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Article

Codeployment of Passive Samplers and Mussels Reveals Major Source of Ongoing PCB Inputs to the Anacostia River in Washington, DC

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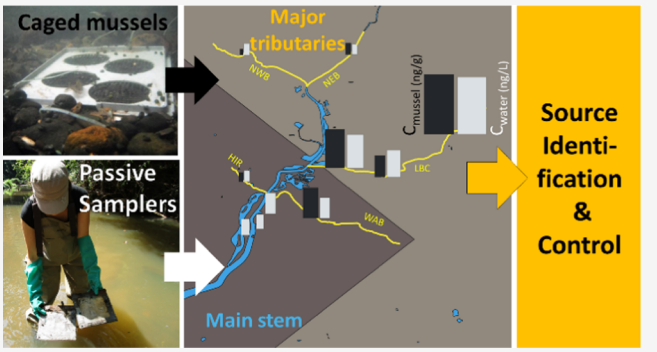
ABSTRACT: Remedial investigations of sites contaminated with legacy pollutants like polychlorinated biphenyls (PCBs) have traditionally focused on mapping sediment contamination to develop a site conceptual model and select remedy options. Ignoring dissolved concentrations that drive transport and bioaccumulation often leads to an incomplete assessment of ongoing inputs to the water column and overestimation of potential effectiveness of sediment remediation. Here, we demonstrate the utility of codeployment of passive equilibrium samplers and freshwater mussels as dual lines of evidence to identify ongoing sources of PCBs from eight main tributaries of the Anacostia River in Washington, DC, that has been historically polluted from industrial and other human activities. The freely dissolved PCB concentrations measured using passive samplers tracked well with the accumulation in mussels and allowed predictions of biouptake within a factor of 2 for total PCBs and a factor of 4 for most congeners. One tributary was identified as the primary source of PCBs to the water column and became a focus of additional ongoing investigations. Codeployment of passive samplers and mussels provides strong lines of evidence to refine site conceptual models and identify ongoing sources critical to control to achieve river water quality standards and reduce bioaccumulation in the aquatic food web.



KEYWORDS: *passive sampling, bioaccumulation, source identification, PCB, freshwater mussel, Elliptio*

INTRODUCTION

Thousands of waterbodies in the United States are still impaired by polychlorinated biphenyls (PCBs)[1] including many in Maryland (MD) and the District of Columbia (DC). Past and current discharges into the Anacostia River, from its 456 sq. km. mostly urban and industrial watershed,[2] have caused elevated concentrations of toxic pollutants in water, sediments, and biota. Within MD and DC, advisories still warn the public to restrict the consumption of fish largely because of high concentrations of PCBs.[3,4]

The DC Department of Energy and Environment (DOEE) initiated a Remedial Investigation/Feasibility Study (RI/FS)[2,5] to evaluate the nature and extent of contamination in the Anacostia River and evaluate options for cleanup. DOEE is also supporting concurrent efforts to understand the sources of contaminant loading from the watershed into the tidal river. While legacy contaminated sediments are often considered the primary source of PCBs to the aquatic food web, ongoing inputs from the urban landscape, especially in the dissolved form, can also be a major contributor at many sites. For example, recent work at a wastewater treatment plant[6] demonstrated that dissolved PCBs in the effluent were a major source of PCBs to an urban river.

Past work by Velinsky et al.[7,8] documented increased total loadings of a range of pollutants during storm events, including PCBs, polycyclic aromatic hydrocarbons (PAHs), and organochlorine pesticides (OCPs), such as chlordane. While much of the sediment load and associated pollutants are delivered during episodic storms, exposure and accumulation in aquatic species are continuous over time and reflective of long-term ambient concentrations, especially the freely dissolved species (C_{free}).[9−13] Recent modeling work[14] also demonstrates that C_{free} in surface water can contribute to more than half of the ultimate bioaccumulation of PCBs in most fish species (a combination of direct exposure through ventilation and

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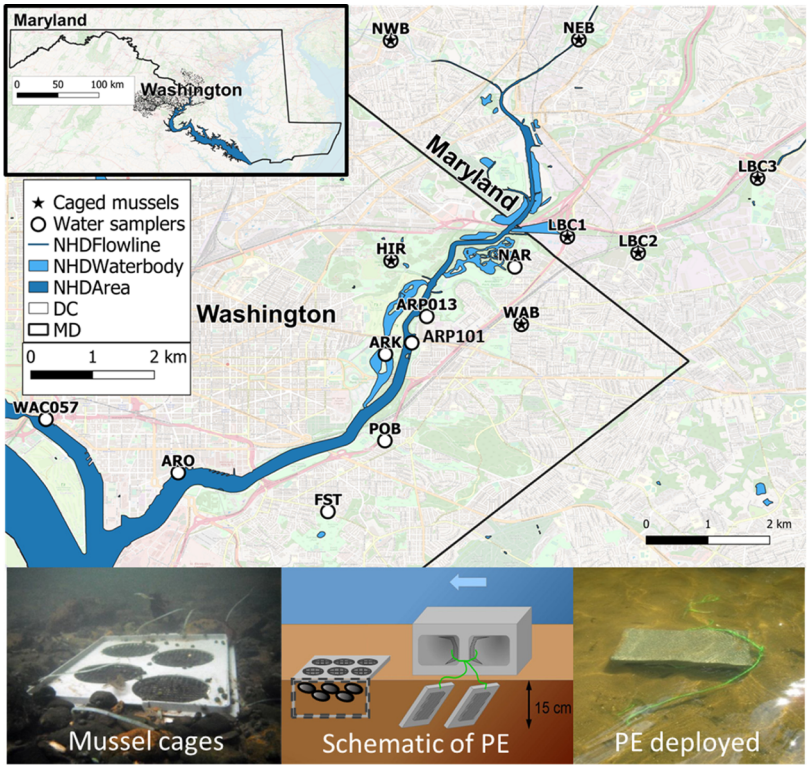

Figure 1. Top: Deployment locations for mussels and passive samplers in the Anacostia River and tributaries. Bottom: Schematic of deployment devices for mussels and passive samplers and pictures from the field. Map prepared with ©OpenStreetMap layer in qGIS.

indirect exposure through the pelagic food web). In addition to accurately predicting bioaccumulation and toxicity, C_{free} controls pollutant exchange with the surface sediment and the atmosphere.[15−18]

Understanding pollutant dynamics at contaminated sites can be greatly aided by the strategic use of passive sampling as demonstrated for the DDT-contaminated Palos Verdez Shelf Superfund[18] site and the PCB-impacted Lower Duwamish River.[19,20] Multiple studies have also demonstrated the use of passive sampling [using polyoxymethylene, polyethylene, and poly(dimethylsiloxane) polymers] to evaluate the effectiveness of sediment remediation.[16,21,22] The time-integrated C_{free} measured by passive sampling can provide useful inputs for assessing bioaccumulation, as demonstrated in recent work by Khairy et al.,[23] for the tidal Passaic River. Yet, use in the regulatory context has been limited due to the lack of precedent and solid demonstrations that are tied closely to a regulatory need. A critical review by Booij et al.[24] also noted the need for greater utilization of passive sampling in the regulatory context. Especially lacking are coordinated demonstrations of passive sampling with other assessment methodologies for remedial investigations of polluted sites.

