UMBC

PCB Source Tracking In Anne Arundel County Phase II

Final Report prepared for

Anne Arundel County

FEBRUARY 2024

By Upal Ghosh, Nathalie Lombard, Louis Cheung, Oindrila Ghosh
UMBC | 1000 HILLTOP CIRCLE, BALTIMORE, MD

Acknowledgements

This work was performed in collaboration with personnel from the Anne Arundel County (AACo), Maryland Department of Environment (MDE), and University of Maryland Baltimore County (UMBC).

Key personnel involved in this work include:

Douglas Griffith	AACo	pwgrif04@aacounty.org
Ginger Ellis	AACo	pwelli16@aacounty.org
Dennis Rasmussen	MDE	dennis.rasmussen@maryland.gov
Leonard Schugam	MDE	leonard.schugam@maryland.gov
Louis Cheung	UMBC	ba65171@umbc.edu
Oindrila Ghosh	UMBC	ij63854@umbc.edu
Nathalie Lombard	UMBC	nlombard@umb.edu
*Upal Ghosh	UMBC	ughosh@umbc.edu

*Point of Contact

List of Abbreviations and Acronyms

AACo	Anne Arundel County
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
$C_{free\ sed}$	Freely dissolved concentration of bed sediments
$C_{free\ SS}$	Freely dissolved concentration of suspended sediments
C_{pw}	Freely dissolved PCB concentration in sediment porewater
C_{sed}	PCB concentration in bed sediment
C_{SS}	PCB concentration in suspended sediments
C_{w}	Freely dissolved PCB concentration in water column
DI	Deionised
ECD	Electron Capture Detector
FD	Ferndale Branch
MDE	Maryland Department of Environment
MS	Mass Spectrometry
NG	North Glen tributary
NRC	National Response Center
OC	Organic Carbon
PCB	Polychlorinated Biphenyls
PE	Low density Polyethylene
PRC	Performance Reference Compound
Sed	Bed sediments
SS	Suspended Sediments
S.WC	Storm water column passive sampling,
SW-WLA	Storm water Waste Load Allocation
QA/QC	Quality Assurance/ Quality Control
TMDL	Total Maximum Daily Load
UMBC	University of Maryland Baltimore County
WQC	Water Quality Criteria
WQS	Water Quality Standard

Contents

List of Tables and Figures

1 Introduction

The Maryland Integrated Report of Surface Water Quality (MDE 2010) listed the Baltimore Harbor, Curtis Creek/Bay, and Bear Creek portions of the Patapsco River Mesohaline Tidal Chesapeake Bay Segment as impaired for Polychlorinated Biphenyls (PCBs) in sediment and fish tissue. As a result, a PCB TMDL was established in 2011 to reduce PCB loads into the Baltimore Harbor and ultimately achieve its goal of designated use for fishing.

Following the completion of an action strategy to address the PCB Stormwater Wasteload Allocation (SW-WLA) set forth in the PCB TMDL Anne Arundel County (AACo) initiated a collaborative effort in 2020 with UMBC and MDE to assess local water quality impairments from PCBs and determine current PCB loads to address existing TMDL requirements. UMBC, MDE, and AACo collectively developed and implemented a PCB monitoring plan (Phase 1) in the Sawmill Creek catchment to characterize the potential sources of contamination in the watershed. The study identified both North Glen tributary and Ferndale Branch as tributaries of concern (Lombard et al., 2021). In North Glen tributary, PCB sources were tracked back to sediments located at the station PT7-RW-01. In Ferndale Branch, highest PCB concentrations were measured in the water column at the station PT7-RW-03, and in sediments at the upstream station PT7-RW-04 (above TMDL endpoint of 39 ng/g sediments). The station PT7-RW-04 was identified as a potential PCB source from bed sediments to the overlying water.

As a result of these findings, a Phase 2 study to further track down PCB sources was proposed in both tributaries of concern, i.e. North Glen tributary and Ferndale Branch. The Phase 2 sampling strategy included:

1. Repeat deployment of passive samplers in the water column at and around the section of concerns to further track down freely dissolved PCB sources.
2. Joint deployment of passive samplers in the sediment porewater to verify if bed sediments are acting as a PCB source to the overlying water column through PCB diffusive flux.
3. Measure PCB concentrations in suspended sediments collected during storm events at outfalls located and/or connected to suspected land sources.
4. Measure freely dissolved PCB concentrations during storm events at selected locations using a novel short-term passive sampling approach. Use information collected to further track potential ongoing PCB sources from land.

2 Material and Methods

2.1 Sampling locations

Sampling was performed in the Sawmill Creek watershed, catchment PT7, and included 11 monitoring sites. The sampling locations and analysis performed per site are listed in **Table 1** and shown in **Figure 1.** Monitoring site PT7-RW-03 was moved about 200 m downstream due to stream restoration construction activity occurring during Phase 2 monitoring.

Table 1: Sampling locations and number of analysis.

Site ID	Stream	Longitude	Latitude	WC	PW	S.WC	SS	Sed	TOC
NG-OF1	NG	-76.6288	39.18456				1		1
NG-OF2	NG	-76.6249	39.18415				1		1
PT7-RW-01	NG	-76.6248	39.18386	1	1			1	1
NG-02	NG	-76.6235	39.18274	1	1			1	1
NG-03	NG	-76.6231	39.18252	1	1			1	1
FD-OF0	FD	-76.6385	39.18281				1		1
PT7-RW-04	FD	-76.6329	39.17927	1	1			1	1
OD-02	OD	-76.6335	39.17885					1	1
OD-01	FD	-76.6319	39.17864	1	1	2	1	1	2
PT7-RW-03	FD	-76.6247	39.1786	1	1	2	1	1	2
FD-01-17	FD	-76.6239	39.1788	1	1				
Sum analysis	**42**			**7**	**7**	**4**	**5**	**7**	**12**

FD: Ferndale Branch, NG: North Glen Tributary, OD: Olen Drive Tributary, PW: Porewater passive sampling, Sed: bed sediments, SS: Suspended Sediments, S.WC: Stormwater passive sampling, TOC: Total Organic Carbon, WC: Water column passive sampling.

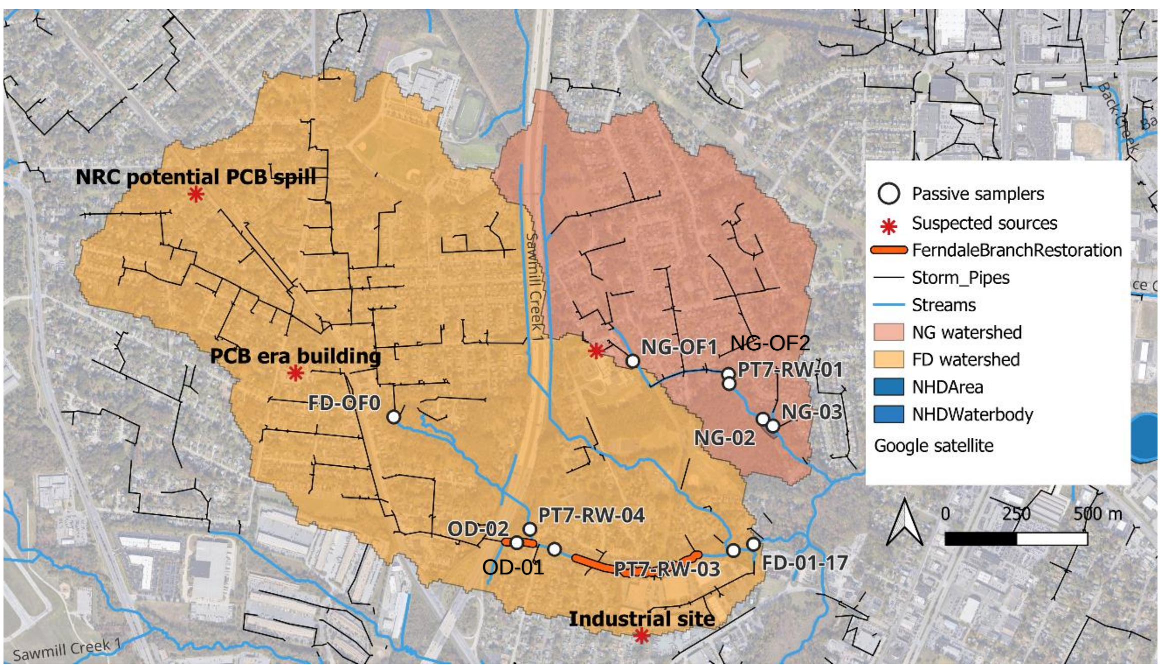


Figure 1: Map of sampling locations.

2.2 Water column and sediment porewater measurements

Freely dissolved PCB concentrations in surface water were measured using a recently published guidance document on passive sampling (USEPA, 2017).

