Proposal for
PCB source tracking in Anne Arundel County-Phase 3 (2024)

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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.

The Anne Arundel County (AACo) is assessing local water quality impairments from PCBs and determining 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 that were responsible for an increase of freely dissolved PCB concentrations at their confluence with Sawmill Creek (Lombard et al., 2022). 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 PCB source from bed sediments to the overlying water. A subsequent Phase 2 study also supported by AACo performed a more detailed assessment of the North Glen tributary and Ferndale Branch. (Lombard et al., 2024). An overall recovery was observed in both streams in 2022 compared to 2020. In Ferndale Branch, a 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, was observed. 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. A decrease was also observed in the sediments, and water column of North Glen tributary, but PCB levels in the water column were still above EPA WQC 1E-5.

Key recommendations from the Phase 2 study were continued monitoring at key points in the Ferndale Branch and North Glen Tributaries to document continued decrease in concentrations over time, stormwater sampling to evaluate impacts of short-term events, and extension of the approach to selected additional watersheds.

In consultation with AACo officials, the following scope was developed to perform additional monitoring in 2024/25.

Sampling Plan

Sampling locations are shown in Table 1 and Figures 1-4. These proposed locations can be adjusted based on any additional review and recommendations from AACo.

Sawmill Creek phase 3

Ferndale Branch

- Monitoring at PT7-RW-03 and FD-01 in Fall 2024 to confirm the decrease in water column concentration

North Glen Tributary

- Monitoring at PT7-RW-01 and SM-01 in Fall 2024 to confirm the decrease in water column concentration. The location SM-01 is better suited to check for impacts downstream.
- Stormwater passive sampling for two storm events to identify PCB sources that would explain elevated PCB levels in the water column (above EPA WQC 1E-5)

Cabin Branch phase 1

Restoration project in 2026-2027. We will monitor before and after the restoration effort. Monitoring stations proposed by AA county. Only water column measurement is proposed during Phase 1 to identify sections of the waterbody with PCB sources. Stormwater suspended sediments will be collected at the most downstream location during a storm event to assess storm driven inputs in the system.

Marley Creek phase 1

Restoration project in 2026-2027. We will monitor before and after the restoration effort. Monitoring stations proposed by AA county. (Ongoing bacteria monitoring). The number of sites and their locations will be refined after reconnaissance with AACo personnel. Only water column measurement is proposed during Phase 1 to identify sections of the waterbody with PCB sources. Stormwater suspended sediments will be collected at the most downstream location during a storm event to assess storm driven inputs in the system.

Table 1. Sampling locations and number of samples

Site ID	Xlong	Ylat	Coordinate Refence System	Watershed	Phase	WC	SS	Sh.WC	All
PT7-RW-01	-76.62484	39.18386	EPSG:4326-WG84	Sawmill Creek	3	1		2	3
SM-01	-76.616575	39.18274	EPSG:4326-WG84	Sawmill Creek	3	1			1
PT7-RW-03	-76.62467	39.1786	EPSG:4326-WG84	Sawmill Creek	3	1			1
FD-01	-76.623853	39.1788	EPSG:4326-WG84	Sawmill Creek	3	1			1
CB1	1425550.11	562297.7	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Cabin Branch	1	1	2		3
CB2	1424167.52	561560.1	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Cabin Branch	1	1			1
CB3	1419427.18	559637.3	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Cabin Branch	1	1			1
CB4	1416996.56	558339.4	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Cabin Branch	1	1			1
CB5	1413893.5	557808.1	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Cabin Branch	1	1			1
CB6	1410039.8	556760.5	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Cabin Branch	1	1			1
MC1	1425265.38	540881.8	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Marley Creek	1	1	2		3
MC2	1425363.61	540023.9	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Marley Creek	1	1			1
MC3	1424669.75	539924.9	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Marley Creek	1	1			1
MC4	1423896	538152.5	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Marley Creek	1	1			1
MC5	1423526.48	537773.9	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Marley Creek	1	1			1
MC6	1422898.77	536336.5	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Marley Creek	1	1			1
MC7	1420830.07	535820.4	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Marley Creek	1	1			1
MC8	1419554.48	534648.3	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Marley Creek	1	1			1
MC9	1419053.65	534474	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Marley Creek	1	1			1
MC10	1418861.79	534257.6	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Marley Creek	1	1			1
MC11	1417403.42	533490.6	EPSG:6488-NAD83(2011)/Maryland (ftUS)	Marley Creek	1	1			1
Total						21	4	2	27