Biomonitoring programs provide complementary information on bioavailable pollutants in the aquatic environment. Bivalves, such as mussels, are useful indicators at the lower trophic level of the aquatic food web. They are filter feeders that bioaccumulate pollutants through the water column and through the ingestion of particles, including suspended sediments, algae, and invertebrates.[25,26] They are effective as regional monitors of bioaccumulative organic pollutants because they lack the capacity to efficiently metabolize most organic pollutants.[27,28] Caged freshwater mussel *Elliptio complanata* has been used for the past 20 years to monitor contamination in the Lake Huron−Lake Erie corridor,[29] including the Detroit River.[30,31]

To address the need to advance passive sampling into regulatory frameworks, the present study was designed to supplement an ongoing remedial investigation and demonstrate the combined use of paired passive sampling and freshwater mussel monitoring to fill existing data gaps in the overall conceptual site model for PCB sources and bioaccumulation in an urban river. Polyethylene (PE) passive samplers were deployed in the Anacostia River and the eight main tributaries over a 2-year period to determine the spatial distribution of dissolved concentrations in surface water and sediment porewater and monitor seasonal changes. Caged mussels were deployed in two subsequent summers at the tributary water sampling locations to directly measure the uptake of PCBs in a lower trophic level organism. The results were interpreted to determine dominant ongoing tributary sources to the river that are the primary drivers for biouptake at the base of the aquatic food web and inform management decisions.

MATERIALS AND METHODS

Sampling Locations. A monitoring program was implemented in 2016 and 2017 at the five major tributaries of the Anacostia River and at two locations within the main stem of the river as shown in Figure 1. The deployment location map in Figure 1 was prepared using National Hydrography Dataset (NHD) from USGS,[32] TIGER/Line State Boundary from Census Bureau[33] shapefiles, and ©OpenStreetMap (OSM) layer in qGIS. At least one sampling site was selected per tributary to the extent possible near US Geological Survey (USGS) gage stations. Four additional monitoring campaigns were conducted from Spring 2017 to

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Winter 2017/2018 and included the monitoring of three additional minor tributaries, three additional locations within the main stem, and an additional location within Lower Beaverdam Creek (LBC) to further track down sources of PCB within that tributary. Details of sampling site locations and deployment dates are provided in Supporting Information (SI) Table S1. Monitoring included water column analysis for all deployments, porewater analysis of surface sediments (0−15 cm), and tissue analysis of caged mussels during summer deployments only.

Passive Sampler Preparation, Deployment, and Retrieval. Low-density polyethylene (PE) sheets (Husky, Poly-America, TX) were prepared and used for passive sampling as described in USEPA (2017).[34] Briefly, the sheets were cut into 15 by 15 cm squares (1.1 ± 0.11 g, n = 178, average based on five deployment records), precleaned in acetone/hexane (50/50 v/v) for 24 h, and loaded with the following PCB performance reference compounds (PRCs): PCB#29 (2,4,5-trichlorobiphenyl), PCB#69 (2,3′,4,6-tetrachlorobiphenyl), PCB#155 (2,2′,4,4′,6,6′-hexachlorobiphenyl), and PCB#192 (2,3,3′,4,5,5′,6-heptachlorobiphenyl) in a mixture of methanol/water (80:20 v/v).[35] After loading for at least 15 days on a shaker,[36] the samplers were soaked in deionized (DI) water overnight to remove the methanol, then enveloped in stainless steel mesh for the water column passive sampler, and mounted into frames for the sediment porewater passive sampler. Two passive samplers were inserted into the surface sediments (top 15 cm) to measure the sediment porewater concentration and two were left in the overlying water housed inside a hollow cinder block to measure the water column concentration (Figure 1). The passive samplers were retrieved after 2−3 months of deployment, rinsed with DI water to remove any particles, transferred to 40 mL VOA-certified vials, and kept refrigerated until further processing.

Passive Sampler Extraction, Cleanup, and Analysis. The passive samplers were processed for analysis following methods described by Sanders et al.[23] Cleanup of passive sampler extracts followed EPA SW-846 Methods 3630C (silica gel cleanup), and 3660B (sulfur removal with copper) followed by analysis in an Agilent 6890 N gas chromatograph (GC) with an electron capture detector.[37] PCB #14 and #65 were used as surrogates and spiked (30 μL of stock solution at 500 μg/mL) at the first extraction step. PCBs were quantified using PCB #30 and #204 as internal standards and were spiked in the concentrated eluate at 4 μg/L before analysis. Additional analytical details are provided in the SI QA/QC section. Samples that exhibited surrogate recovery inferior to 70% for passive samplers were removed from analysis and analyte values below MDL were reported as 0. In this document, ∑PCBs refer to the sum of 119 congeners (Table S2). The 119 congeners measured account for the vast majority of congeners found in the environment,[38] and this was confirmed by comparison of ∑PCB concentrations measured in Anacostia River sediments using the full 209 congeners[5] (Figure S1). The congeners not included in our analysis accounted for 4−20% of the total concentration measured using all 209 congeners (see the SI for details).

Mussel Deployment, Retrieval, and Analysis. Full description of the procedure used is provided in the SI. Briefly, adult Eastern elliptio (60−80 mm) in length n = 336 (2016) and n = 408 (2017) were collected one day before deployment from the reference site Zekiah Swamp in Charles County (MD). The mussels were labeled by affixing Hallprint Fish Tags (one tag per valve), depurated overnight in spring water to clear the guts from ingested particulate, and then deployed in cages (Figure 1) at each Anacostia River tributary in early June 2016 and 2017 (Table S1). Within Lower Beaverdam Creek, only LBC2 was monitored in 2016, and LBC1 and LBC3 were added in 2017. Five (2017) to six (2016) cages containing 8 mussels each were deployed per site. Sites were checked approximately weekly or after major storm events to remove debris and ensure that all cages were intact, and water quality data were recorded during each site visit. Six of the 8 mussels from each cage were collected after 91 days deployment. The two remaining mussels were collected after 146−154 days. Three cages (out of 45 deployed) were lost in 2017 due to storm events or theft prior to the 91 days retrieval (two at NWB, one at the ZEK reference location), and two mussels were unaccounted for at LBC2 on the 154 days retrieval. Retrieved mussels were depurated overnight, shucked and soft tissues homogenized using a Polytron PT 1035 with 10 mm dispersing aggregate, freeze-dried, and analyzed for protein and carbohydrate content,[39] lipid content,[40] and PCBs.[41] Shell length, width, and height were also recorded to the nearest mm, as well as the total weight to the nearest 0.1 g before and after retrieval.