2.2.1 Passive sampler preparation

Passive samplers were prepared using 50.8 um thick low density polyethylene sheets (PE) from Husky (Bolton, Ontario). The PE were cut into 6x6 inch (15x15 cm) sheets and then cleaned by solvent extraction. Cleaned PE were spiked in a mixture of methanol/water (80/20 v/v) with known amount of performance reference compounds (PRCs) (Booij et al., 2002). The following PCBs were used as PRC as they cover a wide range of hydrophobicities, are not present in the environment, and are not already used as analytical internal standards or surrogates:

PCB29 - 2,4,5-Trichlorobiphenyl
PCB69 - 2,3',4,6-Tetrachlorobiphenyl
PCB121 - 2,3',4,5',6-Pentachlorobiphenyl
PCB155 - 2,2',4,4',6,6'-Hexachlorobiphenyl
PCB192 - 2,3,3',4,5,5',6-Heptachlorobiphenyl

The PE soaked in PRC solution were left on a shaker at room temperature until equilibrium, then the PE samplers were soaked in deionized (DI) water overnight to remove methanol. Lastly, the samplers were dried, the water column samplers were encased in stainless steel mesh, then wrapped in aluminum foil and stored in a freezer the day before deployment (USEPA, 2017).

2.2.2 Passive sampler deployment, monitoring and retrieval

Past work from UMBC with PE showed high reproducibility between duplicates, with a median coefficient variation of 13% (n=226) (Ghosh et al., 2020). Only one passive sampler replicate was therefore deployed per site. For the porewater sampler, a mesh encased PE sampler was secured onto steel frames, then attached with screw and bolts to the bottom part of the U-post. The U-post was then hammered down into the sediments until the PE was fully inserted in the sediments. For the water column sampler, a mesh encased PE was attached to the top part of the U-post with ropes (**Figure 1**). The passive samplers were left to equilibrate in the field for 125-126 days. At retrieval, the passive samplers were lightly cleaned on site to remove particulates, placed into pre-cleaned 40 mL vials and transported back to UMBC in a cooler. The passive samplers were further cleaned at UMBC using a clean tissue and DI. water to remove surface contamination and placed into new pre-cleaned 40 mL vials. Deployment and retrieval dates are indicated in **Table 2**.

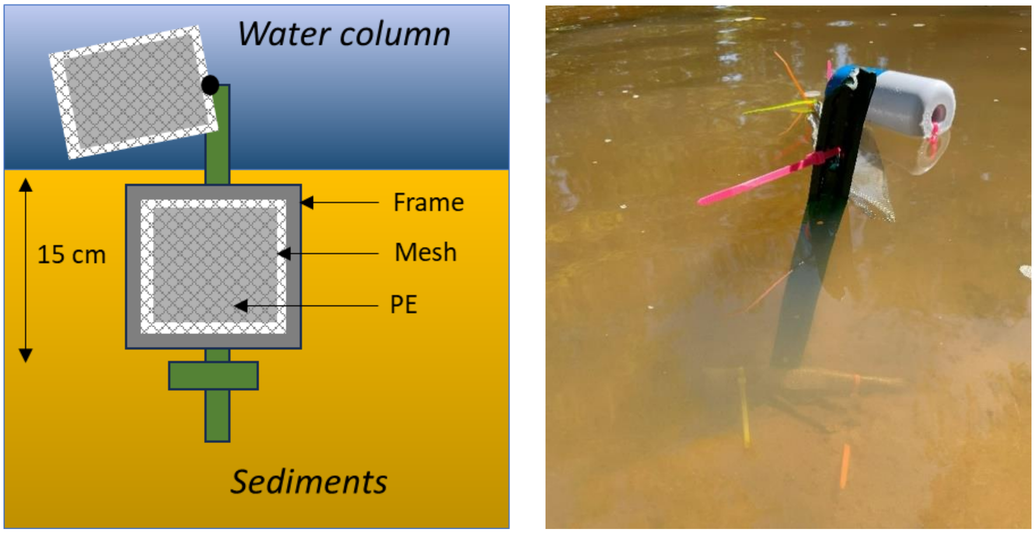


Figure 2: Deployment device for water column and porewater passive samplers.

Left panel: schematic representation of the deployment device. Right panel: picture of water column deployment in a shallow stream.

2.2.3 Passive sampler extraction and PCB analysis

All passive samplers were stored at 4 ^{o}C in closed glass vials until extraction. PCBs were extracted from the passive samplers using 30 mL of hexane, spiked with a known amount of PCB surrogate mixture containing 3,5-Dichlorobiphenyl (PCB 14) and 2,3,5,6-Tetrachlorobiphenyl (PCB 65) for QA/QC, and in presence of anhydrous sodium sulfate to remove any residual water. The samples were then placed on an orbital shaker for 24 hours, solvent was collected and extraction with fresh hexane was repeated for two additional times to ensure complete recovery of PCB analytes from the PE sheet. Once extraction was complete, the PE sheets were dried and weighed to normalize analyte concentration in the passive sampler (quantified as nanogram per gram in PE). The final combined extracts were concentrated down to 1 mL using nitrogen evaporation, treated with activated copper (EPA method 3660B), then cleaned through a 3% deactivated silica gel column (EPA SW-846 method 3530C) to remove interferents and the separation of PCBs. Internal standards, 2,4,6- Trichlorobiphenyl (PCB 30) and 2,2',3,4,4',5,6,6'- Octachlorobiphenyl (PCB 204) were added to all samples at the end of sample processing. PCB analysis was performed at the congener level based on USEPA SW846 method 8082A on an Agilent 6890N gas chromatograph (Restek, Bellefonte, PA, USA) with an electron capture detector (ECD) and a fused silica capillary column (Rtx-5MS, 60 m x 0.25 mm i.d, 0.25 um film thickness). A total of 119 most commonly found PCB congeners, (87 PCB congeners and congener groups) were measured using this method. Samples with surrogate PCB 14 and 65 recoveries below 70% were excluded from analysis.

2.3 Storm event water column passive sampling

Freely dissolved PCB concentrations were measured over a 24 h period during stormflow in order to evaluate the contribution of stormwater runoffs to the overall freely dissolved concentrations measured over a 3 month period. Short-term passive sampling of stormwater runoffs is a modification of the standard passive sampling approach developed in Ghosh's lab (Ghosh et al, 2023). Sampler preparation, impregnation and deployment was identical to regular passive sampling approach as described above, except a thinner PE of 18 µm thickness (0.7 mil) was used to achieve faster equilibrium, and stable isotope-labelled PCB were used as PRC:

^{13}C-labelled PCB congener 37
^{13}C-labelled PCB congener 47
^{13}C-labelled PCB congener 54
^{13}C-labelled PCB congener 111
^{13}C-labelled PCB congener 138
^{13}C-labelled PCB congener 178

PCB analysis was performed on an Agilent 7890B gas chromatograph with a fused silica capillary column (Rtx-5MS, 60 m x 0.25 mm i.d, 0.25 µm film thickness) equipped with an Agilent 5977B mass spectrometer (MS) detector and a high efficiency source. Three C13 labeled PCB congeners, PCB 9*, 118*, and 188* were used as internal standards and added to all samples before analysis. Peak identification and integration was performed with Agilent MS Quantitative software in the Selected Ion Monitoring (SIM) mode. A total of 204 PCB congeners (162 PCB congeners and congener groups) was measured using this method. Deployment and retrieval data and time are shown in **Table 2**.

Table 2: Deployment, retrieval and collection dates

Site ID	Stream	PE and/or SS traps deployment date (MM/DD/YY)	PE and/or SS traps retrieval date (MM/DD/YY)	Bed sediment grab collection date (MM/DD/YY)	Storm event PE deployment date and time (MM/DD/YY - HH:MM)	Storm event PE retrieval date and time (MM/DD/YY - HH:MM)
NG-OF1	NG	7/28/2022	11/30/2022	NA	NA	NA
NG-OF2	NG	7/28/2022	11/30/2022	NA	NA	NA
PT7-RW-01	NG	7/28/2022	11/30/2022	10/26/2023	NA	NA
NG-02	NG	7/28/2022	11/30/2022	10/26/2023	NA	NA
NG-03	NG	7/28/2022	11/30/2022	10/26/2023	NA	NA
FD-OF0	FD	7/27/2023	11/30/2022	NA	NA	NA
PT7-RW-04	FD	7/27/2023	11/30/2022	10/26/2023	NA	NA
OD-02	OD	NA	NA	6/7/2022	NA	NA
OD-01	FD	7/27/2023	11/30/2022	10/26/2023	10/31/2022-12:30	11/01/2022-15:15
PT7-RW-03	FD	7/27/2023	11/30/2022	10/26/2023	10/31/2022-13:20	11/01/2022-16:00
FD-01-17	FD	7/27/2023	11/30/2022	10/26/2023	NA	NA

2.4 Freely dissolved PCB water concentration calculations

The freely dissolved PCB concentration in water column C_w was calculated using the following equation (Perron et al., 2013):

$$C_w = \frac{C_{p,t}}{(1-e^{-k_e}) \times K_{pw}}$$ Equation 1

Where, C_w (ng/L) is the water column concentration, $C_{p,t}$ (ng/g) is the target compound concentration in the polymer at the time t, K_{pw} is the partition coefficient of the target compound between water phase and polymer and k_e is the mass transfer coefficient (d^{-1}).