Legend: WC: water column, SS: Suspended Sediments during storm event, Sh.WC: short term water column

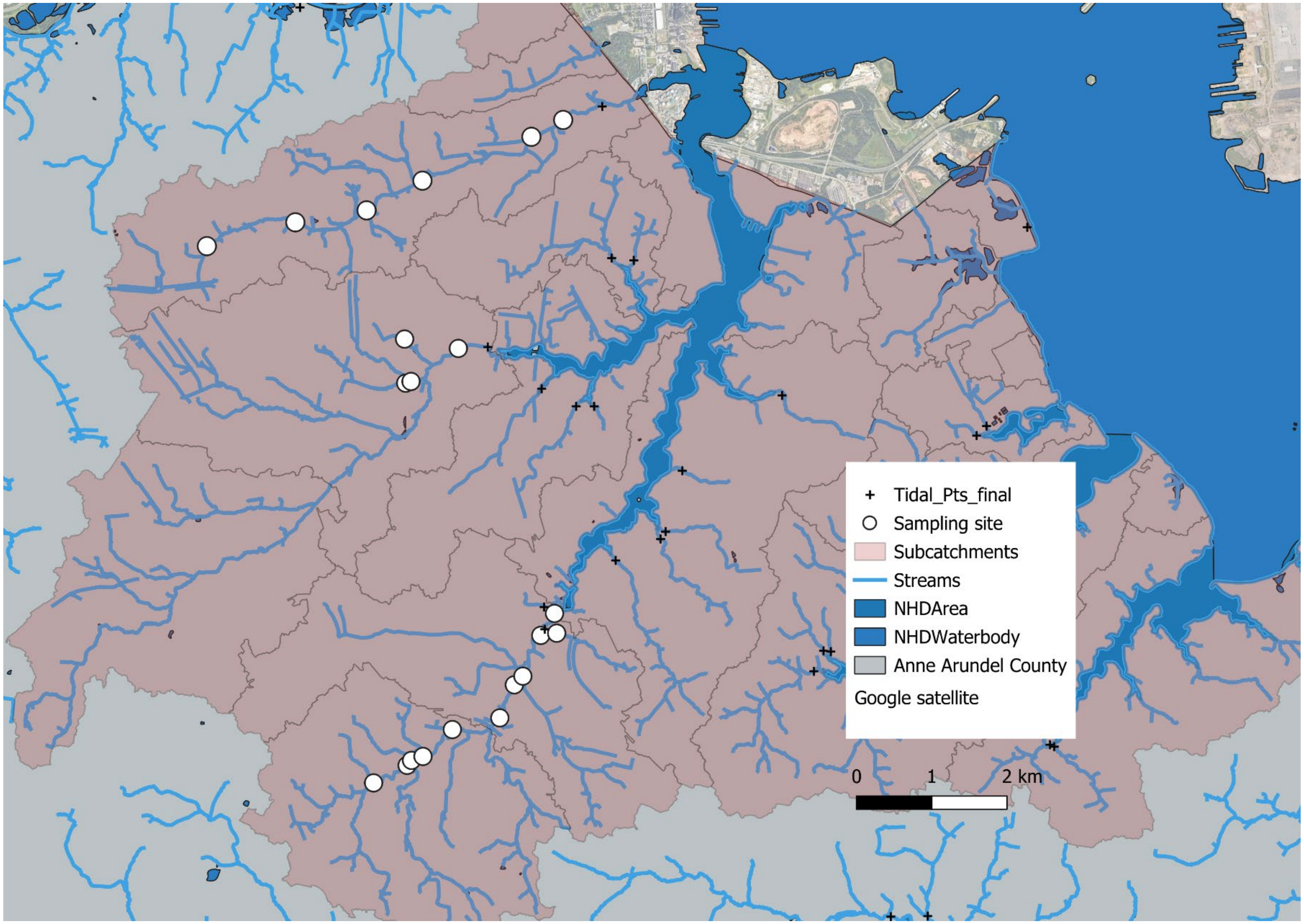

Figure 1: Overview of PCB sampling in 2024

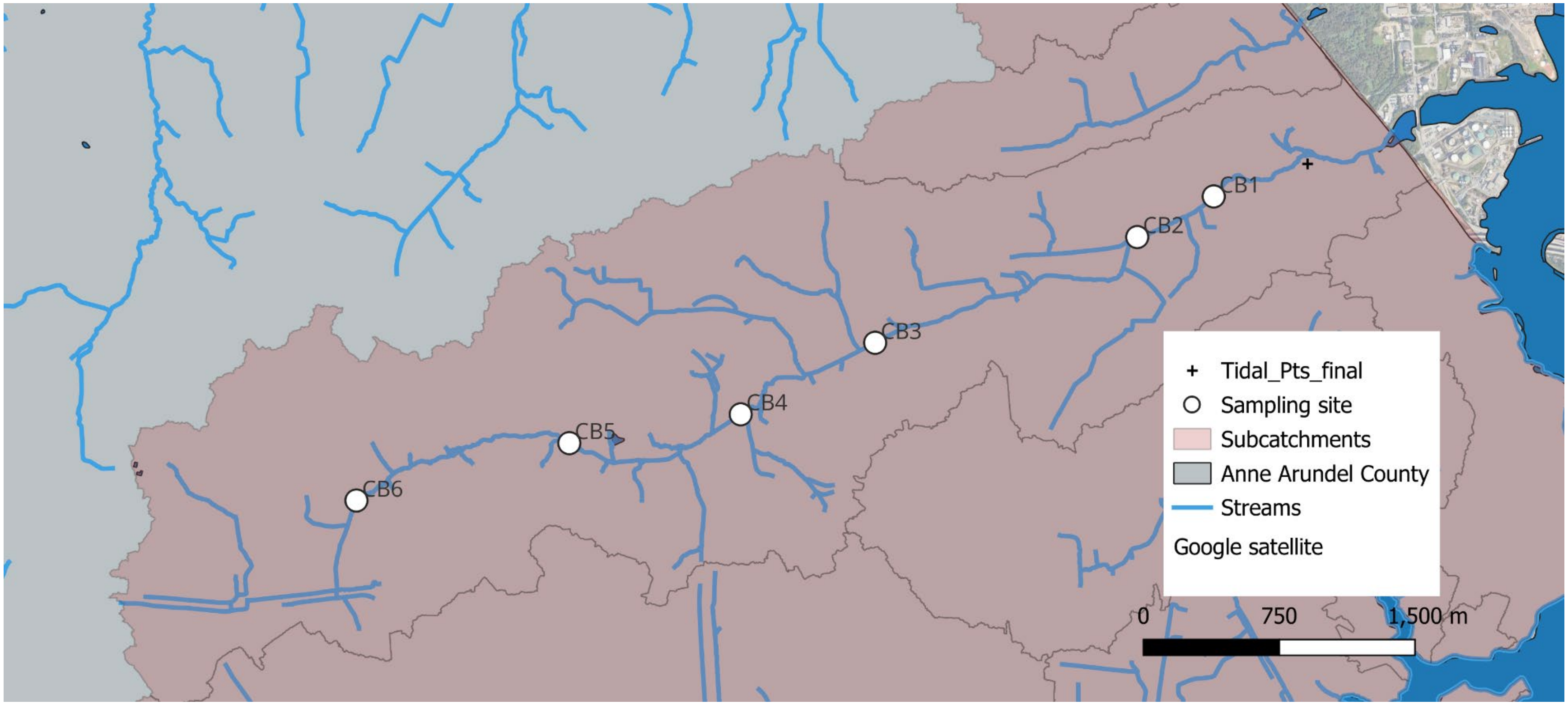

Figure 2: PCB sampling in Cabin Branch, Phase 1

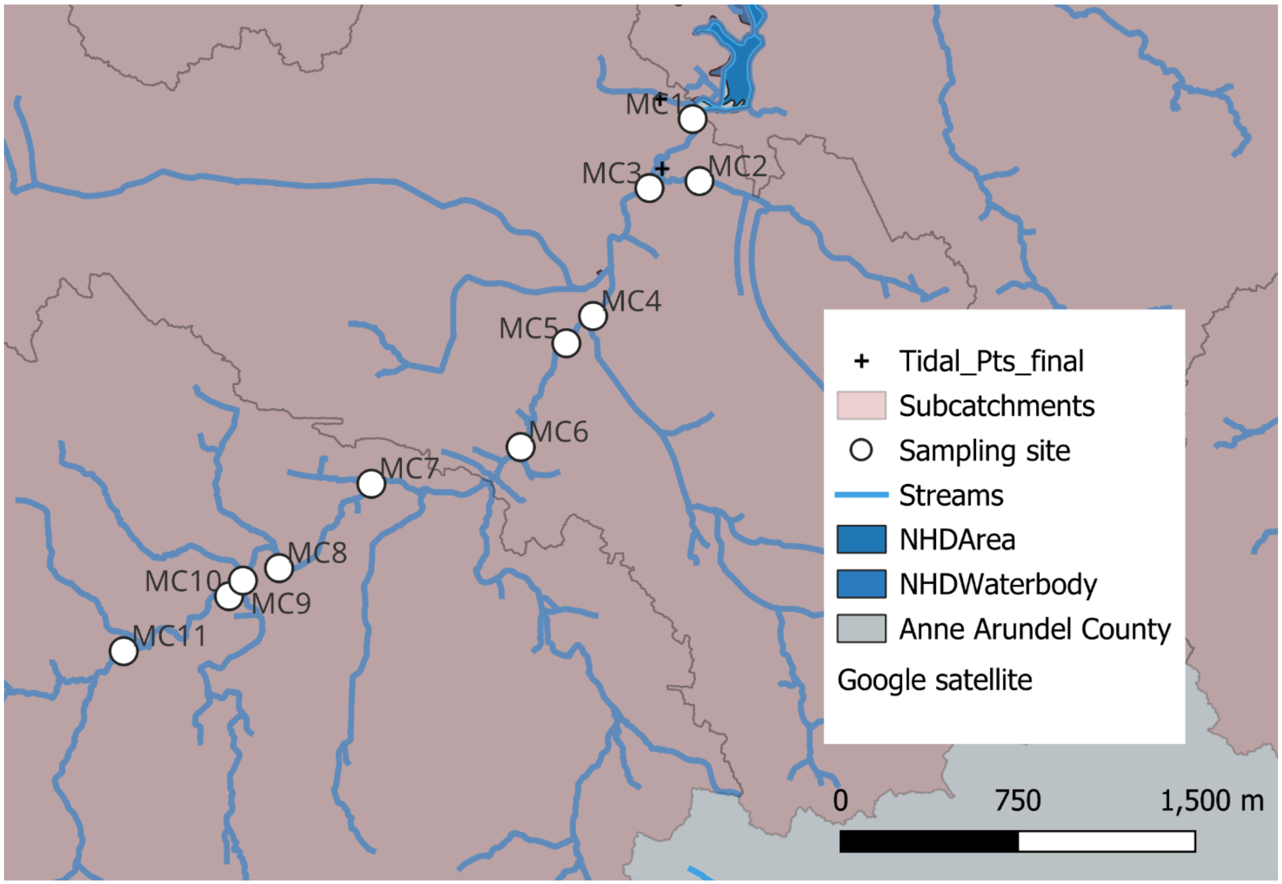

Figure 3: PCB sampling in Marley Creek, Phase 1

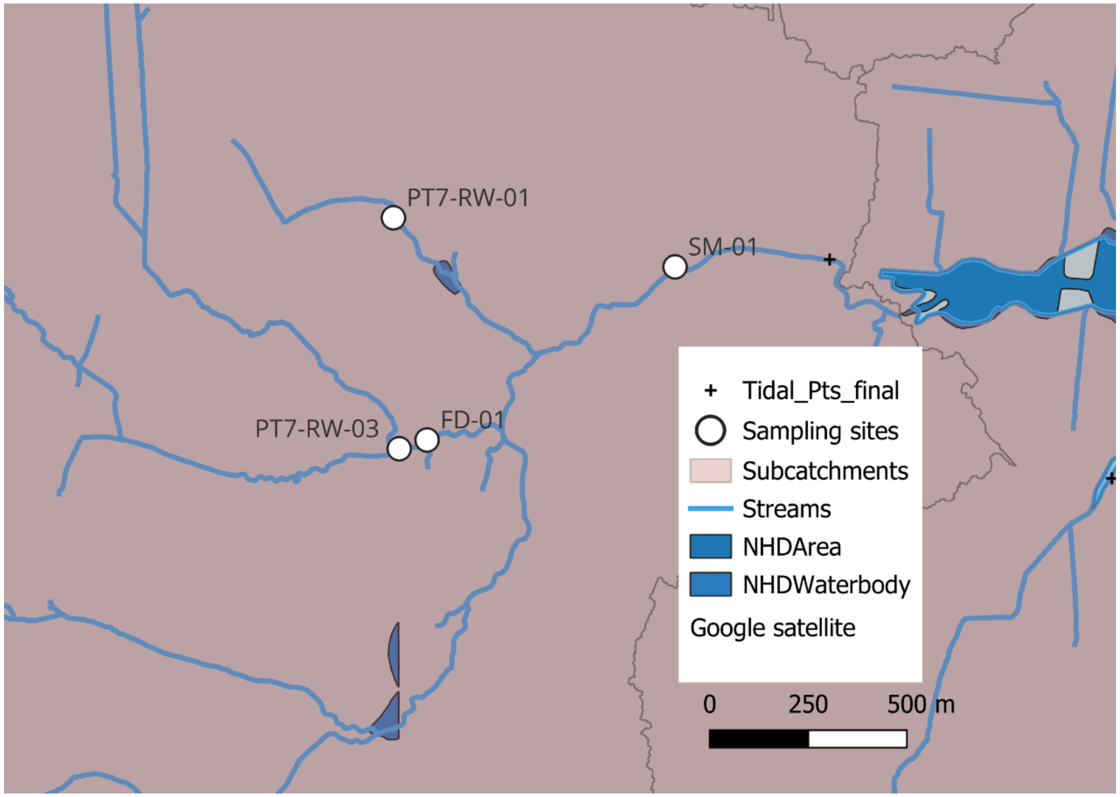

Figure 4: PCB sampling in Sawmill Creek, Phase 3

Material and Methods

Water column and porewater measurements. The freely dissolved concentrations of PCBs in surface water and sediment porewater will be measured using an integrative passive sampling approach. This sampling approach allows measurement of average concentrations of the freely dissolved hydrophobic contaminants such as PCB in surface water that serve as the driving force for uptake in fish. Besides, passive sampling yields a time-average concentration that is representative of pollutant concentration during base