C_{free} Calculation and Analysis. *Water Column.* The ∑PCB C_{free} in the water column (C_w) was calculated after correction of each congener for nonequilibrium based on PRC loss as described elsewhere[42] and is also provided in the SI. Target analytes with a fractional equilibrium (f_{eq}) value below 0.1 were not reported due to uncertainty linked with low uptake and high nonequilibrium correction factors, i.e., above 10.[13,43,44] When required, the partition coefficients were corrected for the average water temperature during the deployment period using the Van't Hoff equation as described in the SI. Relative change in C_{free} between two consecutive seasons was calculated as described in the SI, and statistical comparisons were performed between season n and season n + 1 for each site using t-tests, 2 tails, and unequal variance with statistical significance reported at p-value < 0.05.

Porewater. The C_{free} in sediment porewater (C_{pw}) was estimated from the concentrations measured in the PE samplers using the approach of Fernandez et al.[17] The calculations were performed with PRC correction software created by the same authors. Target analytes with f_{eq} below 0.1 were not reported.[13,43] No temperature correction was applied as the average water temperature was close to standard temperature conditions (298 ± 1 K).

Porewater—Water Column Diffusive Flux. The magnitude of the diffusive flux was estimated as described by Beckingham and Ghosh.[16] A similar mass transfer coefficient between the sediment porewater and water column was estimated for all tributaries (Table S3), and a value of 2 cm/day as measured for the Grasse River was used[16,45] to illustrate the major difference of flux across the tributaries. Error propagation of the diffusive flux was calculated as follows

$$\frac{\delta F}{F} = \sqrt{\left(\frac{\delta C_{pw}}{C_{pw}}\right)^2 + \left(\frac{\delta C_w}{C_w}\right)^2} \quad (1)$$

PCB Homolog and Congener Comparison. Heatmap with clustering analysis was performed on relative PCB homolog concentrations in R using the pheatmap package.[46] Principal component analysis (PCA) was performed on relative PCB

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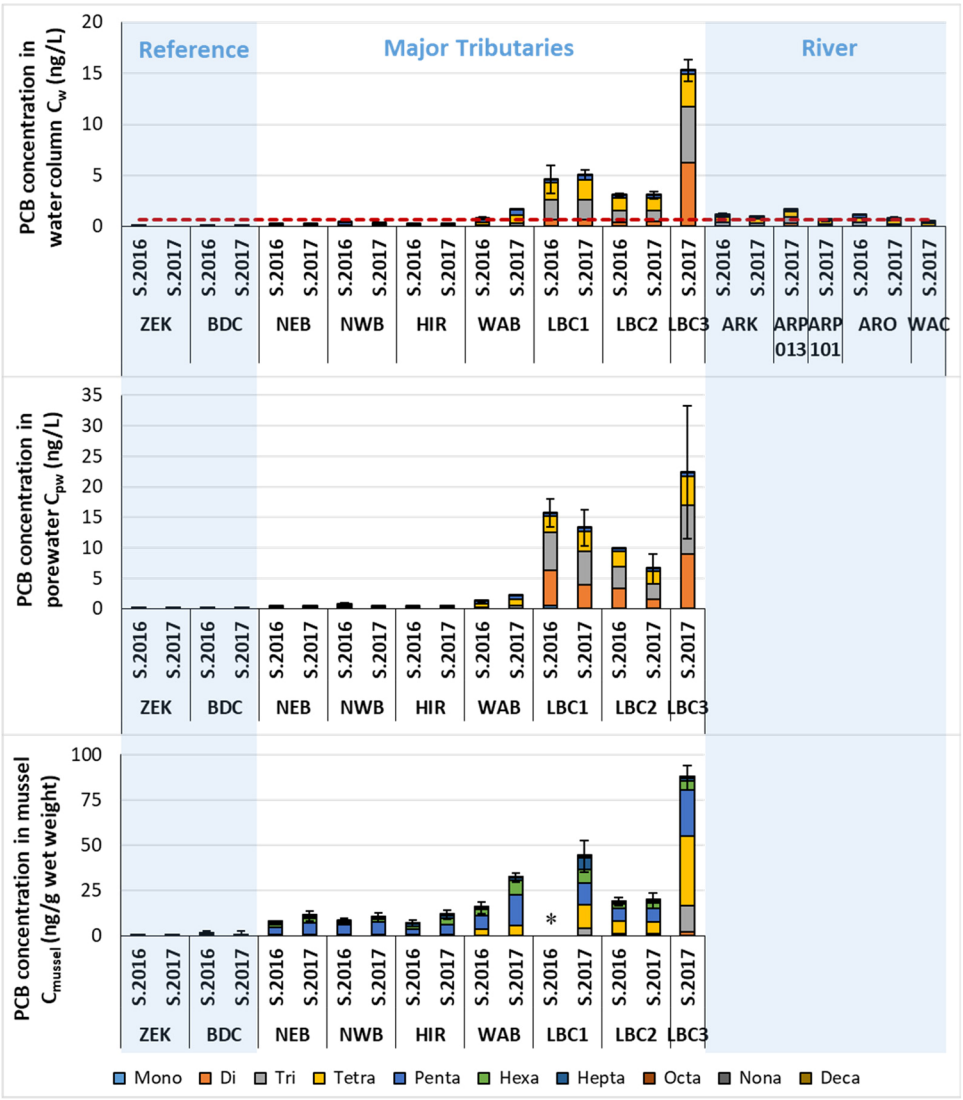

Figure 2. PCB concentration total (mean ± standard deviation) and distribution by homolog in (a) surface water, (b) sediment porewater, (c) mussel at two reference sites (ZEK and BDC), the five main tributaries of the Anacostia River (NEB, NWB, HIR, WAB, and three locations in LBC), and at five locations in the main Anacostia River (ARK, ARP013, ARP101, ARO, and WAC) in Summer (S.) 2016 and 2017. * indicates no data. The dashed red line at 0.64 ng/L indicates the USEPA ambient water quality criteria for PCBs for the protection of human health at 10^{-5} incremental risk of cancer (through fish consumption). PCB homolog concentrations are presented in Table S5.

concentrations at the PCB homolog and at individual congener levels using the factoextra package[47] and biplot graphical representation. PCB concentrations and PCB diffusive flux measured are presented in Tables S4 and S5.