With k_e determined as follows:

$$k_e = ln\left(\frac{C_{prc,t}}{C_{prc,int}}\right) \times \frac{1}{t}$$ Equation 2

Where $C_{prc,t}$ is the concentration of PRC compound in polymer at time t, and $C_{prc,int}$ is the initial concentration of PRC compound in polymer, and t is the time of deployment (d). Polymer partition constants K_{pw} for PCBs were based on published consensus values in Ghosh et al. (2014).

The fractional equilibrium f_{eq} was calculated for each target analyte as follows:

$$f_{eq} = 1 - e^{-ke*t}$$ Equation 3

Target analytes with f_{eq} below 0.1 were not reported due to uncertainty linked with low uptake and high non-equilibrium correction factor, i.e. above 10.

The freely-dissolved concentrations in sediment porewater C_{pw} was calculated from the concentrations measured in the PE samplers, fractional equilibrium f_{eq} calculated with the PRC correction software (Fernandez et al., 2012), and Kpw such as:

$$C_{pw} = \frac{C_{p,t}}{f_{eq} \times K_{pw}} \qquad \text{Equation 4}$$

Similarly to C_w, target analytes with f_{eq} below 0.1 were not reported due to uncertainty linked with low uptake and high non-equilibrium correction factor, i.e. above 10

For both C_{pw} and C_w calculations, K_{pw} partition coefficients were corrected for the average water temperature during the deployment period using the Van't Hoff equation:

$$K_{pw}(T) = K_{pw}(298) \times \exp\left(\frac{\Delta H_{pw}}{R} \times \left(\frac{1}{298} - \frac{1}{T}\right)\right) \qquad \text{Equation 5}$$

Where K_{pw} (T) is the PE-water partitioning coefficient at any temperature T (K), K_{pw} (298) is the PE-water partitioning coefficient at standard reporting temperature of 298 K, ΔH_{pw} is the enthalpy of PE-water partitioning (kJ/mol), and R is the universal gas constant, 0.008314 kJ/(mol.K).

Average water temperature was estimated based on the USGS daily data for the deployment period. No temperature records were available in the Sawmill Creek watershed. Water temperature from Herring Run at the USGS gage # 01585219 was used, and a water temperature correction of T=292K was applied for the regular passive sampler data and T=288K was applied for the storm passive sampler data.

2.5 Pollutant flux from sediment to water column

The magnitude of diffusive flux of pollutants between the sediment porewater and water column was calculated from the freely dissolved concentration of the pollutant in these two phases as shown below (Beckingham and Ghosh, 2013):

$$F_{pw \to w} = k_{BL} \times (C_{pw} - C_w) \qquad \text{Equation 6}$$

Where $F_{pw \to w}$ is the flux due to molecular diffusion of pollutants between the sediment porewater and overlying/surface water (ng/m^2/day), k_{BL} is the mass transfer coefficient for transport through the sediment-water interface or benthic boundary layer (m/day), C_{pw} and C_w are the freely dissolved concentration of the pollutants in the sediment porewater and overlying/surface water, respectively (ng/m^3). The mass transfer coefficient, k_{BL}, is site-specific and is a strong function of flow velocity (Thibodeaux, 1996). A mass transfer coefficient of 2 cm/day, as measured in Grasse River (Alcoa, 2001) and applied for Anacostia River Tributaries diffusive flux calculation (Lombard et al., 2023), was used in this study. Site specific determination of the mass transfer coefficient can improve the prediction of PCB flux from sediments.

2.6 Sediment measurements

2.6.1 Bed Sediment collection

Stream channel sediments were sampled by MDE using a petite ponar stainless steel sampler that measures 6” W x 6” L. Three grab samples were taken at each sampling site - one near left bank, one mid steam, and one near the right bank location. Sediment from the top 2" of the ponar sampler of each grab were mixed to create a composite sample for each sampling site. Sediment samples were placed in a cooler, transported back to the UMBC laboratory and stored at 4 ^{o}C until processing. MDE staff collected all bed sediments samples, except at OD-02, where sediments were sampled by UMBC team before stream restoration project construction began. Sediments were sampled with a trowel at 3 locations surrounding OD-02, within 3 meters distance, where high organic content was observed, then mixed in a stainless-steel bowl, to create a composite sample.

2.6.2 Suspended sediments collection

Suspended sediments were collected using sediment traps as shown in **Figure 2**. The sediment trap device was deployed in the stream for the duration of passive sampler deployment to collect suspended sediments from multiple storm events. Suspended sediments collected (**Figure 3**) were transferred in a 250 mL wide mouth jar, transported back to UMBC in a cooler, sieved through a 2 mm USA standard test sieve, then freeze dried and stored in a freezer until analysis. Mass of dried sediments collected is presented **in Table 3**.

2.6.3 Sediment sample preparation and PCB extraction

Sediment samples were first manually homogenized using a clean metal stirring rod. Homogenized samples were then sieved using a 2 mm sieve to remove large particles. Next, all sediments were freeze dried for at least 24-hours before extraction and then stored at -4°C. Approximately 1 gram of dry sediment was extracted using a 1:1 v/v hexane:acetone mixture. Extraction was conducted using ultrasonication per EPA method 3550B. Following extraction, extract cleanup followed EPA method 3660B (activated copper cleanup) and 3630C (3.3% deactivated silica gel cleanup).

2.6.4 TOC analysis

Total organic carbon in sediment samples were measured with a Total Organic Carbon Analyzer (TOC-V CPH model) using the Non-Purgeable Organic Carbon mode and detection performed with a NDIR detector. Methods for these analyses followed prior source tracking work performed in the Anacostia River tributaries (Ghosh et al. 2020).

Table 3: Mass of suspended sediments collected per site.

Site ID	NG-OF1-SS	NG-OF2-SS	FD-OF0-SS	OD-01-SS	PT7-RW-03-SS
mass SS < 2mm (g)	11.3	51	24.4	67.8	233.1
mass SS > 2mm (g)	4.5	2.4	3.4	4.5	14.5
mass SS total	15.8	53.4	27.8	72.3	247.6

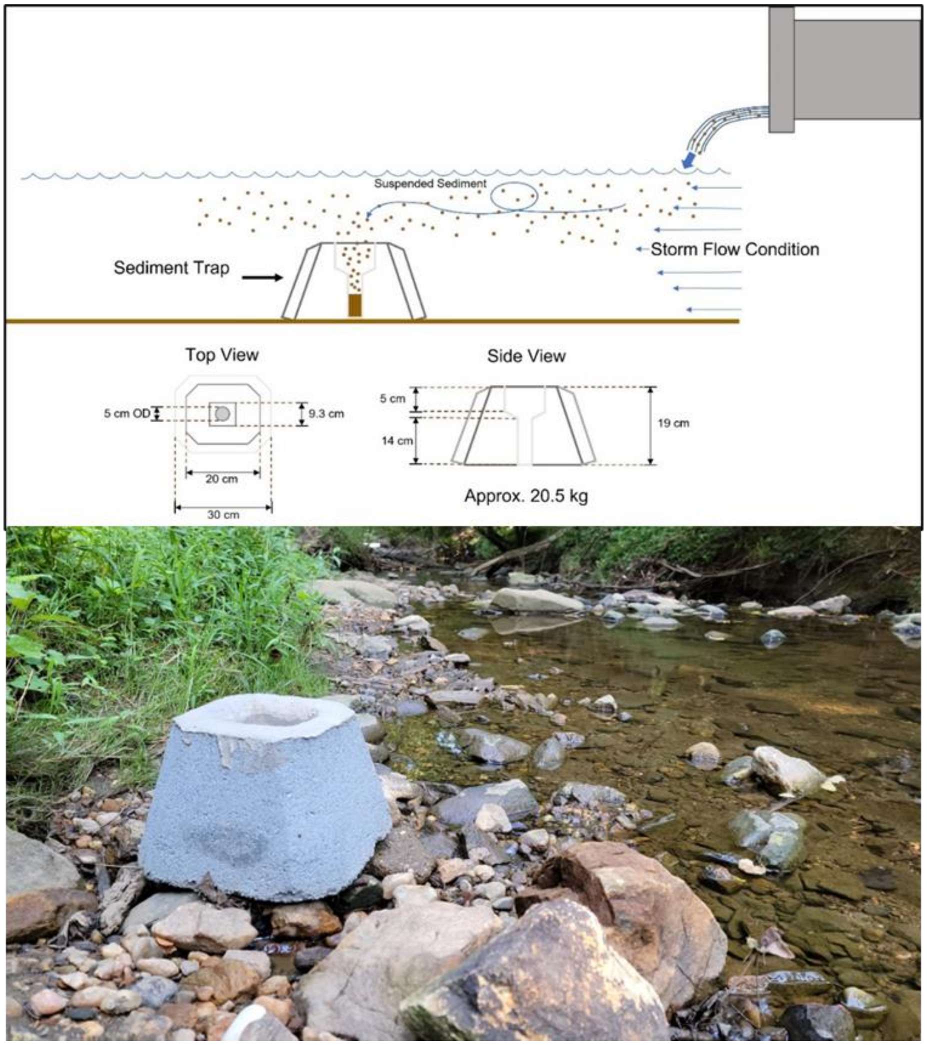


Figure 3: Sediment trap design. Top: schematic representation of the sediment trap in stormflow conditions. Bottom: picture of sediment trap in stream during baseflow conditions.