flow and episodic rainfall events during the deployment time of the passive samplers. In this proposed work, a recently published guidance document on passive sampling (U.S. EPA/SERDP/ESTCP. 2017) will be followed to measure freely dissolved concentrations of PCBs in surface water. UMBC partnered with several collaborators to develop this guidance on passive sampling. The sampling method would entail design of the size of samplers based on project data quality objectives, preparation of polyethylene passive sampling strips with performance reference compounds, placement at the selected locations after encasing in deployment devices, retrieval after a 2-3 month period of deployment, extraction, analysis, and interpretation of the results.

Passive samplers will be prepared using 1 g of 51 mm thick polyethylene (LDPE) sheets pre-cleaned by solvent extraction followed by the impregnation with five PCB performance reference compounds in the laboratory. The deployment method shown in Figure 2 was developed especially targeting flashy urban streams where the depth of water is often very shallow during baseflow and flow velocities are extremely high during stormflow that can result in loss of samplers. Similar approach will be used and adapted to the stream configuration. The deployment of only one sampler was requested per location for the present project. After retrieval of the passive samplers from the field, they will be cleaned on site using a clean tissue and DI water to remove surface contamination and placed into pre-cleaned 40 mL glass vials. All passive samplers will be placed into a cooler marked for return to UMBC. All samples will be stored at 4 ºC in closed glass vials until extraction. Extraction of all stored samples will be completed within 1 month of generation of the sample. Cleanup and analysis of passive samplers will follow methods described in the analytical section below.

For each deployment, a set of three unexposed passive samplers will be extracted and measured to determine the initial concentration of the performance reference compounds and any background contamination. The loss of performance reference compounds during the deployment period will be used to correct for non-equilibrium as described in Sanders et al. (2019).

Details of sampler preparation, deployment, and retrieval are provided in Appendix A.

Short-term passive sampling. Freely dissolved PCB concentrations will be measured over a 24h period during stormflow versus baseflow conditions in order to evaluate stormwater runoffs contribution to the overall freely dissolved concentrations measured over a 3 month period. Samplers preparation, impregnation and deployment is similar to regular passive sampling approach as described above, except LDPE of 25um will be used, and will be impregnated with labelled PCB performance reference compounds. To enhance sensitivity of the lower chlorinated compounds, PCB analysis will be performed on a GC-MS.