Bioaccumulation Prediction. Kinetic uptake model for mussels was based on Arnot and Gobas,[48] and the assumptions described in the SI lead to eq 2

$$\frac{dC_{mussel}}{dt} = (k_1 C_w + k_d(f_p C_{plankton} + f_s C_{sediment}) - (k_2 + k_e)C_{mussel} \quad (2)$$

where k_1, k_2, k_d, and k_e are, respectively, the ventilation uptake, ventilation elimination, dietary uptake, and fecal egestion rate constants (day^{-1}) estimated at the congener level (Table S12); $C_{plankton}$, $C_{sediment}$, and C_{mussel} are, respectively, the PCB congener concentration in plankton, sediment, and mussel (g/kg); f_p and f_s are, respectively, the fraction of plankton and sediment in mussel's diet.

Thermodynamic equilibrium models were also tested using either K_{lipid} only (eq 3) or K_{lipid} and $K_{protein}$ (eq 4) as partitioning coefficients

$$C_{lipid} = K_{lipid} * C_{free} \quad (3)$$

$$C_{org} = C_{free} * (f_w + K_{lipid} * f_{lipid} + K_{protein} * f_{protein}) \quad (4)$$

where C_{lipid} and C_{org} are the concentrations of the target pollutant in lipid and organism (ng/kg), respectively; K_{lipid} is the partitioning coefficient of the target pollutant between water and lipid (L/kg); C_{free} (ng/L) in surface water (w) or porewater (pw); $K_{protein}$ is the partitioning coefficient of the target pollutant between water and protein; and f_w, f_{lipid}, and $f_{protein}$ are, respectively, the fractions of water, lipid, and protein in wet tissue. C_{org} was divided by f_{lipid} to allow comparison with the model in eq 3 and measured C_{lipid} values. For K_{lipid}, the partitioning coefficient between octanol and water (K_{ow}) using Hawker et al.[49] values and the partitioning coefficient between triolein (a lipid model) and water (K_{tw}) using Hung et al.[50]

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values were tested. The partitioning coefficient between polymer and lipid (K_{PL})[51] was also tested, with C_{free} in eq 3 being replaced by $C_{PE,PRC\ corr.}$, i.e., the concentration of the target pollutant measured in PE corrected for PRC loss (ng/kg of PE) and K_{lipid} by $1/K_{PL}$. An average K_{PL} value of 0.0938 ± 0.00935 (kg/kg) was used for all PCB congeners analyzed in this study. For $K_{protein}$, the correlation with K_{ow} given by Endo et al.[52] was used. No temperature correction was applied as the average water temperature was close to standard temperature conditions (298 ± 1 K). Accuracy of the predictions was determined using the congener level model bias, which is the geometric mean of predicted to measured ratios for each congener. Values closer to 1 indicate better agreement between modeled and measured values. Root mean square error (RMSE) was also calculated using the lipid normalized data (Table S14).

RESULTS AND DISCUSSION

PCB C_{free} in Water Column during Summer. *Reference Sites.* As shown in Figure 2a, both reference sites, Zekiah Swamp (ZEK), located 25 miles south from the confluence of Anacostia River and Potomac River, and Beaverdam Creek (BDC) located in the most agricultural and forested portion of the Anacostia watershed, exhibited low PCB C_{free} below the USEPA ambient water quality criteria for the protection of human health via fish consumption, associated with a cancer risk of 10^{-6} of 0.064 ng/L (WQC 10^{-6}). Note that the USEPA WQC is for total PCBs in water including PCBs associated with particulate and dissolved organic carbon (DOC) present at national default values of 0.5 and 2.9 mg/L respectively.[53]

Five Major Tributaries. ∑PCB concentrations measured in surface water of the five major tributaries during Summer 2016 (S.2016) were above WQC 10^{-6} (Figure 2a). The lowest ∑PCB concentrations were measured at the two main upstream branches of the Anacostia River, Northeast Branch (NEB), and Northwest Branch (NWB) and at Hickey Run (HIR) with concentrations ranging from 0.21 to 0.41 ng/L. The highest concentrations were measured at the Lower Beaverdam Creek (LBC) locations, followed by the Watts Branch location (WAB), which were even above the WQC 10^{-5} incremental cancer risk (Figure 2a). The major tributary of concern was LBC, where PCB C_{free} were 6−21 times higher than at the other tributaries and 4 times higher than at the Anacostia River sites ARO and ARK monitored in 2016. The tributary measurements replicated in Summer 2017 (S.2017) produced similar results (concentrations within a factor of 1.5), except at WAB, where average concentrations measured in 2017 were about 2 times higher than those measured in 2016. However, the changes were not significant (*t*-test, *p*-value > 0.05) and LBC still exhibited about 3 times higher PCB C_{free} than at WAB. The measurements performed at LBC1 (4.6 ± 1.4 ng/L in S.2016, 5.0 ± 0.50 ng/L in S.2017) were within the range of concentrations reported by Velinsky et al.[7] (3.8 ± 0.43 ng/L pre-rain; 7.1 ng/L post-rain in Spring/early Summer) almost 10 years earlier (see the SI for details). The persistence of high PCB concentrations in the water column of LBC would suggest an ongoing and uncontrolled source within that tributary.

Minor Tributaries. To complete water column PCB C_{free} mapping of the Anacostia watershed, three minor tributaries of the Anacostia River were added to the 2017 campaign: Nash Run (NAR), Pope Branch (POB), and Fort Stanton (FST). The monitoring of these minor tributaries showed low PCB C_{free} similar to those measured in NEB, NWB, and HIR with concentrations ranging from 0.20 to 0.35 ng/L in S.2017. In addition, the estimated discharge from these 3 minor tributaries contributed 1.3% of the net annual discharge of the 5 main tributaries based on the 2017 discharge data (Table S6). Thus, their potential impact on the Anacostia River C_{free} can be considered minor compared to the major tributaries.

Anacostia River. PCB C_{free} measured in the Anacostia River were above EPA WQC 10^{-5}. Even though high spatial variability has been reported in surface sediment concentrations (at least by a factor of 10),[2,54] the water column concentrations measured at the sites were similar and averaged 0.91 ± 0.29 ng/L in S.2017 (n = 5, Table S7). Such homogeneity of water concentration observed from the middle part to the lower part of the Anacostia River supports the hypothesis of a well-mixed system within that area of the tidal river. One of the sites ARP013, however, showed a distinct pattern from other sites with concentrations at least 2 times higher and significantly different from those measured at other Anacostia River sites (ANOVA, Tukey, *p*-value = 0.018 to 0.043). PCB homolog distribution at ARP013 was also distinct from the profile detected in ARK, ARO, and ARP101 with a higher abundance of di-chlorobiphenyls (12%) compared to the other sites (Figure S2). This was confirmed by additional measurements across seasons in the next section. A local source of contamination from PCB-impacted sediments in a cove is likely causing elevated water column concentrations at this site and is part of a separate ongoing investigation.[55] Still, water column concentrations measured at ARP013 were 3 times lower than that measured at the tributary LBC1, which emphasizes LBC1 as a major ongoing source of contamination to the River.