Figure 4: Picture of the suspended sediments collected at each site.

3 Monitoring Results and Discussion

To compare with the previous study conducted in 2020 (Lombard et al., 2021), a water temperature correction was applied to both 2020 and 2022 passive sampler datasets. Note that data presented in the previous report was not temperature corrected (Lombard et al., 2021). PCB concentrations measured during Phase 1 and Phase 2 are summarized in Appendix 6.

3.1 North Glen Tributary

3.1.1 Water column

Like the previous study, the highest freely dissolved PCB concentrations were measured in the North Glen Tributary (NG) at the most upstream site PT7-RW-01 (**Figure 4, Figure 5**). PCB concentrations measured in 2022 (1.7 ng/L) were 30% lower than that measured in 2020 (2.4 ng/L after temperature correction). PCB concentrations measured in the NG stream were still above EPA recommended water quality criteria (WQC) of 0.64 ng/L for a cancer risk of 10 in a million (10E-5) at all monitoring sites, and above the targeted TMDL endpoint water quality standard (WQS) of 0.27 ng/L for the Baltimore Harbor &Curtis Creek/Bay TMDL.

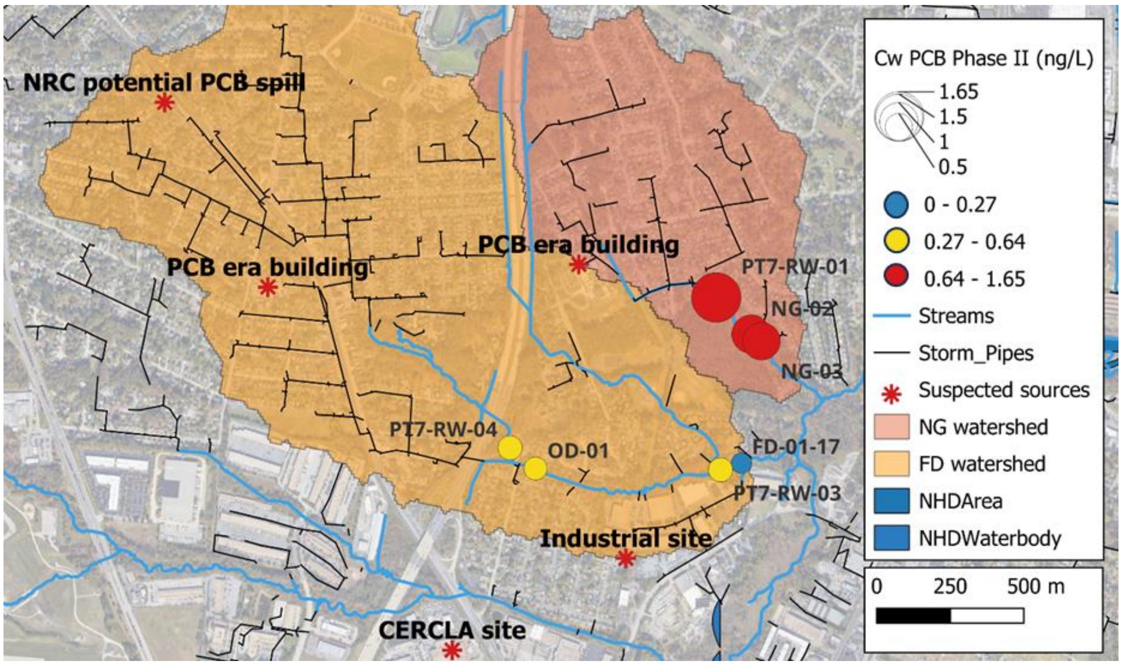


Figure 5: Map of the freely dissolved PCB concentrations measured in water column in Fall 2022

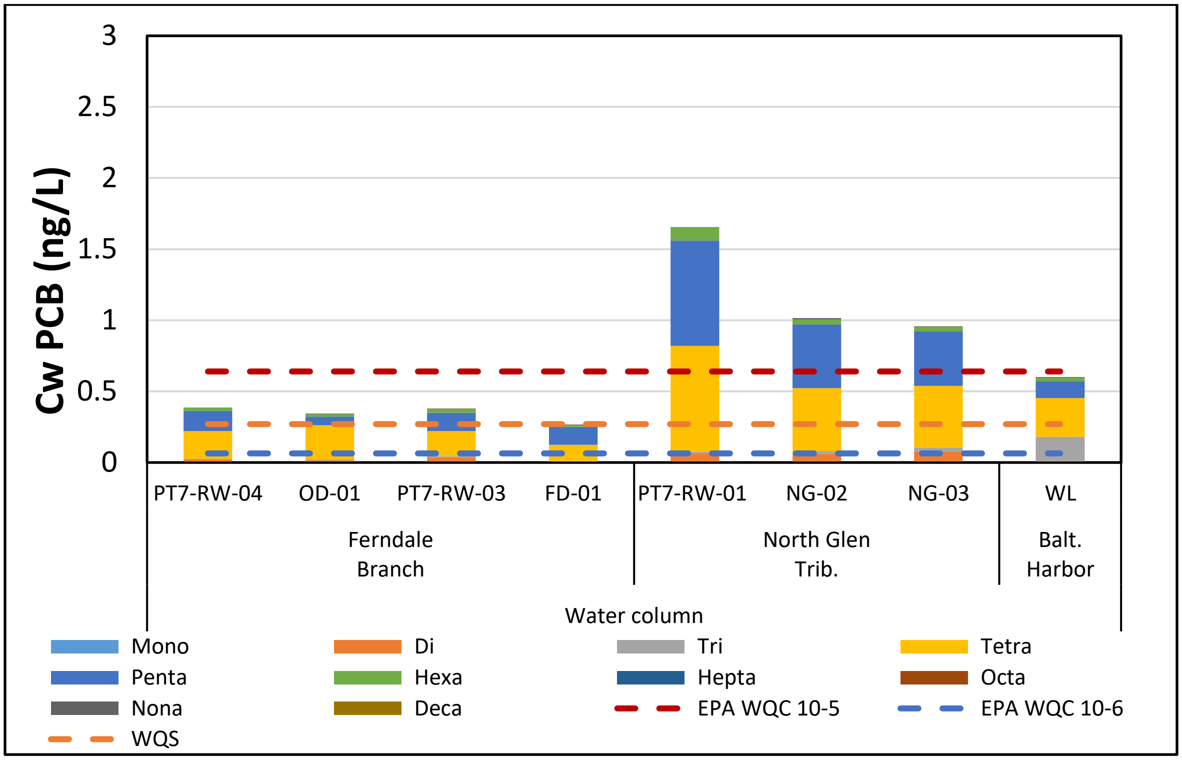


Figure 6: Freely dissolved PCB concentrations measured in the water column during Fall 2022

3.1.2 Sediment porewater

Sediment porewater samplers were installed to measure freely dissolved PCB concentration in the top 0-6 inch (0-15 cm) surface sediments. PCB concentrations in the sediment porewater were similar to that observed in the water column (**Figure 6**). The calculated PCB diffusive net flux is below +/- 10 ng/m^2/day (**Figure 7**). For comparison, the Lower Beaverdam Creek, tributary of the Anacostia River located in D.C area, exhibits significant diffusive flux of at least +100 ng/m^2/day. Surface porewater sediments and water column in NG are consequently close to equilibrium, which suggests the sediments do not act as a source of PCBs to the water column at this site.