Sediment collection and preparation. Suspended sediments delivered during storms will be collected at the most downstream locations of the two new watersheds, Cabin Branch and Marley Creek, using sediment traps as shown in **Figure 5**. The sediment trap device will be left for the duration of passive sampler deployment to collect suspended sediments from multiple storm events. Samples will be 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.

TOC analysis. PCBs strongly associate with natural organic carbon in sediments, and distribution in sediment often is driven by the fraction of organic carbon present. The measurement of total organic carbon allows normalization of PCB concentration in sediment t organic carbon content and allows better comparison of sediment PCB data across a range of sites. Total organic carbon in sediment samples will be measured with a Total Organic Carbon Analyzer (TOC-V CPH model) using the Non-Purgeable Organic Carbon (NPOC) mode and detection performed with a NDIR detector. Methods for these analyses will follow prior source tracking work performed in the Anacostia River tributaries (Ghosh et al. 2020). Details are provided in Appendix D

PCB extraction cleanup and analysis. Passive samplers will be extracted for PCBs using 30 mL additions of hexane then placed on an orbital shaker overnight. The solvent will be collected, and new solvent will be added after each extraction. This process will be repeated three times. The cleanup method used in this project will follow the methods used in Ghosh et al. (2019) that is based on EPA SW-846 methods 3630C (Silica gel cleanup), and 3660B (sulfur removal with copper). For the sediment extraction, UMBC will use the methods outlined in EPA publication SW-846 (Test Methods for Evaluating Solid Waste, Physical/Chemical Methods) methods 3630C (Silica gel cleanup), 3665A (sulfuric acid cleanup) and 3660B (Sulfur removal with copper).

Most PCB analysis will be performed 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 µm film thickness). PCB standards for calibration are purchased as hexane solutions from Ultra Scientific (North Kingstown, RI, USA). Internal standards, 2,4,6-trichlorobiphenyl (PCB#30) and 2,2',3,4,4',5,6,6'- octachlorobiphenyl (PCB#204) will be added to all samples. A total of 129 most commonly found PCB congeners are measured using this method. Note that the remaining congeners not included in the analysis are either not present in typical commercial PCB mixtures or are present at very low concentrations. In some cases, peaks coelute which are identified and reported as the sum of congeners. Detection limits for individual PCB congener in tissue and sediment samples range from 0.001 – 0.1 ng/g with lower detection limits for the more chlorinated congeners. Detection limits for water concentration using passive sampling range from 1-10 pg/L (or 0.001-0.01 ppt) with lower detection limits for the higher chlorinated congeners. Further details and QAQC for the PCB analysis are provided in Appendix B and C.

Short time passive sampler PCB analysis will be 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 detector and a high efficiency source. PCB standards for calibration are purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA). Three C13 labeled PCB congeners, PCB 9*, 118*, and 188* will be used as internal standards and added to all samples before analysis. Peak identification and integration are performed with Agilent MS Quantitative software in the Selected Ion Monitoring (SIM) mode. A total of 189 most commonly found PCB congeners and congener groups will be measured using this method. The method detection limits for individual PCB congeners in samples range from 0.03–0.13 µg/L, and a nine-point calibration leads to a linear calibration with R2>0.998 for all compounds. The calibration range is 0.2 to 50 µg/L for lower chlorinated congeners and 0.6 to 150 µg/L for the higher chlorinated ones.

Water concentration calculations. Concentrations measured in passive samplers will be normalized by the mass of PE deployed and corrected for nonequilibrium when necessary as described in Sanders et al. (2019). The freely-dissolved concentrations in the water column (Cw), will be estimated using the approach as described in the Appendix B.

