PCB Source Tracking In Anne Arundel County

Report prepared for

Anne Arundel County

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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).

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List of Abbreviations and Acronyms

AACo	Anne Arundel County
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
Cpw	Freely dissolved PCB concentration in sediment
Csed	PCB concentration in sediment
Cw	Freely dissolved PCB concentration in water column
DI	Deionised
FD	Ferndale Branch
IB	Irving Branch
LRP	Land Restoration Program
MB	Muddy Branch
MDE	Maryland Department of the Environment
NG	North Glen tributary
NRC	National Response Center
OC	Organic Carbon
PCB	Polychlorinated Biphenyls
PE	Low density Polyethylene
PRC	Performance Reference Compound
QA/QC	Quality Assurance/ Quality Control
SM	Sawmill Creek
TAS	Targeted Action Strategy
TMDL	Total Maximum Daily Load
UMBC	University of Maryland Baltimore County
WQC	Water Quality Criteria
WQS	Water Quality Standard

Contents

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 total maximum daily load (TMDL) was established in 2011 to reduce PCB loads into the Baltimore Harbor and ultimately achieve its goal of designated use for "fishing" as well as "marine and estuarine aquatic life and shellfish harvesting." One major challenge for TMDL implementation is the identification of PCB sources that are contributing to the elevated concentrations in fish and shellfish.

The freely dissolved PCB concentration in water controls biological uptake and is critical for determining dominant sources that result in uptake into biota. However, dissolved concentrations of PCBs are challenging to measure directly due to ultra-low concentrations in water and the presence of colloids and dissolved organic carbon that sorb the PCBs and interfere with the measurement. Passive sampling has emerged as an alternative technique to measure freely dissolved concentrations of hydrophobic chemicals without interference from colloidal particles and dissolved organic carbon (USEPA 2012a; Ghosh et al. 2014).

Legacy deposits of contaminated sediments can be an important source of PCBs to the water column. Their impact on the freely dissolved PCB concentrations however depends on the fraction and type of organic carbon present in the sediments. Combined measurements of PCBs in sediments and fraction of organic carbon of the sediments provide a better understanding of how the sediments affect the freely dissolved concentrations in porewater and therefore the exchange with surface water and uptake in the biota.

Anne Arundel County (AACo) is interested in assessing local water quality impairments from PCBs and determining current PCB loads to address existing TMDL requirements. The County has collaborated with Biohabitats, Maryland Department of the Environment (MDE), and University of Maryland, Baltimore County (UMBC) to develop a Targeted Action Strategy (TAS) that aims to first investigate and then address sources of PCBs within the Baltimore Harbor, Curtis Creek/Bay, and Bear Creek PCB TMDL watershed. The TAS (AACo, 2019) laid out a plan for the proposed measurement and interpretation of ongoing PCB inputs from the County catchments. An initial desktop assessment created a list of 21 catchments, of which the Sawmill Creek catchment (identified as catchment "PT7" in the TAS) was selected for a pilot monitoring program. The key factors for choosing this catchment included good access, a mix of potential PCB sources (based on desktop screening of databases from National Response Center NRC, Land Restoration Program LRP, Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) sites, and PCB-era buildings), and the possibility of using a trackback strategy to identify and eventually eliminate ongoing sources.

UMBC, MDE, and AACo collectively developed a PCB monitoring plan in the Sawmill Creek catchment to characterize the potential sources of contamination in the watershed. Water column and sediment PCB monitoring locations were identified based on a desktop review. A plan was developed to measure PCB concentration in the water column using time-integrated passive sampling (USEPA, 2017) following recent work performed by UMBC to track ongoing pollutant sources in the Anacostia River (Ghosh et al. 2020). Objectives of the study were to:

1. Measure freely dissolved PCBs in the water column at several locations using passive samplers deployed for a 2-3 month period, and compare the values with the USEPA water quality criteria for Human Health protection (0.64 ng/L), and the water column TMDL endpoint (0.27 ng/L).
2. Assess if the Sawmill Creek catchment is a major source of PCB contamination to the Baltimore Harbor by comparing freely dissolved PCB concentration released by the catchment to PCB concentrations that exists within the Harbor.
3. Measure PCB concentration in sediment at the sampling locations to identify any dominant PCB source in surface sediments in the study area.

A summary of the study approach and methods are provided below with details available in a workplan submitted to AA County (Lombard and Ghosh, 2021).

2 Material and Methods

2.1 Sampling locations

A trackback approach was used in the Sawmill Creek catchment (AA 2019). Sampling was performed in the catchment at fifteen locations in Sawmill Creek and its tributaries, two locations in downstream tidal area (Furnace Creek, and Curtis Creek), and two reference sites. Reference sites were located in: Sewell Spring Branch, a direct tributary to the Severn River, and 2) an un-impacted stream of Back River (BR-50, MDE, 2012). The sampling locations are shown in **Figures 1a-c** and listed in Table 1.

2.2 Water column 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 (15 x15 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). This mixture was left on a shaker for one month at room temperature, then the PE samplers were submerged in deionized water overnight to remove methanol. Lastly, the samplers were dried, encased in stainless steel mesh, then wrapped in aluminum foil and stored in a freezer until 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. Samplers were encased in stainless steel meshes and either securely attached to a cinder block with a zip tie or attached to a green post as seen in **Figure 2** and were left to equilibrate for 82 to 96 days. Deployment devices used per site and deployment dates are indicated in **Table 2.** After retrieval of the passive samplers from the field, they were cleaned on site using a clean tissue and deionized (DI) water to remove surface contamination and placed into pre-cleaned 40 mL vials. All passive samplers were placed into a cooler marked for return to UMBC.

2.2.3 Passive sampler extraction and PCB analysis

All samples were stored at 4 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-Di-chlorobiphenyl (PCB 14) and 2,3,5,6-Tetra-chlorobiphenyl (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 contaminant 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 ensure the removal of 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 and a fused silica capillary column (Rtx-5MS, 60 m x 0.25 mm i.d, 0.25 ìm film thickness). A total of 119 most commonly found PCB congeners, and congener groups were measured using this method. Samples with surrogate PCB 14 and 65 recoveries below 70% were excluded from analysis.