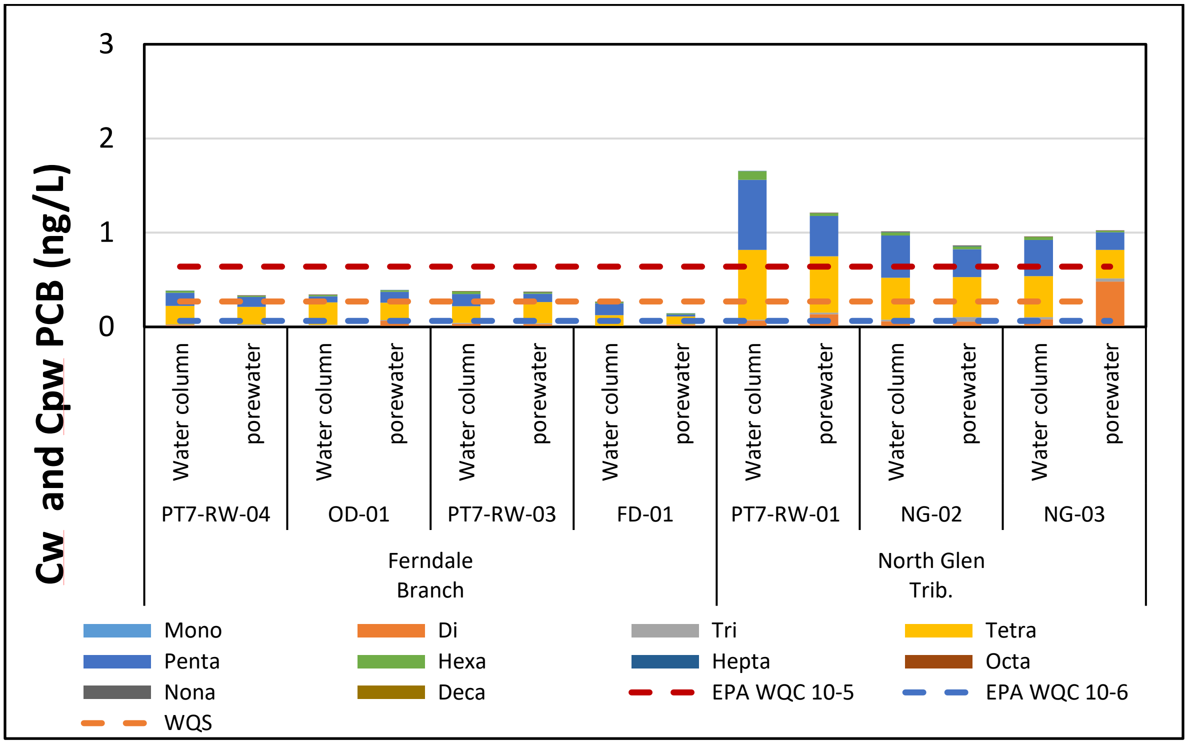


Figure 7: Freely dissolved PCB concentrations in the sediment porewater (Cpw) compared to that in the water column (Cw) in Fall 2022

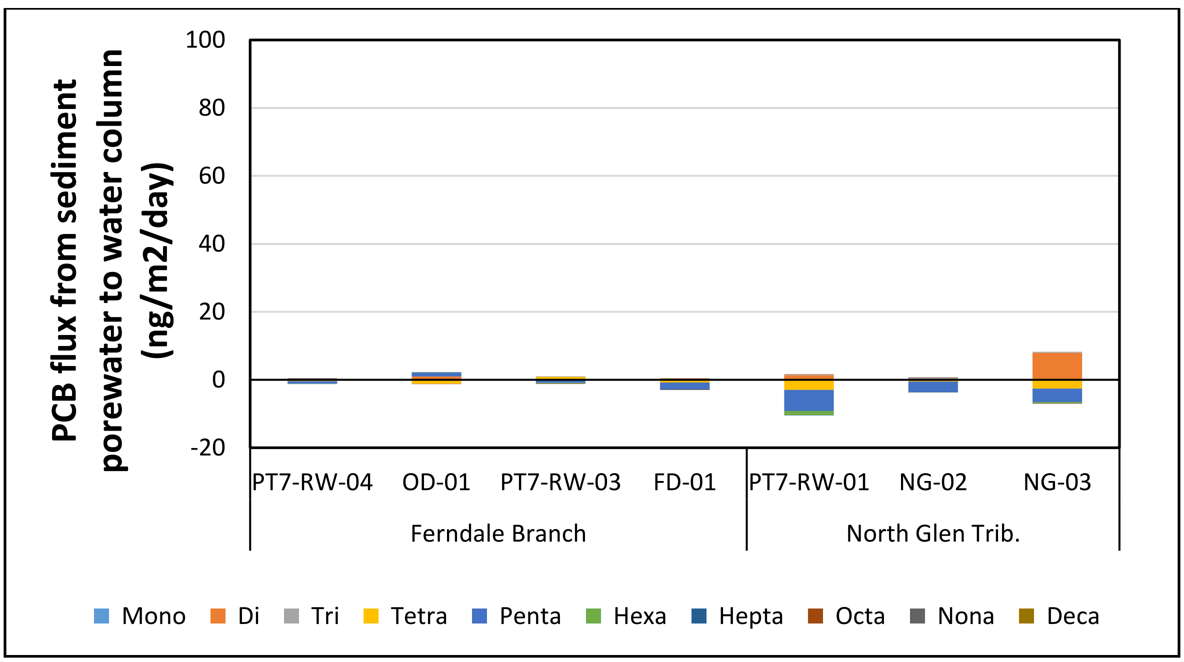


Figure 8: PCB diffusive flux from porewater to water column in Fall 2022

3.1.3 Bed sediments

PCB concentrations in surface bed sediments (C_{sed}) of PT7-RW-01 have decreased from 51 ng/g in 2020 to 2.4 ng/g in 2022 (**Table 4**), suggesting deposition of cleaner sediments at that location or spatial heterogeneity at that location. Higher PCB concentrations (3 to 7 times higher) were observed in the downstream locations NG-02 and NG-03. PCB concentrations in NG-02 and NG-03 surface sediments remained low, respectively 4.8 and 12 ng/g (**Table 4, Figure 8**), and all PCB concentrations measured in bed sediments of NG stream were below the targeted TMDL endpoint of 39 ng/g.

Table 4: PCB concentration and organic carbon content (foc) in sediments

Site ID	Stream	Average sum 119 PCB (ng/g)		Average sum 119 PCB (ng/g OC)	Av OC content (%)	
Bed sediments						
PT7-RW-04	FD	5.8	± 1.3	716	0.8%	± 0.08%
OD-02	FD	12	± 2.7	446	2.6%	± 0.44%
OD-01	FD	8.8		404	2.2%	± 0.46%
PT7-RW-03bis	FD	4.8		296	1.6%	± 0.08%
PT7-RW-01	NG	2.4		1035	0.23%	± 0.034%
NG-02	NG	4.8		353	1.4%	± 0.19%
NG-03	NG	12		3425	0.34%	± 0.05%
Suspended sediments						
FD-OF0	FD	42		279	15%	± 1.0%
OD-01	FD	13	± 5.3	432	2.9%	± 1.5%
PT7-RW-03	FD	3.4		2117	0.16%	± 0.042%
NG-OF1	NG	3.1		284	1.1%	± 0.71%
NG-OF2	NG	2.7		329	0.82%	± 0.15%

Shaded in red, value above TMDL endpoint of 39 ng/g for PCB concentration in sediments.

Direct measurement of PCB in sediments does not provide a full understanding of its impact on the freely dissolved PCB concentration in the water phase and thus on PCB uptake into the biota. The impact of PCB concentration in sediment on the freely dissolved PCB concentrations will depend on the fraction of PCBs that will desorb from the sediment into the water phase and is linked to the total organic carbon content. A more relevant PCB concentrations comparison between sediments require first a normalization by total organic carbon content (OC) present in the sediments**.**

After normalization, PCB concentration in the organic fraction of the sediments at PT7-RW-01 (1035 ng/g OC) decreased by a factor of 32 than that measured in 2020 (33,668 ng/g OC). Downstream stations NG-02 and NG-03 had normalized PCB concentration within a factor of 4 of that at PT7-RW-01. All normalized PCB concentrations were equal to or lower than that measured in 2020 at the downstream Sawmill Creek downstream station SM-01 (~3,500 ng/g

OC). These results confirm that the newly deposited sediments in NG are cleaner and do not act as a source of PCB contamination to the downstream waterbody.

3.1.4 Suspended sediments

Suspended sediments (SS) captured by the sediment traps at NG-OF1 and NG-OF2 exhibited low PCBs concentrations (C_{SS} of ~3 ng/g) (**Table 4**). The similar/lower PCB concentrations measured in the suspended sediments compared to the downstream bed sediments agrees with the deposition of clean sediments in the downstream NG monitoring sites.

The suspended sediments also exhibited low PCB concentration in the organic fraction of the sediments (~300 ng/g OC), equivalent to that measured at NG-02 and lower than that measured at PT7-RW-01 and NG-03. It is worth mentioning that high sedimentation was observed during deployment at NG-02 (difficulty to locate samplers, U-post fully buried, **Appendix 1**). These results suggest a faster natural attenuation and recovery at NG-02 compared to PT7-RW01 and NG-03 due to the volume of suspended sediments settling at NG-02.