Seasonal Change of the Water Column PCB C_{free}. Seasonal measurements performed from Spring (Sp.) 2017 to Winter (W.) 2017/2018 showed an increase in PCB C_{free} between Spring and Summer 2017, then a decrease between Summer and Fall 2017 that was consistent across most tributaries and the river (Figures S3 and S4). Those changes were however not statistically significant for most of the studied sites, and the PCB C_{free} remained within a factor of three for all seasons. Only WAB showed a significant decrease of PCB C_{free} in Fall 2017 (*t*-test, *p*-value = 0.015). The seasonal decrease can be attributed to (1) decrease of temperature,[56,57] (2) significant increase of dissolved organic carbon (DOC) levels observed across tributaries (Figure S5) due to organic matter degradation from leaves, and (3) new organic matter sink for PCBs created by seasonal leaf debris. Given the changes observed across seasons, it is prudent to perform long-term monitoring during the same season to avoid the seasonal effect. Interestingly, the continuous increase of PCB levels observed in Fall 2017 at LBC1 (and to a lesser extent at ARP013) is in contradiction with the expected seasonal trend and may suggest an ongoing source of contamination still active in Fall 2017 at those locations. The minor seasonal changes do not affect the general trend observed during two consecutive summers and confirm LBC1 as a major source of ongoing contamination to the Anacostia River across seasons. Technical limitations were encountered for C_{free} measurements in W.2017/18 due to lower concentrations and exchange rate of PCB between PE and water that was likely caused by lower diffusivity at colder temperatures (SI). This led to uncertainty associated with high correction factors (>10)[13,42,44] for 35% of the PCB congeners (penta- to deca-chlorobiphenyls) versus

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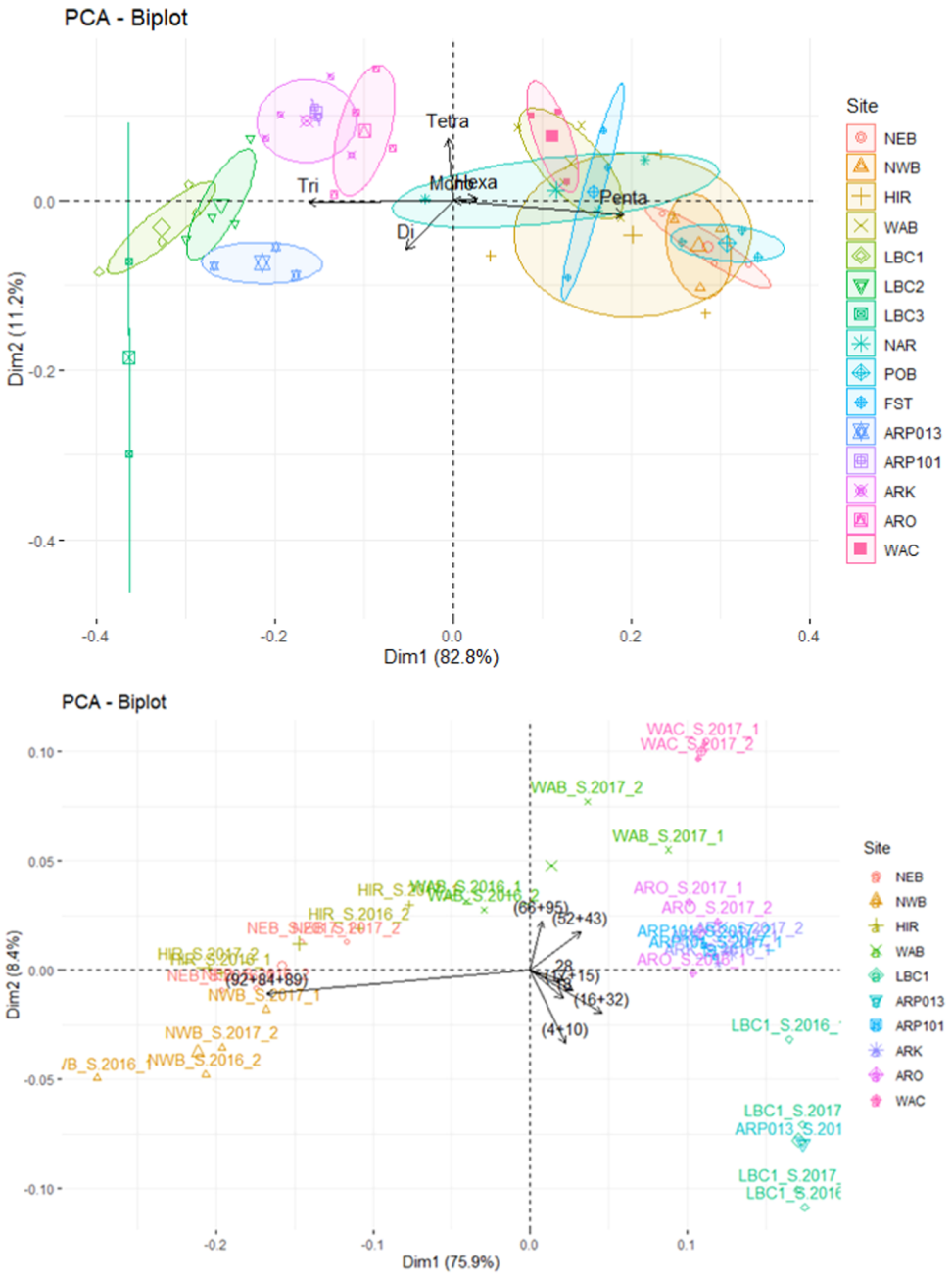

Figure 3. PCA biplot at the homolog (top) and individual congener (bottom) level across the season and across sites. W.2017/18 data was excluded from analysis. Minor tributaries were excluded from the analysis at the individual congener level. At the homolog level, 94% of the variance is explained by the first two dimensions. About 83% of the variance is explained by dimension 1, which is mainly positively correlated with penta- and negatively correlated with trichlorobiphenyls. At the congener level, 84% of the variance is explained by the first two dimensions, with about 76% explained by dimension 1, mainly negatively correlated with the pentachlorobiphenyl congeners (92 + 84 + 89).

less than 15% (hepta- to deca-chlorobiphenyls) for the other seasons. Data for W.2017/18 were likely biased low for a few locations, where penta-homologs were the second dominant homolog group (see the SI for details).