2.2.4 Freely dissolved PCB water concentration calculations

To calculate PCB water column concentration C_w, the following equation is applied (Perron et al, 2013)

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

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:

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

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 PCB concentrations in water were reported in this document for a standard temperature of 298 K or 25ºC.

2.3 Sediment measurements

2.3.1 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 ºC until processing.

2.3.2 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 1.7 mm sieve tray to remove any non-sediment matter. 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).

2.3.3 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).

2.3.4 PCB porewater concentration estimation

PCB concentrations in the porewater of sediment can be estimated from PCB concentrations in sediment and fraction of organic carbon as follow (USEPA, 2012):

$$C_{pw} = C_{sed} / (K_{OC} * f_{OC}) \qquad \text{equation 3}$$

Where C_{sed} is the PCB concentration in sediments in ug/kg, C_{pw} is the PCB concentration in porewater in ug/L, Koc is the partitioning coefficient of compound between OC and water (L/kg), and f_{OC} is the fraction of organic carbon present in sediments. Koc from Nguyen et al. (2005) were used in this study.

3 Sawmill Creek Watershed Monitoring Results

3.1 Freely dissolved PCB concentrations in the water column

Freely dissolved PCB concentrations measured in the water column of the Sawmill creek watershed are presented in **Figure 3**. Freely dissolved concentrations measured in the reference waterbodies, i.e. un-impacted streams of Back River and Severn Run, were below EPA water quality criteria (WQC) and below TMDL water quality standard (WQS) as expected.

3.1.1 Curtis Bay/Creek

Freely dissolved PCB concentrations measured in the water column of Curtis Creek (PT7-TD-02) were above TMDL endpoint WQS of 0.27 ng/L (**Figure 3**), which is consistent with the fish consumption advisory in place in the Patapsco/Baltimore Harbor, due to high PCB levels detected in fish (https://mdewin64.mde.state.md.us/WSA/FCA/index.html). Similar PCB concentrations were detected in the water column of Furnace Creek (PT7-TD-01) (**Figure 3**), but its PCB homolog distribution was shifted towards higher proportion of penta-chlorobiphenyls (44%) compared to Furnace Creek (31%) (**Table 3, Figure S1**), suggesting that different PCB sources are affecting the water column in those two sections of the Curtis Bay.

PCB levels measured in the Curtis Bay/Creek (0.42 ± 0.0079 ng/L) were at least 2 times lower than the average PCB concentration detected in the water column of upper Back River in 2018 and 2019 (about 1 ng/L, Majcher et al., 2021). This suggests that PCB reductions required for reaching the TMDL endpoints water quality standards (WQS) will be lower in Curtis Bay compared to the Back River.

3.1.2 Sawmill Creek Catchment

Sawmill Creek showed PCB concentrations at and above the TMDL water quality standard (WQS) of 0.27 ng/L at the three downstream locations, i.e. SM-03 to SM-01. Within the Sawmill Creek, the most downstream location, SM-01, showed PCB concentrations 1.2 to 2.3 higher than the upstream locations, suggesting possible PCB inputs along the creek. PCB levels measured at the most downstream location, i.e. SM-01 (0.41 ng/L) was similar to the level detected in Furnace Creek and Curtis Bay (0.42 ± 0.0079 ng/L).. However, PCB homolog distribution observed at SM-01 differed from those detected at Furnace Creek and Curtis Creek, suggesting that Sawmill Creek is not the only contributor and other PCB sources may be influencing PCB levels in Furnace Creek and Curtis Creek (**Table 3, Figure S1**).

3.1.3 PCB trackback in Sawmill Creek's Tributaries

PCB levels measured in the water column of each tributary is described from downstream to upstream location along Sawmill Creek.

The Sawmill Creek tributary flowing through North Glen Park (called in this document **"North Glen" tributary**) showed the highest PCB levels (2.6 ± 0.93 ng/L) measured in the watershed and was above EPA WQC for an associated cancer risk of 10 in a million (10^{-5}). Water column concentrations measured in the creek were at least 5 times higher (NG-01) to 8 times (PT7-RW-01) higher than those measured in the Sawmill Creek (0.30 ± 0.099 ng/L). North Glen tributary is therefore a tributary of concern and partly explains the increased PCB levels measured between SM-02 and SM-01 stations. Similar homolog distribution centered on penta-chlorobiphenyls was observed between the two locations monitored in the North Glen tributary (**Table 3**), but 1.7 times higher concentrations were measured in the upstream station PT7-RW-01, suggesting PCB sources near PT7-RW-01.

Ferndale Branch also showed high PCB levels (0.96 ± 0.56 ng/L) in the water column that were above EPA WQC of 10^{-5}. Concentrations detected at the most downstream station of the Ferndale Branch, i.e. FD-01, showed PCB levels 2 to 5 times higher than those detected in Sawmill Creek. Ferndale Branch is therefore contributing to the PCB concentration increase observed between SM-02 and SM-01. PCB homolog distribution observed at SM-01 is closer to that of FD-01 than that of NG-01, suggesting that the Ferndale Branch has a higher relative contribution to PCB levels at SM-01 compared to the North Glen tributary. Their relative contribution can be confirmed by a mass balance approach, but would require flow records per tributary for the deployment period considered.

Within the Ferndale Branch, the highest PCB levels were observed downstream of PT7-RW-04, suggesting a PCB source nearby the station PT7-RW-03 where highest levels were monitored. The unnamed tributary of Ferndale Branch is not a tributary of concern, as PCB detected there were below EPA WQC and TMDL endpoint.

Muddy Bridge Branch showed PCB levels of 0.23 ± 0.015 ng/L which are below the TMDL endpoint, and lower than that detected at SM-03 (after its confluence to Sawmill Creek), but higher that that detected at SM-04 (before its confluence to Sawmill Creek). Muddy Branch therefore has very low PCB concentrations and has minimal contribution to the downstream sections of the watershed. .

Irving Branch has PCB levels below EPA WQC and is not a tributary of concern.

