuary of the Chesapeake Bay. Environ. Sci. Technol. 33, 2138–2144. https://doi.org/10.1021/es981324e.

Bamford, H.A., Ko, F.C., Baker, J.E., 2002. Seasonal and annual air - water exchange of polychlorinated biphenyls across Baltimore harbor and the northern Chesapeake Bay. Environ. Sci. Technol. 4245–4252. https://doi.org/10.1021/es0206893.

Booij, K., Smedes, F., Van Weerlee, E.M., 2002. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. Chemosphere 46, 1157–1161. https://doi.org/10.1016/S0045-6535(01)00200-4.

Brunciak, P.A., Dachs, J., Franz, T.P., Gigliotti, C.L., Nelson, E.D., Turpin, B.J., Eisenreich, S.J., 2001. Polychlorinated biphenyls and particulate organic/elemental carbon in the atmosphere of Chesapeake Bay, USA. Atmos. Environ. 35, 5663–5677. https://doi.org/10.1016/S1352-2310(01)00222-9.

Chesapeake Bay Program, 1999. Chesapeake Bay Basin Toxics Loading and Release Inventory. Annapolis, MD.

Chesapeake Bay Program, 2020. Chemical contaminants | Chesapeake Bay Program, 1.24.20 [WWW Document]. URL. https://www.chesapeakebay.net/issues/chemical_contaminants. accessed.

DOEE, 2016. Fish Consumption Advisory Information, 1.24.20 [WWW Document]. URL. https://doee.dc.gov/sites/default/files/dc/sites/ddoe/service_content/attachments/Fish Advisory 2-2-2016.pdf. accessed.

DOEE, 2019a. For a Cleaner Anacostia River - the Anacostia, 1.24.20. River Sediment Project [WWW Document]. URL. https://doee.dc.gov/publication/cleaner-anacostia-river-anacostia-river-sediment-project. accessed.

DOEE, 2019b. River-wide Feasibility Study Report. Anacostia River Sediment Project, Washington, DC (Washington, D.C).

DOEE, 2019c. Remedial Investigation Report. Anacostia River Sediment Project, Washington, DC. Washington, D.C.

DOEE, 2019d. Surface Water Model Report: Anacostia River Sediment Project Hydrodynamic and Fate and Transport Modeling. Washington, D.C.

Ghosh, U., Kane Driscoll, S., Burgess, R.M., Jonker, M.T.O., Reible, D., Gobas, F., Choi, Y., Apitz, S.E., Maruya, K.A., Gala, W.R., Mortimer, M., Beegan, C., 2014. Passive sampling methods for contaminated sediments: practical guidance for selection, calibration, and implementation. Integrated Environ. Assess. Manag. 10, 210–223. https://doi.org/10.1002/ieam.1507.

Ghosh, U., Lombard, N., Bokare, M., Pinkney, A.E., Yonkos, L., Harrison, R., 2020. Passive Samplers and Mussel Deployment, Monitoring, and Sampling for Organic Constituents in Anacostia River Tributaries: Final Report 2016-2018 (Washington, D.C).

Guo, J., Romanak, K., Westenbroek, S., Li, A., Kreis, R.G., Hites, R.A., Venier, M., 2017. Updated polychlorinated biphenyl mass budget for Lake Michigan. Environ. Sci. Technol. 51, 12455–12465. https://doi.org/10.1021/acs.est.7b02904.

Haywood, H.C., Buchanan, C., 2007. Total Maximum Daily Loads of Polychlorinated Biphenyls (PCBs) for Tidal Portions of the Potomac and Anacostia Rivers in the District of Columbia, Maryland, and Virginia (Rockville, MD).

Hornbuckle, K.C., Jeremiason, J.D., Sweet, C.W., Eisenreich, S.J., 1994. Seasonal variations in air-water exchange of polychlorinated biphenyls in Lake Superior. Environ. Sci. Technol. 28, 1491–1501.

Hu, D., Lehmler, H.J., Martinez, A., Wang, K., Hornbuckle, K.C., 2010. Atmospheric PCB congeners across Chicago. Atmos. Environ. 44, 1550–1557. https://doi.org/10.1016/j.atmosenv.2010.01.006.

Joyce, A.S., Fernandez, L.A., Burgess, R.M., 2020. In situ investigation of performance reference compound-based estimates of PCB equilibrated passive sampler concentrations and Cfree in the marine water column. Environ. Toxicol. Chem. 39, 1165–1173. https://doi.org/10.1002/etc.4714.

Khairy, M., Lohmann, R., 2012. Field validation of polyethylene passive air samplers for parent and alkylated PAHs in Alexandria, Egypt. Environ. Sci. Technol. 46, 3990–3998. https://doi.org/10.1021/es300012u.