Evaluation of Tributary Impact on PCB C_{free} in the Anacostia River. A loading evaluation was performed using the average flow discharge data collected during S.2017 (Table S7) and the average PCB C_{free} measured in S.2017. Even though LBC contributed only 15% of the total tributary discharge, it contributed 77% of the C_{free} PCB load (420 mg/day) from all main tributaries for S.2017, confirming the dominant impact of LBC on the Anacostia River dissolved PCBs. LBC impact on the Anacostia River was further evaluated by the comparison of PCB profiles of the tributaries and the Anacostia River across seasons (Figures S2 and S6). LBC sites showed a very distinct PCB signature with a majority of tri- (36−42%) and tetra- (37−40%) chlorobiphenyls, whereas other main tributaries showed PCB homolog distributions either centered on pentachlorobiphenyls (51−56%) as observed for NEB, NWB, and HIR or centered on tetra- (41%) and penta- (39%) chlorobiphenyls (WAB) (Figure S2). Those distinct PCB signatures were further confirmed by clustering analysis performed at the homolog and at the congener level (Figures 3 and S7). The PCB congeners

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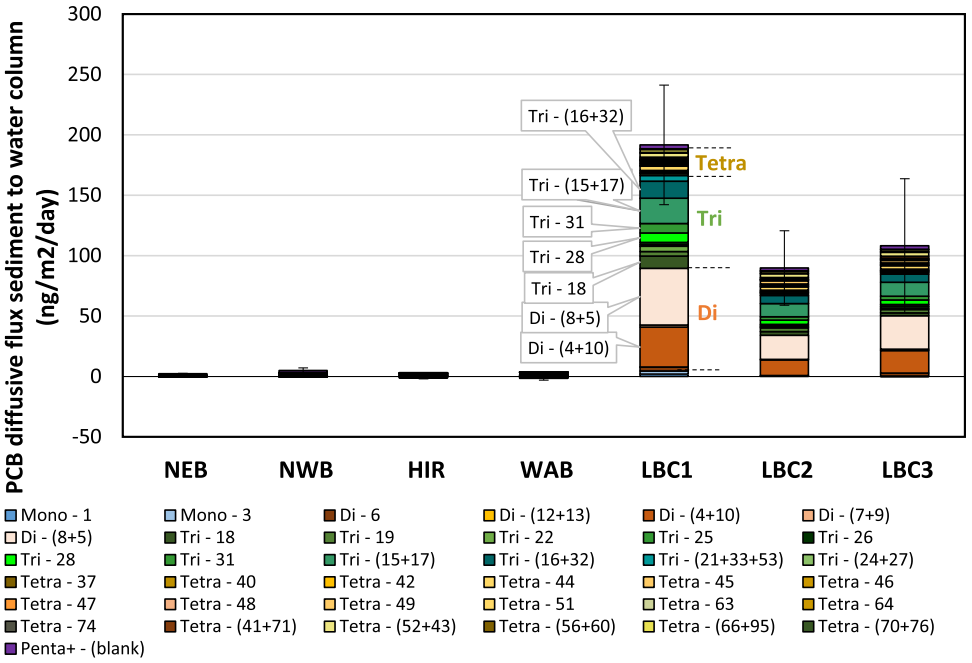

Figure 4. PCB diffusive flux between porewater and water column. PCB flux is presented at the congener level for mono- to tetra-chlorobiphenyl. Higher-molecular-weight congeners were grouped within Penta+. PCB congeners with a relative contribution to the PCB flux above 2% at LBC1 are labeled on the graph.

driving the cluster separation of (1) NEB and NWB, (2) WAB, and (3) LBC1 are, respectively, by (92 + 84 + 89) for the first cluster, (66 + 95) and (52 + 43) for the second cluster, and several lower-molecular-weight PCBs (i.e., (4 + 10), (16 + 32), (17 + 15), 18, 28) for the third cluster (Figure 3). The Anacostia River sites ARK, ARO, and ARP101 showed PCB homolog profile that clustered closer to the LBC sites compared to other tributaries for every season (Figure S7), explained by the presence of trichlorobiphenyls (Figure 3). Similarity of profile may also indicate past contamination from similar (ratios of) Aroclor mixtures and similar weathering. But considering multiple lines of evidence including being an upstream source with elevated PCB concentrations, it is likely that the LBC has a significant contribution to the elevated concentration of PCBs in the Anacostia River. There was also some differentiation from LBC1 due to the lower proportion of di- and higher proportion of tetra-chlorobiphenyls (Figure 3), which might indicate the influence of additional PCB sources or transformation of the PCBs during transport. A full mass balance comprised of water, solid, and air phases would be required to accurately account for all of the potential exchanges. Interestingly, Anacostia River site ARP013 clustered away from ARK, ARO, and ARP101 but grouped with LBC1 due to its higher proportion of di-chlorobiphenyls compared to the other main stem sites and is in line with the local source contamination suggested in the previous section. The river site WAC also clustered away from ARO, ARK, and ARP101 and grouped with WAB sites due to a higher proportion of higher chlorinated compounds compared to the other main stem sites. This specific PCB profile might be explained by its unique location within the Washington Channel, which receives outflow from the tidal basin and drains in the south of the Anacostia River. LBC1 influence on WAC might be diluted from tidal influence of the Potomac River and the outflow from the tidal basin located upstream.

Tributary Sediments as a Potential Source of PCB Contamination. PCB C_{free} measured in the sediment porewater followed the trends observed in the water column (Figure 2b). The lowest concentrations were detected at the reference sites ZEK and BDC as expected, intermediate concentrations above EPA WQC 10^{-6} at NEB, NWB, HIR, and WAB, and the highest concentration at LBC1. Similar porewater C_{free} (within a factor of 2) were measured in both years. The porewater concentrations were low and similar to the water column concentrations (within a factor of 2) at most of the major tributaries, suggesting that sediment and water column are near equilibrium, except at LBC1, where porewater concentrations were high (13 ng/L) and a factor of 2.6 more than the water column. The PCB diffusive flux from porewater to the water column at LBC1 was about 30−90 times higher than that observed in the other tributaries and was driven by di- ((4 + 10), (8 + 5)), and tri- (18, 28, 31, (15 + 17), (16 + 32)) chlorobiphenyls (Figure 4). Interestingly, those are some of the same PCB congeners responsible for the distinct PCB congener signature in LBC compared to other tributaries (Figure 3). These overall results suggest that bed sediment of LBC1 is an important source of contamination to the overlying water.