3.2 PCB concentrations in the sediments

Legacy deposits of contaminated sediments can be an important source of PCBs to the water column. PCB analysis of surface sediment at each of the sampling locations provide an assessment of whether high concentration regions exists within the study area that may need further evaluation. PCB concentrations measured in sediments and their organic carbon content are presented in the **Table 4**.

3.2.1 PCB concentrations in sediments

PCB concentrations measured in the sediments of Furnace Creek (96 ng/g) were nearly half of the concentrations detected within that area (BSM50, about 1km east) in 1996, (Back River TMDL, 2012). In Curtis Creek (about 1 ng/g), PCB concentrations were at least 200 times lower than previous measurements collected in a similar area (BSM45, CB, about 400 m north and west) (Back River TMDL, 2012). Only 5 stations showed PCB concentrations above the TMDL endpoint of 39 ng/g PCB in sediments: upstream station of North Glen tributary (PT7-RW-01), upstream station of Ferndale Creek (PT7-RW-04), two stations in Sawmill Creek (SM-03 and SM-01) and one station in Curtis Bay/Creek (PT7-TD-01).

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. Their impact 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 (Cf. Equation 3). A more relevant PCB concentrations comparison between sediments require first a normalization by total organic carbon content (OC) present in the sediments**.**

3.2.2 PCB concentrations normalized per organic carbon content of sediments

After normalization of PCB concentration by OC, PCB concentrations in the organic carbon of sediments collected at Sawmill Creek's stations SM-03 and SM-01 (~3500 ng/g OC) were about twice the concentrations detected in the tidal bay (PT7-TD-01, 1439 ng/g OC).

The upstream station of North Glen tributary showed the highest PCB concentrations in the organic carbon of sediments (33,368 ng/g OC) and were about 10 times higher than that detected in the Sawmill Creek. This result confirms North Glen as a tributary of concern. To evaluate the sediment impact on the water column concentrations, it is possible to estimate the sediment porewater concentrations from sediment concentrations using Equation 3. Porewater concentration was estimated at 20 ng/L (**Table 5**), which is about six times higher than water column concentrations measured at that station. This estimate could be refined based on the type(s) of carbon (s) present or by direct measurement, but provide a first assessment of potential PCB flux between the sediment and the water column. For that station, a net PCB flux from sediment porewater to the overlying water column is observed. The downstream station of North Glen tributary (NG-01) showed very low PCB concentrations in the organic carbon of sediments (14 ng/g OC) and corresponding estimated porewater concentration, which indicates that the upstream location sediments are likely the primary PCB source impacting the water column of both North Glen tributary stations.

In Ferndale Branch, the upstream station PT7-RW-04 also showed elevated PCB concentrations in the organic carbon of sediments (3,079 ng/g OC) that could act as a source to the overlying water column based on the sediment porewater concentration calculations. Estimated porewater concentrations (4.1 ng/L) were indeed about nine times higher than water column concentrations, leading to a net PCB flux from porewater to surface water. Potential PCB sources from sediment at PT7-RW-03 is inconclusive as organic fraction of the sediment was too low to perform any normalization. In-situ measurement of porewater concentration at this site can provide better understanding of the nature of the sediment source in this section and the potential to stabilize the pollutants in place and reduce impact on the water quality.

In Muddy Bridge Branch, the two stations PT7-RW-07 and MB-01 showed PCB levels similar to Sawmill Creek and the Tidal Bay. They may contribute to some PCB contamination of the Curtis Bay/Creek through the transport of PCB contaminated sediments. The estimated porewater concentration were about two times higher than the overlying water column, and may also act as a source of PCB to the overlying water, but to a much lesser degree compared to North Glen Tributary and Ferndale Branch.

4 PCB sources identified and future recommendations

The two main tributaries of concern leading to PCB levels above TMDL endpoint in Sawmill Creek are North Glen tributary and Ferndale Branch. Recommendations for PCB source identification in these two tributaries are provided below.

North Glen tributary was identified as a main tributary of concern due to elevated PCB concentrations measured in the water column and in the sediments, being respectively five to ten times higher than downstream locations. PCB source in this tributary was tracked back to the sediments located at the station PT7-RW-01. In addition to the contaminated bed sediments at this location, there is also the possibility of an ongoing source from the landscape and contaminated groundwater in the vicinity of this location.

Ferndale Branch was also identified as a tributary of concern. Even though PCB concentrations measured in this tributary were lower than that of North Glen tributary, the water concentration were still 2 to 5 times higher than that of Sawmill Creek. Its relative contribution to freely dissolved PCB source needs to be confirmed using a mass balance approach. This can involve calculating loads based on estimated annual discharges from each of the tributaries.

The AA County TMDL Action Strategy (AACo 2019) lists several potential sources in the North Glen and Ferndale areas including PCB era buildings that were renovated, an old CERCLA site, and other potential old industrial sites and transformers. Based on our study results, we recommend a second desktop review of current facilities and prior land use in the areas with high water concentrations of PCBs to further nail down potential sources from the land. This effort can include tracing back key outfalls within the stream in the high concentration areas, and potential sampling of groundwater and tributary banks.

Further trackback upstream of PT7-RW-01 is recommended by performing PCB measurements in the water column and sediment, in order to locate the most contaminated area and determine the extent of the contamination. Monitoring stations could include multiple locations within the tributary designed to capture potential releases from known outfalls. This would help trace potential land sources.

For example, based on monitoring results, stormwater sediment samples may be collected from the outfalls (L05O004, M05O017, M05O021) (https://koordinates.com/layer/98929-anne-arundel-county-md-storm-outfall/) located near stations exhibiting the highest PCB concentrations. This would confirm if the PCB source is being transported during storm events, and further identify the potential land source.

If PCB transport from land is confirmed, further sampling of surface soils in suspected old industrial areas, PCB era buildings, or fill material may be needed to further delineate the contaminated area.

The PCB source leading to increased water column concentration at PT7-RW-03 has not been identified yet. Since sediment analysis were inconclusive, porewater analysis is suggested at this station to determine if the sediments act as a PCB source to the overlying water.

While this study did not measure pesticides, several contaminant peaks were identified in the analysis that often come from known organochlorine pesticides. High concentrations of potential pesticides are suspected at the North Glen tributary that need to be confirmed.