Khairy, M., Lohmann, R., 2013. Feasibility of using low density polyethylene sheets to detect atmospheric organochlorine pesticides in Alexandria, Egypt. Environ. Pollut. 181, 151–158. https://doi.org/10.1016/j.envpol.2013.06.031.

Khairy, M.A., Lohmann, R., 2014. Field calibration of low density polyethylene passive samplers for gaseous POPs. Environ. Sci. Process. Impacts 16, 414–421. https://doi.org/10.1039/C3EM00493G.

LimnoTech, 2007. PCB TMDL Model for the Potomac River Estuary - Final Report on Hydrodynamic/Salinity and PCB Transport and Fate Models. Greensboro, NC.

Liu, Y., Wang, S., McDonough, C.A., Khairy, M., Muir, D., Helm, P.A., Lohmann, R., 2016a. Gaseous and freely-dissolved PCBs in the lower Great Lakes based on passive sampling: spatial trends and air-water exchange. Environ. Sci. Technol. 50, 4932–4939. https://doi.org/10.1021/acs.est.5b04586.

Liu, Y., Wang, S., McDonough, C.A., Khairy, M., Muir, D., Lohmann, R., 2016b. Estimation of uncertainty in air-water exchange flux and gross volatilization loss of PCBs: a case study based on passive sampling in the lower Great Lakes. Environ. Sci. Technol. 50, 10894–10902. https://doi.org/10.1021/acs.est.6b02891.

Lohmann, R., 2012. Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. Environ. Sci. Technol. 46, 606–618. https://doi.org/10.1021/es202702y.

Lohmann, R., Dapsis, M., Morgan, E.J., Dekany, V., Luey, P.J., 2011. Determining air-water exchange, spatial and temporal trends of freely dissolved PAHs in an urban estuary using passive polyethylene samplers. Environ. Sci. Technol. 45, 2655–2662. https://doi.org/10.1021/es1025883.

Lombard, N., Bokare, M., Harrison, R., Yonkos, L., Pinkney, A., Murali, D., Ghosh, U., 2022. Co-deployment of Passive Samplers and Mussels Reveals Major Source of Ongoing PCB Inputs to the Anacostia River in Washington DC. Manuscript currently under review.

Mackay, D., Shiu, W.Y., Ma, K.-C., Lee, S.C., 2006. Handbook of Physico-Chemical Properties and Environmental Fate for Organic Chemicals. Taylor & Francis, Boca Raton.

Martinez, A., Hadnott, B.N., Awad, A.M., Herkert, N.J., Tomsho, K., Basra, K., Scammell, M.K., Heiger-Bernays, W., Hornbuckle, K.C., 2017. Release of airborne polychlorinated biphenyls from New Bedford harbor results in elevated concentrations in the surrounding air. Environ. Sci. Technol. Lett. 4, 127–131. https://doi.org/10.1021/acs.estlett.7b00047.

Martinez, A., Awad, A.M., Herkert, N.J., Hornbuckle, K.C., 2019. Determination of PCB fluxes from Indiana Harbor and Ship Canal using dual-deployed air and water passive samplers. Environ. Pollut. 244, 469–476. https://doi.org/10.1016/j.envpol.2018.10.048.

Maryland Department of the Environment, 2021a. Technical Memorandum : 2020 Sampling Report - Lower Beaverdam Creek Polychlorinated Biphenyl (PCB) Source Trackdown Study. Baltimore, MD.

Maryland Department of the Environment, 2021b. Lower Beaverdam Creek PCB Investigation Updated February 2021. Baltimore, MD.

Minick, D.J., Anderson, K.A., 2017. Diffusive flux of PAHs across sediment-water and water-air interfaces at urban superfund sites. Environ. Toxicol. Chem. 36, 2281–2289. https://doi.org/10.1002/etc.3785.

Motelay-Massei, A., Harner, T., Shoeib, M., Diamond, M., Stern, G., Rosenberg, B., 2005. Using passive air samplers to assess urban-rural trends for persistent organic pollutants and polycyclic aromatic hydrocarbons. 2. Seasonal trends for PAHs, PCBs, and organochlorine pesticides. Environ. Sci. Technol. 39, 5763–5773. https://doi.org/10.1021/es0504183.

National Data Buoy Center, 2020a, 1.30.20 NDBC - Station WASD2 Recent Data [WWW Document]. URL. https://www.ndbc.noaa.gov/station_page.php?station=wasd2. accessed.

National Data Buoy Center, 2020b, 1.30.20 NDBC - Station BLTM2 Recent Data [WWW Document]. URL. https://www.ndbc.noaa.gov/station_page.php?station=bltm2. accessed.