3.1.5 Main findings and recommendations

The clean suspended sediments captured in NG monitoring sites, and the decrease of PCB concentrations in newly deposited sediments indicate that runoff during storm events helps with the recovery of the stream. The overall decrease in sediment and suspended sediments observed in 2022 compared to 2020 might be linked to the stormwater retrofit project at Cromwell Elementary School from March 2 to June 14, 2021. During the project, two stormwater pipes half full of sediments were cleaned. PCBs analysis of the removed sediments would be necessary to confirm this hypothesis.

The time integrated PCB concentrations measured in the water column is still above EPA WQC 10E-5 and WQS, suggesting that ongoing inputs from the watershed are impacting the stream. Similar dissolved PCBs in surface water and surface sediment porewater point to the highly disturbed nature of the bed sediments that are mixed up, mobilized, and deposited upon during high flow events. Potential sources of dissolved PCBs in the water column could be unidentified locations of contaminated sediments in the tributary, or in stormwater pipes.

Overall, the findings are that the concentrations are low and trending towards a decline over the last 2 years. Future work can track further changes in water column concentrations, and if the downwards trend is not fast enough, explore additional investigations to identify contaminated surface soil sources in the watershed. Analysis of PCB concentrations in water column baseflow versus stormflow would be recommended to verify if PCB levels measured in streams are linked to stormwater pipes.

3.2 Ferndale Branch

3.2.1 Water column

The 2020 study had indicated an increase in freely dissolved PCB concentrations from 0.33 ng/L at PT7-RW-04 to 1.1 ng/L at PT7-RW-03, indicating an ongoing PCB source between the two sampling locations. Freely dissolved PCB concentrations measured in 2022 at PT7-RW-04 (0.38 ng/L) was similar to that measured in 2020. The downstream site PT7-RW-03, on the other hand, showed a factor of 3 decrease of freely dissolved PCB concentrations (0.38 ng/L) in 2022, to level similar to that measured in the upstream site PT7-RW-04 and the intermediate site OD-1 (0.33 ng/L) (**Figure 4, 5**). The water column data suggests that ongoing PCB sources impacting the water column of PT7-RW-03 may have declined over time. The PCB source reduction led to a 60 % decrease in water column concentration at the downstream FD-01 from 0.63 ng/L in 2020 to 0.26 ng/L in 2022. Freely dissolved PCB concentrations in the Ferndale Branch (FD) are now below EPA WQC 10-5, and near the TMDL endpoint WQS (**Figure 4, 5**).

3.2.2 Sediment porewater

PCB concentrations in the sediment porewater were similar to that observed in the water column (**Figure 6**). The calculated PCB diffusive net flux is below +/- 10 ng/m2/day (**Figure 7**). Surface porewater sediments and water column in FD are consequently in equilibrium, which suggests that the sediments do not act as a source of PCBs to the water column at the sampled locations.

3.2.3 Bed sediments

PCB concentrations in the bed sediments of PT7-RW-04 have dropped from 48 ng/g in 2020 to 6 ng/g in 2022, suggesting deposition of cleaner sediments at that location. PCB concentrations at the downstream locations ranged from 4.8 ng/g (PT7-RW-03) to 8.8 ng/g (OD-01) and were all below the targeted endpoint of 34 ng/g (**Table 4**).

Organic carbon normalized PCB concentrations in FD sediments measured in 2022 (~300-700 ng/g OC) were all lower than that measured in 2020 at FD station PT7-RW-04 (~3000 ng/g OC) and downstream Sawmill Creek station SM-01 (~3500 ng/g OC). The lowest normalized PCB concentration was observed at PT7-RW-03. High sedimentation was observed at this site as demonstrated by the mass of suspended sediments collected at this site compared to OD-01 and FD-OF0 (**Table 3**). This would suggest deposition of cleaner sediments at PT7-RW-03.

The “Olen Drive” (OD) tributary was suspected as a potential source of PCB contamination, but low PCB concentrations were measured in sediments collected at OD-02 before the restoration project (12 ng/g) and in the organic fraction of the sediments (450 ng/g OC) compared to 2020 measurements in FD. The estimated freely dissolved PCB concentration of the sediments (0.21 ng/L) was also below water column levels of PT7-RW-03 (0.38 ng/L). This suggests that Olen Drive tributary bed sediments did not act as a PCB source to the water column.

3.2.4 Suspended sediments

The suspended sediments (SS) captured at the outfall FD-OF0 showed PCB concentrations of 42 ng/g (just above the TMDL targeted endpoint of 39 ng/g) (**Table 4**). The FD-OF0 SS also featured very high organic carbon (15%) (**Table 4**). The corresponding normalized PCB concentration was 280 ng/g OC, which is similar/lower than that measured in the FD bed sediments.

SS captured at downstream locations OD-01 and PT7-RW-03 had lower PCB concentrations (3-13 ng/g), but 1.5 to 7.5 times higher normalized PCB concentrations (430-2100 ng/g OC) than SS captured at FD-OF0. Only SS captured at PT7-RW-03 exhibited higher normalized PCB concentrations than FD sediments, suggesting a potential PCB source between OD-1 and PT7-RW-03. This result should be used with caution as PT7-RW-03 SS exhibited both low PCB concentrations and ultra-low organic carbon content (0.16%) - close to method detection limit

(0.1%). Any impacts of stormwater runoff between OD-01 and PT7-RW-01 were instead interpreted with storm passive sampling results.

3.2.5 Storm passive sampling

Storm passive sampler data were collected at OD-01 and PT7-RW-03 the end of October 2022, about 1 month before retrieval of the regular passive samplers. PCB concentrations measured using a GC-MS are presented in **Table 5**. The GC-MS measurement was also performed for the regular passive sampler to compare PCB concentration and profile in the water column during a storm event (short) versus 4 months averaged (long). PCB concentrations measured with MS or ECD detectors were close (**Table 5**). A shift in the dominant PCB homolog group was noticed, from tetra/penta- homologs for ECD to tri/tetra- homologs for MS (**Table 6**). The shift of homolog profile is partly due to difference in the detector sensitivity, and the different number of PCB congeners analyzed (119 with ECD, 204 with MS). Only MS data are considered in the "short" versus "long" analysis.

PCB concentrations measured in the water column during the storm on 10/31/2022 were 3 (OD1) to 7 (PT7RW03) times higher than the average PCB concentrations measured during the 4 months deployment. Two times higher PCB concentration was measured during storm at PT7-RW-03 compared to the upstream location OD-01, but the difference was not statistically significant (paired t-test, p>0.05). Short- and long-term deployment showed overall similar homolog profile, except at PT7-RW-03, where higher relative concentration of tetra-homolog is noticed. These results might indicate PCB contamination in storm water runoffs between OD-01 and PT7-RW-03. Their impact on water column concentrations is however short and does not affect the longer time average concentrations since the long-term PCB concentration at PT7-RW-03 is similar to that at upstream locations. However, short-term loading during high flow can lead to residual contamination in sediments and elevation of concentrations in porewater and surface water over a more extended period.

Table 5: Comparison of PCB concentrations measured in the water column during storm (short) versus 4 months average (long)

Sample ID	PCB Cw (ng/L) GC-MS		PCB Cw (ng/L) GC-ECD
Long_PT7RW04_WC	0.27		0.38
Long_OD01_WC	0.28		0.34
Long_PT7RW03_WC	0.20		0.38
Short_OD01_WC	0.79	± 0.41	
Short_PT7RW03_WC	1.43	± 0.62	

Table 6: Comparison of PCB homolog profile in the water column during storm (short) versus 4 months average (long)

Sample ID	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
Long_PT7RW04_WC_ECD	0%	5%	1%	51%	37%	5%	0%	0%	0%	0%
Long_OD01_WC_ECD	0%	4%	3%	70%	18%	5%	0%	0%	0%	0%
Long_PT7RW03_WC_ECD	0%	9%	2%	47%	34%	7%	0%	0%	0%	0%
Long_PT7RW04_WC_MS	0%	19%	37%	32%	9%	2%	1%	0%	0%	0%
Long_OD01_WC_MS	0%	19%	41%	29%	8%	2%	1%	0%	0%	0%
Long_PT7RW03_WC_MS	0%	18%	32%	37%	9%	3%	1%	0%	0%	0%
Short_OD01_WC_MS	0%	16%	29%	44%	9%	2%	0%	0%	0%	0%
Short_PT7RW03_WC_MS	0%	8%	20%	66%	5%	1%	0%	0%	0%	0%

3.2.6 Main findings and recommendations

Decrease of the freely dissolved concentrations at PT7-RW-03 suggests that PCB source(s) identified between PT7-RW-04 and PT7-RW-03 in 2020 may not be active in 2022. This PCB source cutoff may be linked to the construction of a stream restoration project in the Ferndale Branch that occurred between PT7-RW-03 and PT7-RW-04 from March 2022 and July 2023 (Griffith, Personal communication). Stream restoration included removal of legacy sediments and addition of wood chips to the bottom substrate, that may have helped reduce the freely dissolved concentrations through PCB partitioning to the wood chips. Further analysis of the wood chip PCB partitioning properties would confirm the hypothesis.