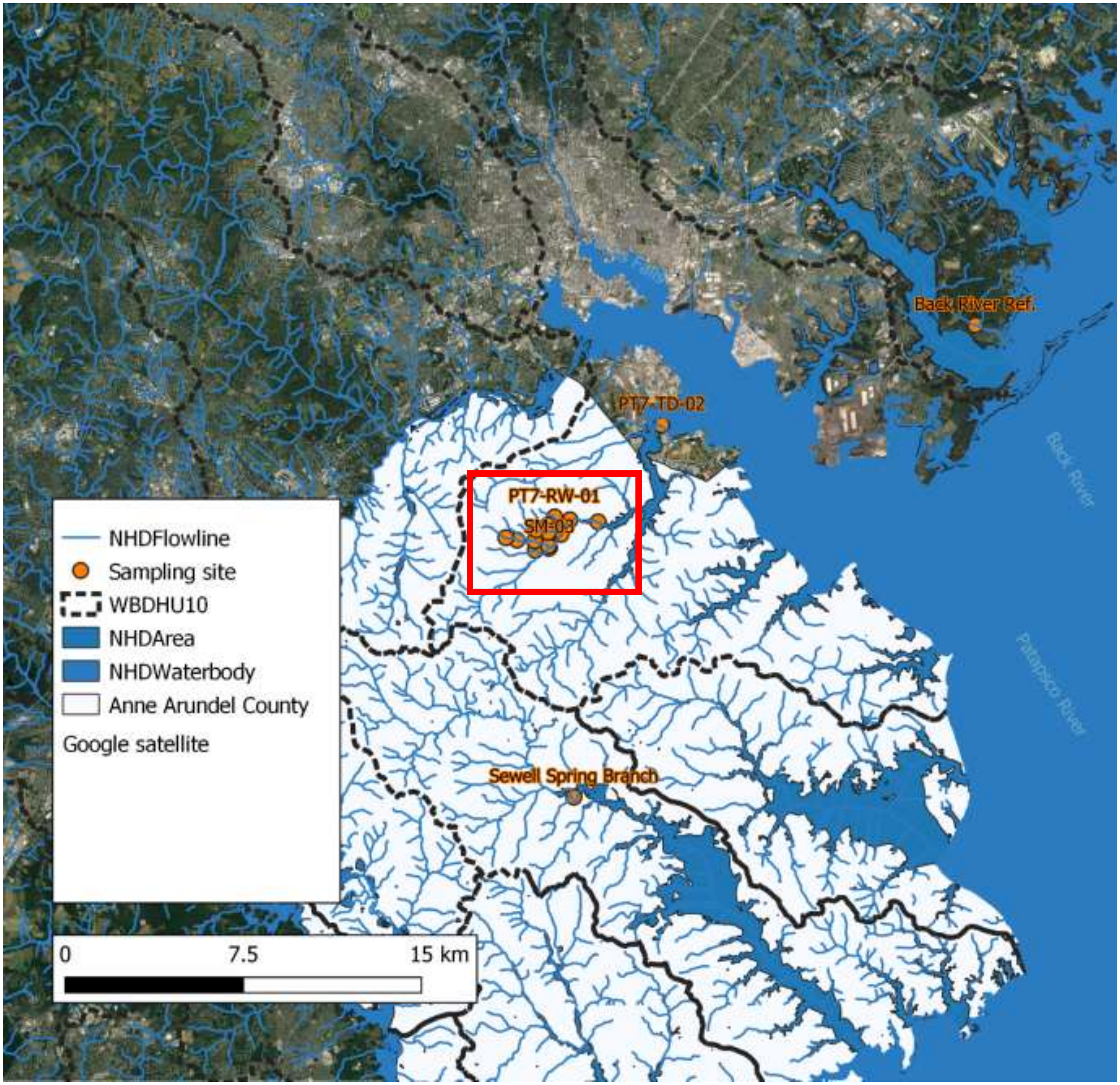

Figure 1a: Sampling locations. Map showing sampling watershed and reference sites in Back River and Severn Run. Red rectangle area shown in more detail in Figure 1b. NHD: National Hydrography Dataset, WBD: Watershed Boundary line.