Nelson, E.D., Mcconnell, L.L., Baker, J.E., 1998. Diffusive exchange of gaseous polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface of the Chesapeake Bay. Environ. Sci. Technol. 32, 912–919. https://doi.org/10.1021/es9706155.

Perron, M.M., Burgess, R.M., Suuberg, E.M., Cantwell, M.G., Pennell, K.G., 2013. Performance of passive samplers for monitoring estuarine water column concentrations: 1. Contaminants of concern. Environ. Toxicol. Chem. 32, 2182–2189. https://doi.org/10.1002/etc.2321.

Pozo, K., Harner, T., Wania, F., Muir, D.C.G., Jones, K.C., Barrie, L.A., 2006. Toward a global network for persistent organic pollutants in air: results from the GAPS study. Environ. Sci. Technol. 40, 4867–4873. https://doi.org/10.1021/es060447t.

Rowe, M.D., Perlinger, J.A., 2012. Micrometeorological measurement of hexachlorobenzene and polychlorinated biphenyl compound air-water gas exchange in Lake Superior and comparison to model predictions. Atmos. Chem. Phys. 12, 4607–4617. https://doi.org/10.5194/acp-12-4607-2012.

Rowe, A.A., Totten, L.A., Xie, M., Fikslin, T.J., Eisenreich, S.J., 2007. Air-water exchange of polychlorinated biphenyls in the Delaware River. Environ. Sci. Technol. 41, 1152–1158. https://doi.org/10.1021/es061797i.

Ruge, Z., Muir, D., Helm, P., Lohmann, R., 2018. Concentrations, trends, and air-water exchange of PCBs and organochlorine pesticides derived from passive samplers in Lake Superior in 2011. Environ. Sci. Technol. 52, 14061–14069. https://doi.org/10.1021/acs.est.8b04036.

Sandy, A.L., Guo, J., Miskewitz, R.J., McGillis, W.R., Rodenburg, L.A., 2012. Fluxes of polychlorinated biphenyls volatilizing from the Hudson River, New York measured using micrometeorological approaches. Environ. Sci. Technol. 46, 885–891. https://doi.org/10.1021/es203446w.

SERDP/ESTCP/U.S. EPA, 2016. Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments. User's Manual, Washington, DC.

Tidwell, L.G., Blair Paulik, L., Anderson, K.A., 2017. Air-water exchange of PAHs and OPAHs at a superfund mega-site. Sci. Total Environ. 603–604, 676–686. https://doi.org/10.1016/j.scitotenv.2017.01.185.

Totten, L.A., Brunciak, P.A., Gigliotti, C.L., Dachs, J., Glenn IV, T.R., Nelson, E.D., Eisenreich, S.J., 2001. Dynamic air-water exchange of polychlorinated biphenyls in the New York-New Jersey harbor estuary. Environ. Sci. Technol. 35, 3834–3840. https://doi.org/10.1021/es010791k.

Totten, L.A., Gigliotti, C.L., Offenberg, J.H., Baker, J.E., Eisenreich, S.J., 2003. Reevaluation of air-water exchange fluxes of PCBs in Green Bay and southern Lake Michigan. Environ. Sci. Technol. 37, 1739–1743. https://doi.org/10.1021/es026093x.

Tsai, P., Hoenicke, R., Yee, D., Bamford, H.A., Baker, J.E., 2002. Atmospheric concentrations and fluxes of organic compounds in the northern San Francisco Estuary. Environ. Sci. Technol. 36, 4741–4747. https://doi.org/10.1021/es011470b.

U.S. EPA, 2018, 9.17.18 National Recommended Water Quality Criteria - Human Health Criteria Table [WWW Document]. URL. https://www.epa.gov/wqc/national-recommended-water-quality-criteria-human-health-criteria-table. accessed.

U.S. EPA, 2020. District Of Columbia Water Quality Assessment Report | Water Quality Assessment and TMDL Information, 1.24.20 [WWW Document]. URL. https://ofmpub.epa.gov/waters10/attains_state.control?p_state=DC#causes. accessed.

U.S. EPA, US Geological Survey, US Fish and Wildlife Service, 2012. Toxic Contaminants in the Chesapeake Bay and its Watershed: Extent and Potential Biological Effects. Annapolis. MD.

Wilson, T.P., 2019. Sediment and Chemical Contaminant Loads in Tributaries to the Anacostia River, Washington, District of Columbia, 2016-17. U.S. Geological Survey Scientific Investigations Report, Reston, VA. https://doi.org/10.3133/sir20195092.

Yan, S., Rodenburg, L.A., Dachs, J., Eisenreich, S.J., 2008. Seasonal air-water exchange fluxes of polychlorinated biphenyls in the Hudson River Estuary. Environ. Pollut. 152, 443–451. https://doi.org/10.1016/j.envpol.2007.06.074.