An overall recovery of the stream was observed compared to 2020, with decrease of PCB concentrations in the bed sediments of PT7-RW-04 below the TMDL endpoint for sediments, as well as freely dissolved PCBs in the water column reaching concentrations near TMDL endpoint WQS. Bed sediments in FD do not act as a source to the water column. PCB contaminated stormwater runoff was detected between OD-01 and PT7-RW-03 but the overall impact on long term PCB concentration is not significant.

Since the downstream site FD-01, located after confluence of the unnamed Ferndale Branch Tributary, reached freely dissolved PCB concentrations in water column below WQS, no further action would be needed. Short term (within a year or 2) and long-term (5-7 years) monitoring at PT7-RW-03 and FD-01 is however recommended to verify that the trends observed in 2022 are not transients. Amongst the concerns are 1) high storms events in the stream that may fully rearrange the bed sediments and increase the impact of contaminated runoffs to the stream 2) the decay of the wood chips that would negatively impact on the water column concentration at PT7-RW-03 if their contribution to the stream recovery is non-negligible.

4 Next steps

The PCB source tracking approach applied in the catchment PT7 successfully identified two tributaries of concerns, Ferndale Branch and North Glen tributary, that were responsible for an increase of freely dissolved PCB concentrations at their confluence with Sawmill Creek. Further source tracking during Phase II indicated an overall (ongoing) recovery of both tributaries.

As next steps, we propose to:

1. Ferndale Branch: Short term (within a year or 2) and long-term (5-7 years) monitoring at PT7-RW-03 and FD-01 to verify that the trends observed in 2022 are not transients.

2. North Glen tributary:
   a. Short term monitoring to track further changes in water column concentrations,
   b. if the downwards trend is not fast enough, analyze PCB concentrations in water column baseflow versus stormflow to verify if PCB levels measured in streams are linked to surface drainage from contaminated sites in the watershed

3. Apply the same PCB source tracking approach to other catchments such as PT3, PTF, and PTG.

5 References

Alcoa. 2001. Comprehensive Characterization of the Lower Grasse River – Executive Summary. http://www.thegrasseriver.com/major_reports.html

Beckingham, B., and Ghosh, U. 2013. Polyoxymethylene Passive Samplers to Monitor Changes in Bioavailability and Flux of PCBs after Activated Carbon Amendment to Sediment in the Field. Chemosphere 91, 1401-1407.

Booij, K., Smedes, F., and van Weerlee, E.M. 2002. Spiking of Performance Reference Compounds in Low Density Polyethylene and Silicone Passive Water Samplers. Chemosphere 46, 1157–1161.

Fernandez, L.A., Lao, W., Maruya, K.A., White, C., and Burgess, R.M. 2012. Passive Sampling to Measure Baseline Dissolved Persistent Organic Pollutant Concentrations in the Water Column of the Palos Verdes Shelf Superfund Site. Environmental Science & Technology 46, 11937–11947.

Ghosh, U.; Damond, J.; Sanders, J.P.; Ghosh, O.; Gilmour, C.C.; Washburn, S. 2023. Actively shaken in-situ passive sampler platform for methylmercury and organics. Final Project Report Submitted to the DoD Strategic Environmental Research and Development Program. Project # ER-2540. Jan 31, 2023

Ghosh, U., S.K. Driscoll, R.M. Burgess, M.T.O. Jonker, D. Reible, F. Gobas, Y. Choi, S.E. Apitz, K.A. Maruya, W.R. Gala, M. Mortimer, and C. Beegan. 2014. Passive sampling methods for contaminated sediments: practical guidance for selection, calibration, and implementation. Integrated Environmental Assessment and Management 10:210-223.

Ghosh U., Lombard N., Bokare M., R., Yonkos L., Pinkney F. 2020. Passive samplers and mussel deployment, monitoring, and sampling for organic constituents in Anacostia River tributaries: 2016-2018. DOEE Final Report.

MDE. 2010. The 2010 Integrated Report of Surface Water Quality in Maryland. Submitted in Accordance with Sections 303(d), 305(b) and 314 of the Clean Water Act. The Maryland Department of Environment, April 2, 2010.

https://mde.maryland.gov/programs/water/tmdl/integrated303dreports/pages/final_approved_2010_ir.aspx

Lombard N., Joshee S., Cheung L., Ghosh U. 2021. PCB Source Tracking in Anne Arundel County. Final Report prepared for Anne Arundel County, Baltimore, MD.

Lombard N.J., Bokare M., Harrison R., Yonkos, L., Murali D., U. Ghosh. 2023. Co-deployment of passive samplers and mussels reveals major source of ongoing PCB input to the Anacostia River. Environ Sci Technol. 10.1021/acs.est.2c06646. Advance online publication. https://doi.org/10.1021/acs.est.2c06646

Perron, M.M., Burgess, R.M., Suuberg, E.M., Cantwell, M.G., and Pennell, K.G. 2013. Performance of Passive Samplers for Monitoring Estuarine Water Column Concentrations 1. Contaminants of Concern. Environmental Toxicology and Chemistry 32, 2182–2189.

Thibodeaux, L.J. 1996. Environmental Chemodynamics: Environmental Movement of Chemicals in Air, Water and Soil. 2d ed., Wiley and Sons, New York.

USEPA. 2017. Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual. EPA/600/R- 16/357. Office of Research and Development, Washington, DC 20460.