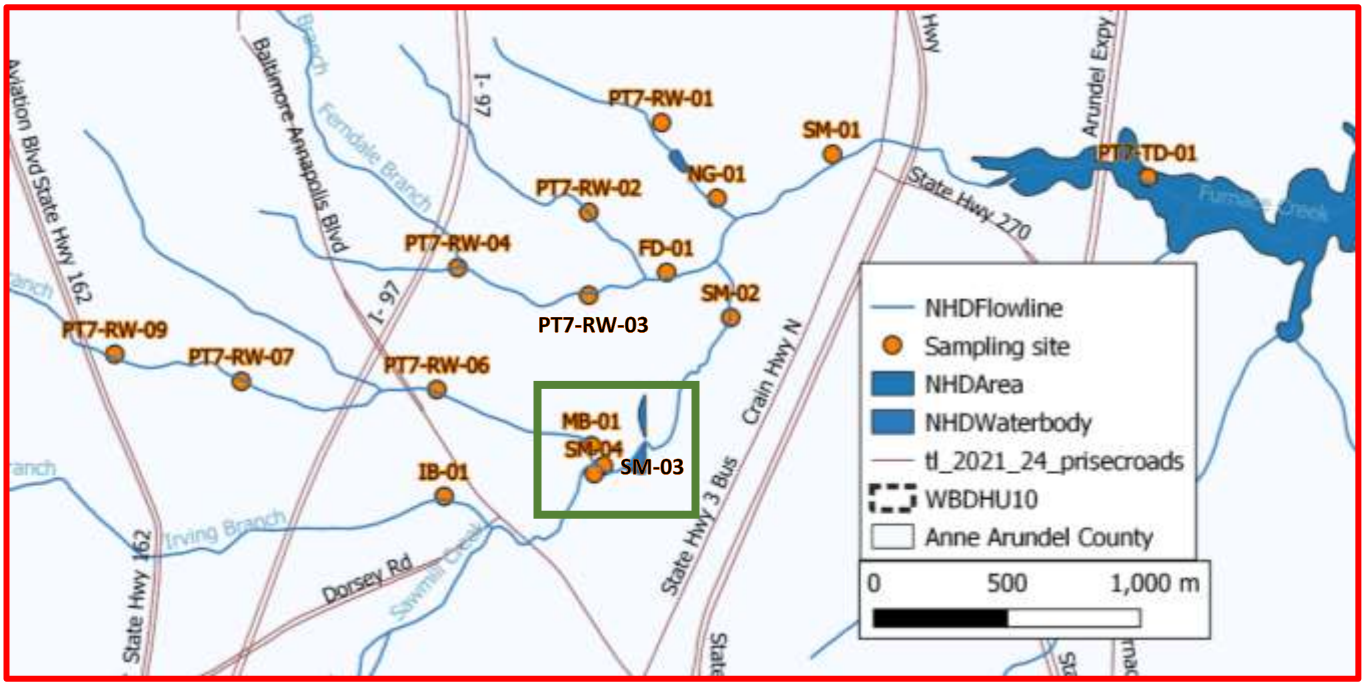

Figure 1b: Sampling locations (continued). Map showing main sampling locations. Detail of area marked in green rectangle shown in Figure 1c. NHD: National Hydrography Dataset, WBD: Watershed Boundary line.

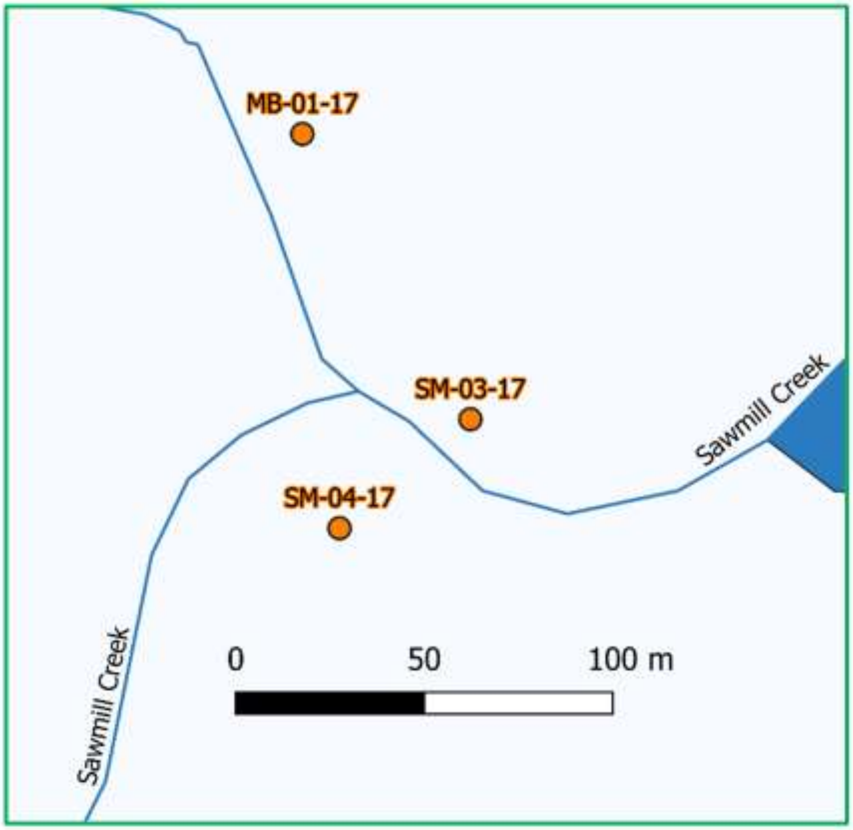

Figure 1b: Sampling locations (continued). Detail map showing sampling sites on Sawmill Creek and its tributaries. NHD: National Hydrography Dataset, WBD: Watershed Boundary line.

Figure 2: Passive sampler deployment. Polyethylene (PE) sheets were enclosed in stainless steel mesh and attached to a cinder block (picture) or to a green post.