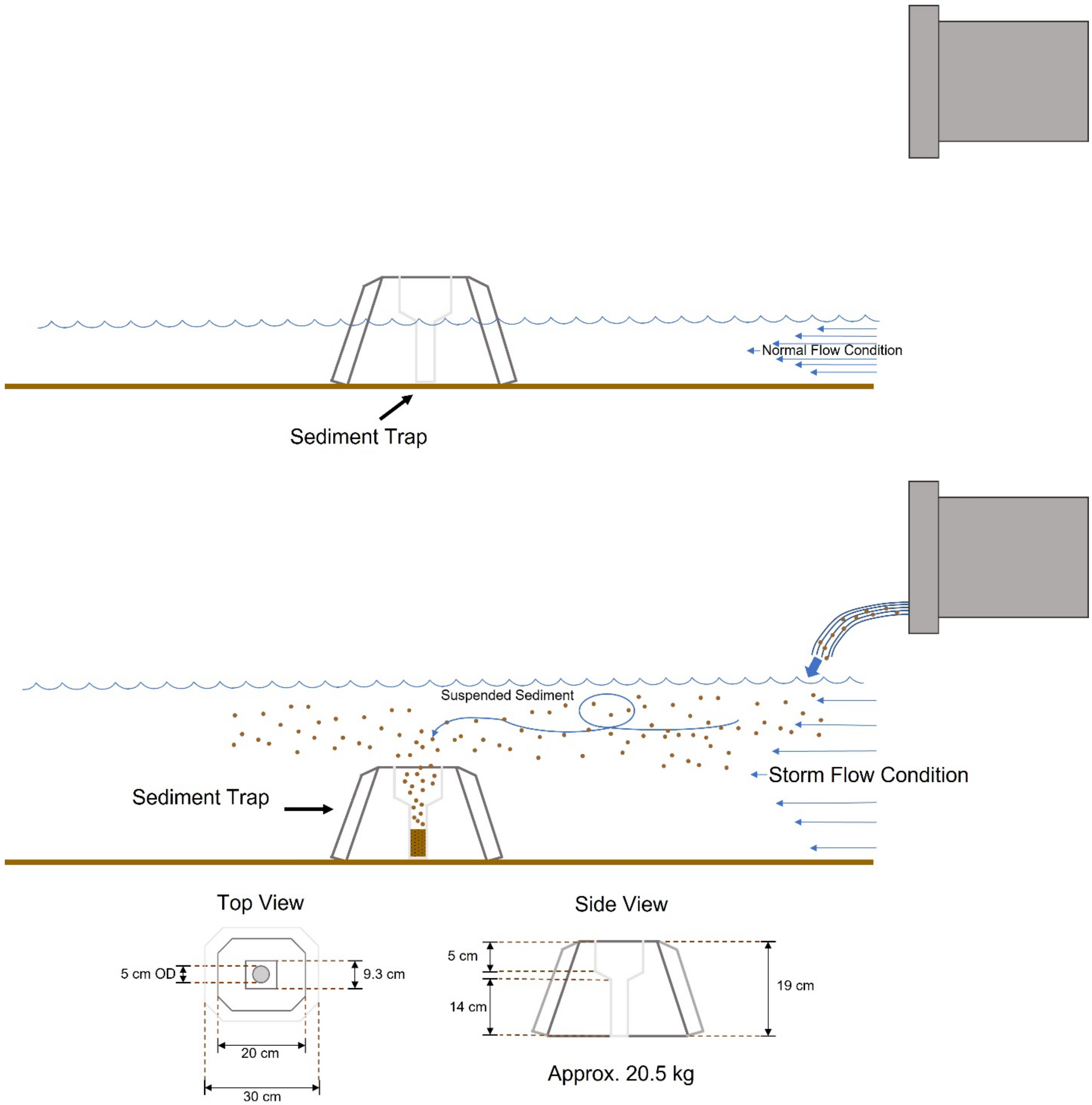

Figure 5: Sediment trap design. Top: normal flow condition, bottom: stormflow conditions.

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BUDGET

The tasks outlined above will be carried out by a team of personnel from UMBC including Dr. Upal Ghosh, Dr. Nathalie Lombard, and an undergraduate student. The team will be supervised by PI, Dr. Upal Ghosh. The total proposed budget is $65,352. A breakdown of the costs are provided below for the two phases of the project. The project duration is anticipated to be Oct 15, 2024 – Oct 14, 2025.

Sawmill Creek Phase 3

Salary + fringe	$8,256
Supplies	$880
Travel	$220
Student tuition and insurance	$0
Total Direct	$9,356
Total Indirect (UMBC indirect rate of 55%)	$5,146
TOTAL	$14,502

Cabin Branch and Marley Creek Phase 1

Salary + fringe	$28,907
Supplies	$3,120
Travel	$780
Student tuition and insurance	$0
Total Direct	$32,807
Total Indirect (UMBC indirect rate of 55%)	$18,043
TOTAL	$50,850