Tracking the Source of PCB Contamination within Lower Beaverdam Creek. Since LBC appeared to be the primary tributary of concern, a trackback approach was applied to identify PCB sources along the tributary. Additional monitoring sites were added about 1.2 miles (1.9 km, LBC2) and 2.9 miles (4.7 km, LBC3) upstream of the initial location LBC1. The most upstream site, LBC3, showed the highest surface water PCB C_{free} (15 ± 1.1 ng/L) measured in the study. Lower concentrations were measured at the intermediate site LBC2 (3.1 ± 0.33 ng/L), but higher concentrations were detected further downstream at LBC1 (5.0 ± 0.5 ng/L) (Table S4). These results suggest two potential hot spots of contamination: at LBC1, located near a

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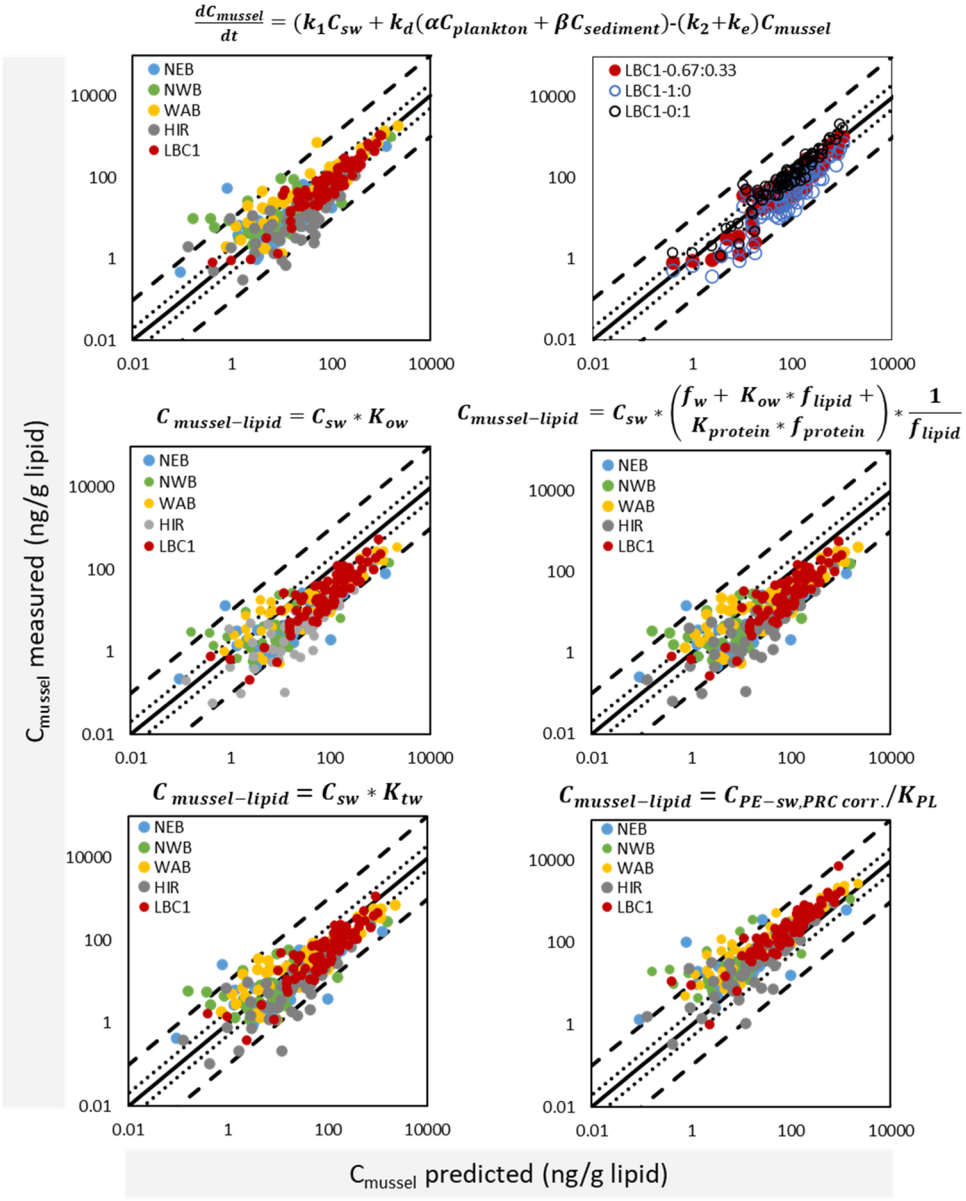

Figure 5. Comparison of measured PCB bioaccumulation in mussels at the congener level with values predicted using kinetic uptake (top) and various equilibrium partitioning models (middle and bottom). Each dot represents an individual or group of PCB congeners (Table S2) measured per site. For the kinetic uptake model, left graph shows predictions using a diet of 0.67 plankton and 0.33 sediment for all tributaries, right graph shows a comparison for LBC with 2 additional feeding conditions of plankton only (1:0) or sediment only (0:1).

metal recycling facility, and at LBC3, located near a Metro station and other industrial units, where surface soil is contaminated with PCBs, resulting in past and ongoing contaminated stormwater/sediment runoff into LBC. Sediment porewater analysis also showed high PCB C_{free} at all LBC sites, which were 3−57 times higher than the concentration measured in sediment porewater of the other main tributaries. The highest porewater concentrations were measured at LBC3, with concentration reaching 22 ± 11 ng/L. PCB flux analysis indicates a flux from the bed sediment to the water column (Figure 4), driven by similar PCB congeners as observed at LBC1 (Figure 3). Results from this study have triggered an ongoing investigation into possible sources of PCBs to LBC.[58]

PCB Bioaccumulation in Freshwater Mussels. Overall, *E. complanata* survival was above 99%, which is in agreement with previous studies.[39,60] Mussel growth of 0.023 to 0.18 mm/wk after 91 days deployment (Tables S8 and S9) was also comparable to previous studies (e.g., 0.044 mm/wk for ∼70 mm *E. complanata* caged 62 days in the St Laurence River, Canada).[59] Protein, carbohydrate, and lipid (2017 only) content were comparable to concentrations reported by Gray and Kreeger[39] for *E. complanata* deployed during similar times of the year in the Delaware and Susquehanna River basins (Tables S10 and S11) and suggest that conditions in the tributaries are suitable for *E. complanata* survival. Overall, high survival and lack of negative impacts confirm the utility of these organisms for studies of contaminant-impacted waters.[26,60−62]

The ∑PCB measured in mussels across sites showed a similar trend as the concentrations measured in the water column and porewater (Figure 2). The lowest concentration measured in the water column of ZEK and BDC was reflected in the lowest ∑PCB concentrations measured in the mussels from these sites, while the highest ∑PCB concentrations

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measured in water phases at LBC were reflected in the highest ∑PCB concentrations measured in the mussels. These results provide an additional line of evidence of a substantial ongoing PCB source at LBC that is bioavailable for uptake into aquatic organisms. PCB concentrations predicted using bioaccumulation models were compared against PCB concentrations actually measured in mussels after 91 days deployment as shown in Figure S8 for PCB totals and homologs, and in Figure 5 for PCB congeners.