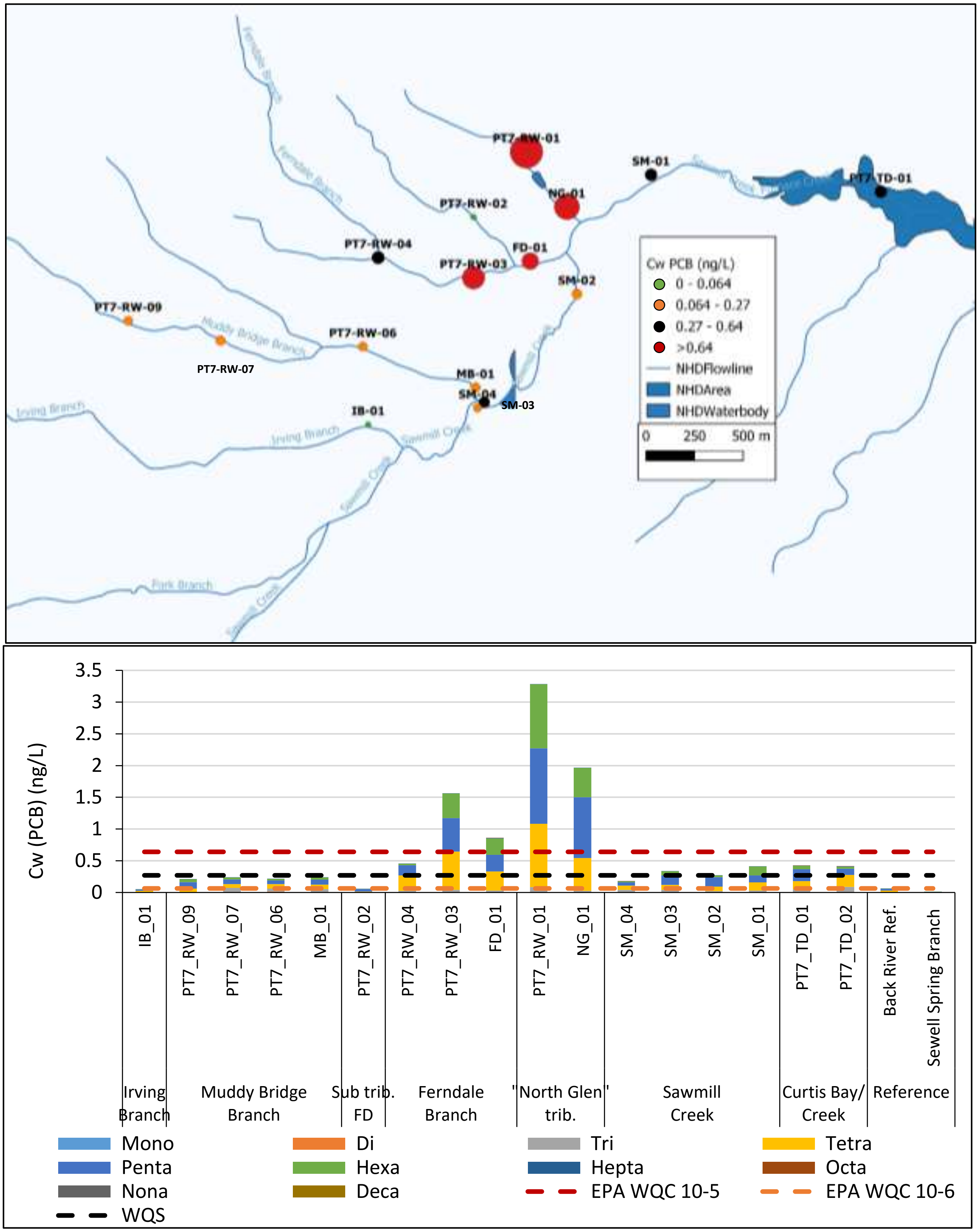

Figure 3: Freely dissolved PCB concentration in the water column of Sawmill Creek watershed

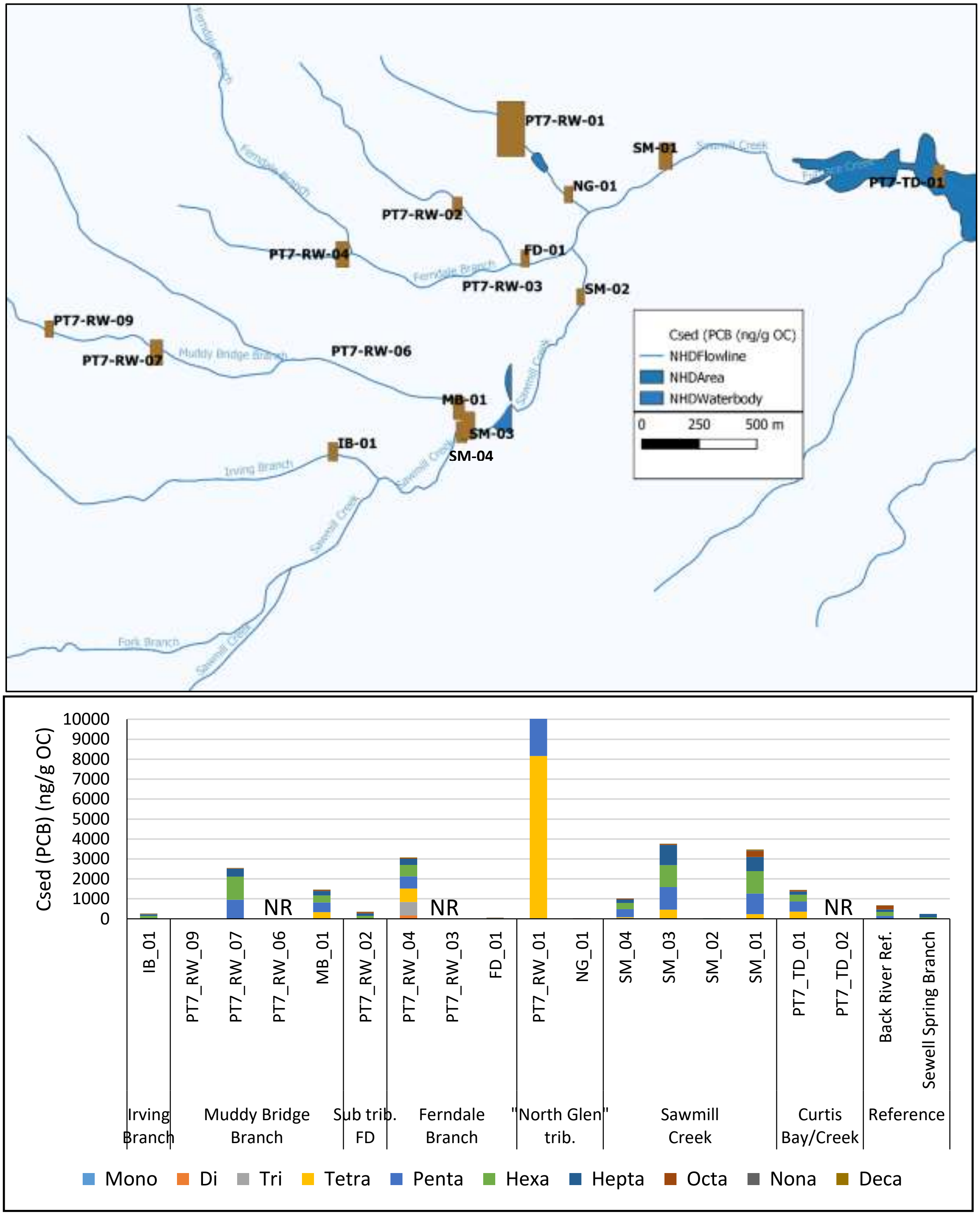

Figure 4: PCB concentrations in the organic carbon of sediments of Sawmill Creek watershed. NR: Not reported because of organic carbon measurement being below MDL.

Table 1: Sampling sites locations and number of analysis.