6 Appendix 1: Monitoring sheet and COC

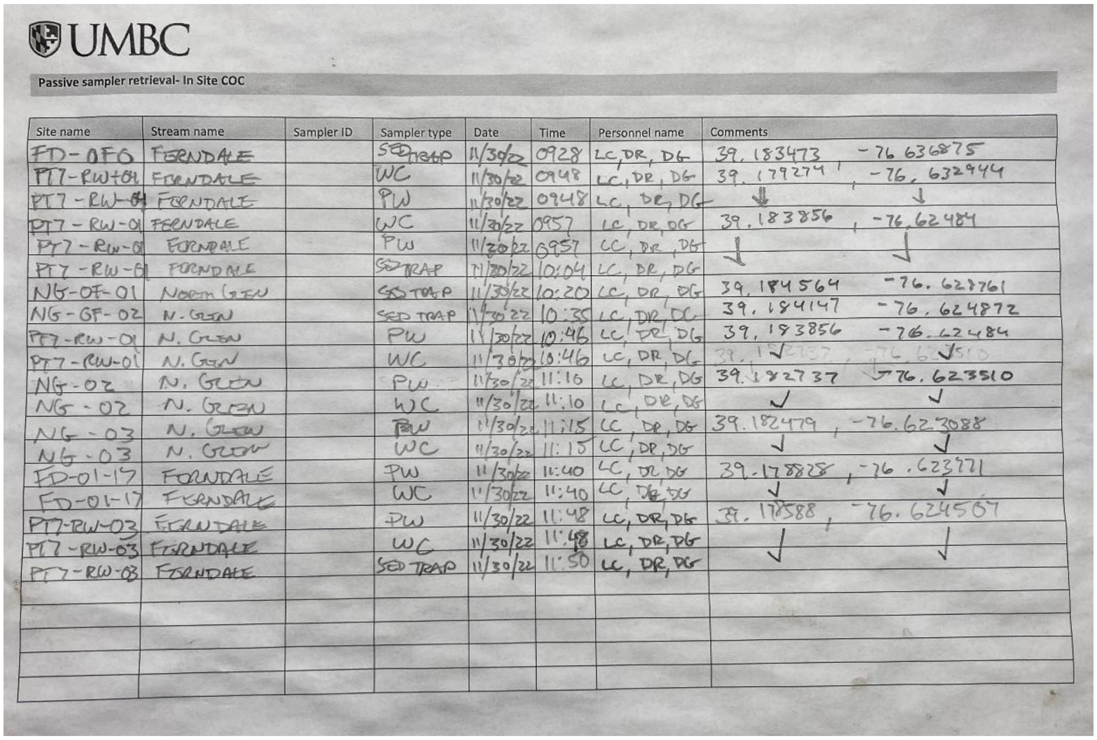
Sawmill Creek PCB Passive Samplers

Station #	Site Visit Log	Lat	Long	Sampler Type	Parking/Station Description	Logger Location
FD-OF-0	INSTALL 7.27 CHECK 8.10, 8.29, 9.14, 10.11 PULLED + FLOW 11.30	39.182807	-76.638479	Sediment Trap Only	Park @ 39.183473, -76.636875. 119 Sauers Lane.	Walk through yard, around sediment pond and behind white shed to stream.
PT7-RW-04	INSTALL 7.27 CLEAN 8.10, 8.29, 9.14, 10.11 SED GRAB 10.26 PULLED + FLOW 11.30	39.179274	-76.632944	Passive Sampler and Pore Water	108 Olen Dr. Can park at same location for this station and for OD-01	About 70 yards upstream of road crossing toward walk bridge
OD-01	INSTALL 7.27 CLEAN 8.10, 8.29, 9.14, 10.11 SED GRAB 10.26 PULLED + FLOW 11.30	39.178643	-76.631914	Passive sampler, Pore Water and Sediment Trap	108 Olen Dr. Can park at same location for this station and for PT7-RW-04	About 70 yards downstream of road crossing
FD-01-17	INSTALL 7.27 CLEAN 8.10, 8.29, 9.14, 10.11 SED GRAB 10.26 PULLED + FLOW 11.30	39.178804	-76.623853	Passive Sampler and Pore Water	150 Penrod Court. Park at same place for this station and for PT7-RW-03. Park at back left corner of building.	Follow flagging across small stream to 2nd stream.
PT7-RW-03	INSTALL 7.27 CLEAN 8.10, 8.29, 9.14, 10.11 SEDGRAB 10.26 PULLED + FLOW 11.30	39.178604	-76.62467	Passive sampler, Pore Water and Sediment Trap	150 Penrod Court. Park at same place for this station and for FD-01-17	About 50 yards upstream of FD-01-17. Need Hip / chest waders

PT7-RW-03 BIS SED 10.26

Sawmill Creek PCB Passive Samplers

Station #	Site Visit Log	Lat	Long	Sampler Type	Parking/Station Description	Logger Location
NG-OF1	INSTALL 7.28 CHECK 8.10, 8.29, 9.14, 10.11 PULLED + FLOW 11.30	39.184564	-76.628761	Sediment Trap Only	525 Wellham Avenue @ George Cromwell Elementary School. Park near fire hydrant.	About 50 yards from school drive, heading toward houses, near white benches.
NG-OF2	INSTALL 7.28 CHECK 8.10, 8.29, 9.14, 10.11 PULLED + FLOW 11.30	39.184147	-76.624872	Sediment Trap Only	1403 Rowe Dr. Park @ 39.183765, -76.625609. Can access this station and PT7-RW-01. Enter woods between guard rail and last house at flagging, through clearing to outfall pipe.	Trap about 10 yards downstream of outfall pipe.
PT7-RW-01	INSTALL 7.28 CLEAN 8.10, 8.29, 9.14, 10.11 SED 10.26 PULLED 11.30 (FLOW SAME AS NG-OF2)	39.183856	-76.62484	Passive Sampler and Pore Water	1403 Rowe Dr. Park @ 39.183765, -76.625609. Can access this station and NG-OF2.	About 30 yards downstream from NG-OF2. Potential to get buried. In between 2 large rocks
NG-02	INSTALL 7.28 CLEAN 8.10 10.11 * SEE BELOW SED 10.26 PULLED + FLOW 11.30	39.182738	-76.623469	Passive Sampler and Pore Water	Park @ North Glen County Park 39.181752, -76.625848. Can access this station and NG-03.	Walk past wooden framed area to right. Walk trail past the lost and found grill to paved path. Go right on paved path and look for flagging to get to stream
NG-03	INSTALL 7.28 CLEAN 8.10, 8.29, 9.14, 10.11 SED 10.26 PULLED 11.30 (FLOW SAME AS NG-02)	39.182524	-76.623062	Passive Sampler and Pore Water	Park @ North Glen County Park 39.181752, -76.625848. Can access this station and NG-02.	Walk about 40 yards downstream from NG-02
*	NG02 COULD NOT BE LOCATED ON 8.29 OR 9.14 (LOUIS WENT OUT AND LOCATED BURIED SAMPLER ON 9.14 WAS THERE, BUT BURIED)					



UMBC

Passive sampler retrieval- In Site COC

Site name	Stream name	Sampler ID	Sampler type	Date	Time	Personnel name	Comments
FD-OFO	FERNDALE		SED TRAP	11/30/22	0928	LC, DR, DG	39.183473 , -76.636875
PT7-RW+01	FERNDALE		WC	11/30/22	0948	LC, DR, DG	39.179274 , -76.632444
PT7-RW-01	FERNDALE		PW	11/30/22	0948	LC, DR, DG	⇊ ↓
PT7-RW-01	FERNDALE		WC	11/30/22	0957	LC, DR, DG	39.183856 , -76.62484
PT7-RW-01	FERNDALE		PW	11/30/22	0957	LC, DR, DG	✓ ✓
PT7-RW-01	FERNDALE		SED TRAP	11/30/22	10:04	LC, DR, DG	
NG-OF-01	NORTH GLEN		SED TRAP	11/30/22	10:20	LC, DR, DG	39.184564 -76.627761
NG-GF-02	N. GLEN		SED TRAP	11/30/22	10:35	LC, DR, DG	39.184147 -76.624872
PT7-RW-01	N. GLEN		PW	11/30/22	10:46	LC, DR, DG	39.183856 -76.62484
PT7-RW-01	N. GLEN		WC	11/30/22	10:46	LC, DR, DG	✓ ✓
NG-02	N. GLEN		PW	11/30/22	11:10	LC, DR, DG	39.182737 -76.623510
NG-02	N. GLEN		WC	11/30/22	11:10	LC, DR, DG	✓ ✓
NG-03	N. GLEN		BW	11/30/22	11:15	LC, DR, DG	39.182479 , -76.623088
NG-03	N. GLEN		WC	11/30/22	11:15	LC, DR, DG	✓ ✓
FD-01-17	FERNDALE		PW	11/30/22	11:40	LC, DR, DG	39.178828 , -76.623771
FD-01-17	FERNDALE		WC	11/30/22	11:40	LC, DR, DG	✓ ✓
PT7-RW-03	FERNDALE		PW	11/30/22	11:48	LC, DR, DG	39.178588 , -76.624507
PT7-RW-03	FERNDALE		WC	11/30/22	11:48	LC, DR, DG	✓ ✓
PT7-RW-03	FERNDALE		SED TRAP	11/30/22	11:50	LC, DR, DG	

7 Appendix 2: Summary Tables of PCB concentrations measured in phase 1 and phase 2

Table S1: PCB concentrations measured in Phase 1 (2020)

Stations ID	Cw (ng/L)		Csed (ng/g)	Csed (ng/g OC)
	No temp. Corr.	After temp. corr.		
Irving Branch				
IB_01_17	0.052	0.038	2.1	266
Muddy Bridge Branch				
PT7_RW_09	0.21	0.15	0.062	6.7
PT7_RW_07	0.24	0.18	3.5	2551
PT7_RW_06	0.22	0.16	0.77	
MB_01_17	0.24	0.18	17	1463
Sub trib. D				
PT7_RW_02	0.056	0.041	3.8	343
Ferndale Branch				
PT7_RW_04	0.45	0.33	48	3080
PT7_RW_03	1.6	1.1	0.88	
FD_01_17	0.86	0.63	1.3	53
"North Glen" Tributary				
PT7_RW_01	3.3	2.4	51	33368
NG_01_17	2.0	1.4	0.3	15
Sawmill Creek				
SM_04_17	0.18	0.046	7.3	1011
SM_03_17	0.34	0.0073	102	3758
SM_02_17	0.27	0.22	0.42	6.6
SM_01_17	0.41	0.30	48	3470
Tidal				
PT7_TD_01	0.43	0.25	96	1440
PT7_TD_02	0.42	0.13	0.84	
Reference				
Back Rvr. Ref.	0.063	0.31	3.9	669
Severn Run Ref.	0.010	0.30	2.6	251

Temp. corr.: temperature correction. Sed: bed sediments, W: Water column

Table S2: PCB concentrations measured in Phase 2 (2022)

Site ID	Cw (ng/L)	Cpw (ng/L)	Csed (ng/g)	Css (ng/g)	Csed (ng/g OC)	Css (ng/g OC)	Cw (ng/L) (MS)	Cw s. (ng/L) (MS)
North Glen Trib.								
NG-OF-01				3.1		284		
NG-OF-02				2.7		329		
PT7-RW-01	1.7	1.2	2.4		1035			
NG-02	1.0	0.86	4.8		353			
NG-03	0.96	1.0	12		3425			
Ferndale Branch								
FD-OF-00				42		279		
PT7-RW-04	0.38	0.33	5.8		716		0.27	
OD-02			12		446			
OD-01	0.34	0.39	8.8	13	404	432	0.28	0.79
PT7-RW-03	0.38	0.37	4.8	3.4	296	2117	0.20	1.4
FD-01	0.26	0.14						

Freely dissolved PCB Cw and Cpw were all temperature corrected. PW: Porewater, Sed: bed sediments, SS: Suspended Sediments, S.: Stormwater, W: Water column.