The kinetic uptake model (SI, Table S12), with a fractional diet of 0.67 plankton (zoo- and phytoplankton in equilibrium with water column) and 0.33 sediment, as specified in the KABAM model for filter feeders,[63] showed the best agreement with measured values, which validates the input parameters used for *E. complanata*, as well as the PCB C_{free} from this study used in the uptake model. ∑PCBs were within a factor of 2, and 64% (NWB) to 97% (LBC1) of the PCB congeners agreed within a factor of 4 using the kinetic uptake model. Lower accuracy was observed for the higher-molecular-weight PCB congeners (hepta- to deca-chlorobiphenyl) (Table S13) and can be attributed to nonequilibrium conditions for those congeners after 91 days deployment and greater uncertainty in their measurement in water. Based on the kinetic uptake model for LBC1 (Figure S9), 72% of the PCB congeners reached near equilibrium (f_{eq} > 0.90) within 91 days and 77% within 120 days. Higher-molecular-weight congeners (hepta- to deca-chlorobiphenyl) require at least a year or more to reach near equilibrium conditions. A deployment period of 90 days is therefore a good compromise between approaching equilibrium and minimizing risks of cage loss due to storms or vandalism. Based on the input parameters, ventilation accounts for 60% of PCB accumulation in the mussels. The model assumes that ventilation of bivalves is primarily (95%) from surface water[48,64] and was confirmed by the agreement between predictions and measured data. This would also suggest that the mussel is in closer equilibrium to surface water than sediment porewater despite its presence buried in the sediment. Changes in the fractional diet had a minor impact on the accuracy of predictions (C_{bias} decreases from 0.77 to 0.48 from plankton only to 1.2 if diet from sediment only, Table S14). However, the inclusion of sediment only in the diet tends to overpredict the PCB concentration in mussels, which further supports the observation that the PCB concentration in the mussel is primarily driven by surface water concentration, which accounts for about 70% of the PCB concentration in the mussel (through ventilation and diet on plankton in equilibrium with water column).

This observation was further confirmed through the assessment of thermodynamic equilibrium models to predict PCB bioaccumulation in the mussel, using various K_{lipid} estimates from the literature in conjunction with surface water PCB concentration only (Figure 5). All thermodynamic equilibrium models were able to predict mussel PCB concentration within a factor of 10. The best congener bias (C_{bias}) was achieved using either the partitioning coefficient K_{tw} from Hung et al.[50] that tends to underpredict (C_{bias} ranging from 0.25 to 0.67) or K_{PL} that was developed for prediction in fish[51] that tends to overpredict (C_{bias} 1.1−2.8). Due to the very low lipid content measured in the mussel (<1% wet weight), PCB partitioning to the nonlipid organic matter (NLOM) compartment such as protein fraction of the mussel was included in the model but led to very small improvement of the accuracy of the model ($K_{ow}C_{bias}$ 0.12−0.34 versus K_{ow}−$K_{prot}C_{bias}$ 0.13−0.37). This can be explained by the protein partitioning coefficient being 40−600 times lower than the lipid partitioning coefficient for the PCB congeners. Using a combination of K_{tw} or K_{PL}, and surface water PCB C_{free}, the thermodynamic equilibrium model allowed the prediction of ∑PCB concentrations in the mussel within a factor of 4 for 44% (HIR) to 96% (LBC sites) of the PCB congeners modeled. RMSE analysis confirmed the kinetic uptake model as a better predictor for concentration in the mussel using a diet of 67% plankton and 33% sediments (Table S14). For the thermodynamic equilibrium model, results are not as clear, as RMSE is scale-dependent, and 10-fold variation in tPCB concentration is observed across all sites (no data normalization was performed, besides normalization for lipid content). Overall, K_{tw} seems to provide higher accuracy (lower RMSE) compared to other partitioning coefficients when data from all sites were combined.

Collectively, these results indicate that mussels are a useful indicator of local PCB levels in the surface water and bioaccumulation potential in the aquatic food web. Mussels equilibrate faster with ambient water concentration than passive samplers (Figure S10), but mussel deployment of minimum 3 months is required to reach near equilibrium concentrations of mono- to hexa-chlorobiphenyls, with longer time for higher-molecular-weight PCBs. Concentrations in mussel or in water can be inferred from one another using simple thermodynamic equilibrium models and the right set of partitioning coefficients of PCBs between water and the organism lipid (K_{tw} in the case of mussel).

Study Implications. Management of PCB contamination has traditionally focused on mapping legacy contamination in sediments and remediation of sediment hot-spots that often fails to achieve risk reduction objectives.[62] This sediment-focused approach leads to an incomplete understanding of the impacts of ongoing dissolved inputs to the water column and overestimation of potential effectiveness of sediment remediation. Controlling ongoing sources is critical for the management of PCB contaminated sites and is at the core of USEPA's contaminated sediment management strategy.[65] However, in practice, the ultralow dissolved concentrations of PCBs make it difficult to adequately monitor ongoing inputs. Novelty of the present study includes the paired deployment of passive sampling with biomonitoring as dual lines of evidence to identify ongoing dissolved PCB sources and demonstrate a path to integrate passive sampling in remedial investigations through an active collaboration with a regulatory agency and a federal stakeholder for the site.

This study identified one tributary as a major source of contamination to the river and demonstrated that codeployment of passive samplers and freshwater mussels together help identify and communicate the importance of controlling ongoing sources as a key component of managing PCB-impacted rivers.

■ ASSOCIATED CONTENT

Data Availability Statement

PCB congener data are available at https://data.mendeley.com/datasets/2sgjj9b7yw/draft?a=88e0ed7e-3667-4d92-8353-b8219ba38abb.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c06646.

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Supporting material and methods for mussel deployment and retrieval, biochemical analysis, C_{free} calculation and analysis, seasonal change analysis, kinetic model assumptions and parameters used, quality assurance and quality control, supporting tables, supporting figures, supporting discussion of passive sampling and grab sampling approach, PCB C_{free} seasonal change (PDF)

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ABBREVIATIONS

ARK	Kingman Island
ARO	Near O St. outfall
ARP	Pepco
BCF	bioconcentration factor
BDC	Beaverdam Creek
C_{free}	freely dissolved concentrations
C_{pw}	concentration in the sediment porewater
C_w	concentration in the water column
DI	deionized water
DOC	dissolved organic carbon
DOEE	Department of Energy and Environment
ECD	electron capture detector
F	fall
FST	Fort Stanton
GC	gas chromatography
HIR	Hickey Run
LBC	Lower Beaverdam Creek
NAR	Nash Run
NEB	Northeast Branch
NWB	Northwest Branch
OCP	organochlorine pesticides
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
PE	low-density polyethylene
POP	Pope Branch
PRC	performance reference compounds
RI/FS	remedial investigation/feasibility study
RMSE	root mean square error
S	summer
SI	Supporting Information
Sp	spring
USGS	US Geological Survey
W	winter
WAB	Watts Branch
WAC	Washington Channel
WQC	water quality criteria
ZEK	Zekiah Swamp

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