Station ID	Waterbody	Longitude	Latitude	WC	S	TOC
SM-01	Sawmill Creek	-76.6166	39.18274	1	1	1
SM-02	Sawmill Creek	-76.621	39.17725	1	1	1
SM-03	Sawmill Creek	-76.6265	39.17226	1	1	1
SM-04	Sawmill Creek	-76.6269	39.172	1	1	1
NG-01	Lowest tributary Sawmill Creek	-76.6216	39.18125	1	1	1
PT7-RW-01	Lowest tributary Sawmill Creek	-76.624	39.1838	1	1	1
IB-01	Irving Branch	-76.6334	39.17123	1	1	1
MB-01	Sawmill creek/Muddy Bridge Branch	-76.627	39.17293	1	1	1
PT7-RW-06	Muddy Bridge Branch	-76.6337	39.17482	1	1	1
PT7-RW-07	Muddy Bridge Branch	-76.6422	39.1751	1	1	1
PT7-RW-09	Muddy Bridge Branch	-76.6477	39.17601	1	1	1
PT7-RW-02	Tributary of Ferndale Branch	-76.6272	39.18078	1	1	1
FD-01	Ferndale Branch	-76.6238	39.17876	1	1	1
PT7-RW-03	Ferndale Branch	-76.6272	39.17799	1	1	1
PT7-RW-04	Ferndale Branch	-76.6328	39.17892	1	1	1
PT7-TD-01	Sawmill Creek/Furnace Creek	-76.6029	39.18196	1	1	1
PT7-TD-02	Curtis Bay	-76.572	39.21844	1	1	1
Sewell Spring Branch Ref.	Sewell Spring Branch	-76.6147	39.07821	1	1	1
Back River Ref.	Back River	-76.4195	39.25605	1	1	1
Number of analysis				19	19	19

WC: Water column, S: Sediment, TOC: Total organic carbon

Table 2: Sampling sites deployment periods

Station ID	Deployment device	Deployment Date	Retrieval Date	Deployment Time (days)
SM-01	Cinder block/rope	8/31/2020	12/4/2020	96
SM-02	Cinder block/rope	9/8/2020	12/4/2020	88
SM-03	Cinder block/rope	8/31/2020	12/4/2020	96
SM-04	Green post/string	8/31/2020	12/4/2020	96
NG-01	Green post/string	9/8/2020	12/4/2020	88
PT7-RW-01	Green post/string	9/8/2020	12/4/2020	88
IB-01		8/31/2020	12/4/2020	96
MB-01	Green post/string	8/31/2020	12/4/2020	88
PT7-RW-06	Green post/string	9/9/2020	12/4/2020	86
PT7-RW-07	Green post/string	9/8/2020	12/4/2020	88
PT7-RW-09	Cinder block/green cable	9/8/2020	12/4/2020	88
PT7-RW-02	Cinder block/green cable	9/8/2020	12/4/2020	88
FD-01		8/31/2020	12/4/2020	96
PT7-RW-03	Cinder block/green cable	9/8/2020	12/4/2020	88
PT7-RW-04	Green post/string	9/8/2020	12/4/2020	88
PT7-TD-01	Cinder block	9/9/2020	12/4/2020	87
PT7-TD-02	Cinder block	9/9/2020	12/4/2020	87
Sewell Spring Branch Ref.	Green post/string	9/9/2020	12/4/2020	87
Back River Ref.	Cinder block	9/14/2020	12/4/2020	82

Table 3: PCB homolog relative concentration in water column

	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
Irving Branch										
IB_01	0%	0%	12%	41%	35%	11%	1%	0%	0%	0%
Muddy Bridge Branch										
PT7_RW_09	0%	0%	0%	28%	49%	21%	1%	0%	0%	0%
PT7_RW_07	0%	0%	31%	24%	31%	13%	1%	0%	0%	0%
PT7_RW_06	0%	7%	21%	33%	27%	11%	1%	0%	0%	0%
MB_01	0%	0%	22%	30%	32%	15%	1%	0%	0%	0%
Sub trib. FD										
PT7_RW_02	0%	0%	1%	26%	67%	5%	0%	0%	0%	0%
Ferndale Branch										
PT7_RW_04	0%	0%	6%	53%	36%	5%	0%	0%	0%	0%
PT7_RW_03	0%	0%	3%	38%	34%	25%	0%	0%	0%	0%
FD_01	0%	0%	3%	35%	31%	30%	1%	0%	0%	0%
"North Glen" trib.										
PT7_RW_01	0%	0%	3%	30%	36%	31%	0%	0%	0%	0%
NG_01	0%	0%	1%	26%	49%	23%	0%	0%	0%	0%
Sawmill Creek										
SM_04	0%	0%	24%	36%	29%	9%	2%	0%	0%	0%
SM_03	0%	0%	12%	23%	45%	19%	1%	0%	0%	0%
SM_02	0%	0%	8%	26%	56%	9%	1%	0%	0%	0%
SM_01	0%	0%	7%	32%	26%	35%	0%	0%	0%	0%
Curtis Bay/Creek										
PT7_TD_01	0%	0%	12%	31%	44%	13%	1%	0%	0%	0%
PT7_TD_02	0%	1%	21%	45%	24%	7%	2%	0%	0%	0%
Reference										
Back Rvr. Ref.	0%	0%	3%	44%	41%	11%	0%	0%	0%	0%
Sewell Spring Branch Ref.	0%	0%	23%	18%	44%	15%	0%	0%	0%	0%

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

Stations ID	Average sum 119 PCB (ng/g)		Average foc	
Irving Branch				
IB_01	2.1	± 0.034	0.0078	
Muddy Bridge Branch				
PT7_RW_09	0.062		0.0093	± 5.7E-05
PT7_RW_07	3.5		0.0014	
PT7_RW_06	0.77		0.00047	
MB_01	17		0.012	
Sub trib. FD				
PT7_RW_02	3.8		0.011	
Ferndale Branch				
PT7_RW_04	48		0.016	
PT7_RW_03	0.88		0.00032	
FD_01	1.3		0.025	
"North Glen" trib.				
PT7_RW_01	51		0.0015	
NG_01	0.30	± 0.12	0.020	
Sawmill Creek				
SM_04	7.3		0.0072	
SM_03	102		0.027	
SM_02	0.42	± 0.22	0.063	
SM_01	48		0.014	
Curtis Bay/Creek				
PT7_TD_01	96		0.067	
PT7_TD_02	0.84		0.00088	
Reference				
Back River Ref.	3.9		0.0059	± 0.0021
Sewell Spring Branch Ref.	2.6		0.010	

Shaded in red, value above TMDL endpoint for PCB concentration in sediments
Shaded in grey, value at or below Method Detection Limit (MDL).

Table 5: Sediment porewater estimates and PCB flux from sediment porewater to water column assessment

Stations ID	Cw (ng/L)	Cpw est. (ng/L)	Concentration gradient (Cpw-Cw)	Concentration ratio (Cpw/Cw)
Irving Branch				
IB_01	0.05	0.04	-0.02	0.70
Muddy Bridge Branch				
PT7_RW_09	0.21	0.00	-0.21	0.02
PT7_RW_07	0.24	0.54	0.30	2.26
PT7_RW_06	0.22	0.24		
MB_01	0.24	0.55	0.31	2.28
Sub trib. FD				
PT7_RW_02	0.06	0.03	-0.02	0.56
Ferndale Branch				
PT7_RW_04	0.45	4.11	3.66	9.05
PT7_RW_03	1.56	1.27		
FD_01	0.86	0.01	-0.85	0.02
North Glen trib.				
PT7_RW_01	3.28	20.05	16.77	6.11
NG_01	1.96	0.01	-1.95	0.01
Sawmill Creek				
SM_04	0.18	0.35	0.18	1.99
SM_03	0.34	1.10	0.76	3.26
SM_02	0.27	0.00	-0.26	0.02
SM_01	0.41	0.79	0.37	1.90
Curtis Bay/Creek				
PT7_TD_01	0.43	0.64	0.21	1.50
PT7_TD_02	0.42	0.23		

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6 Appendices

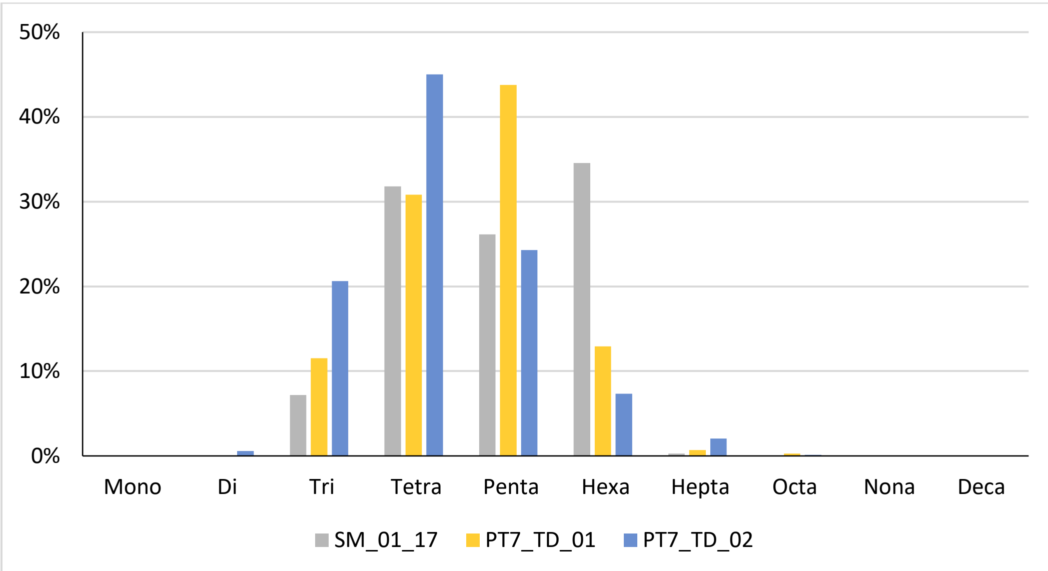

Figure S1: PCB homolog relative concentration in water column of Sawmill Creek (SM-01), Furnace Creek (PT7-TD-01) and Curtis Creek (PT7-TD-02)

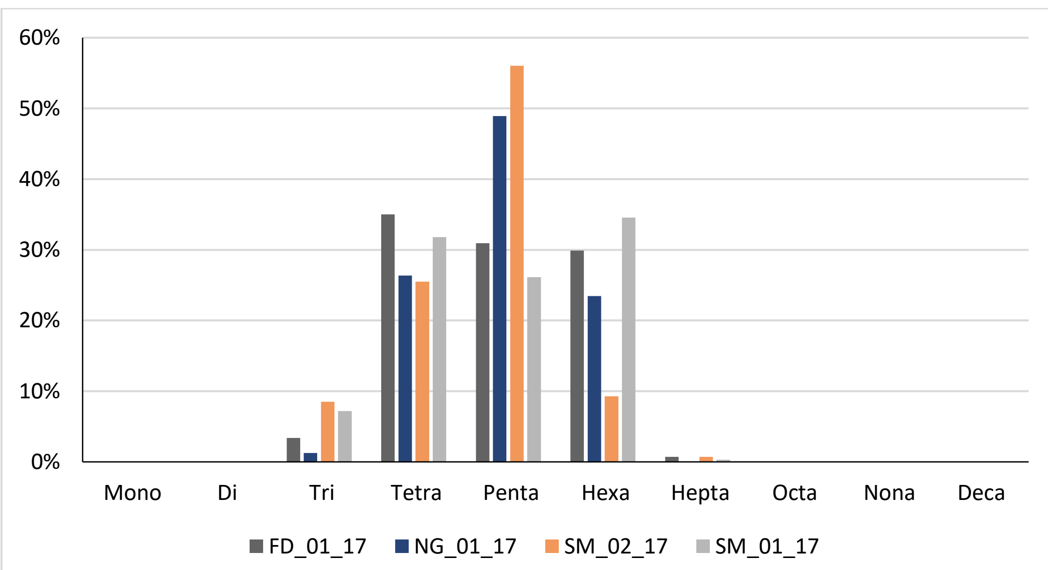

Figure S2: comparison of PCB homolog distribution between Ferndale Branch (FD-01), North Glen tributary (NG-01) with that of Sawmill Creek before (SM-02) and after (SM-01) their confluence.