Proposal for
PCB source tracking in Anne Arundel County-Phase 2

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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.

The Anne Arundel County (AACo) is interested in 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 (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.

For the phase 2 of the study, further track down of PCB sources is proposed in both tributaries of concern, i.e. North Glen tributary and Ferndale Branch. The sampling strategy will include:

1. Repeat the deployment of passive samplers in the water column at and around the section of concerns to further track down freely dissolved PCB sources. This will help in identifying sections where the main PCB sources are, and rule out upstream sections of the tributary as appropriate.
2. Joint-deployment of passive sampler in the sediment porewater to verify if bed sediment are acting as a PCB source to the overlying water column through PCB diffusive flux. Porewater analysis will only be performed at sites where fine-grained sediments with organic carbon are present and sediments are at least 15 cm (6 inch) deep. If in situ porewater analysis cannot be performed, grab sediment samples will be collected instead,

and porewater concentration will be inferred from PCB concentration measured in the sediments, organic carbon content measured in the sediments, and available partitioning coefficient of PCB between water and organic carbon.

3. Measure PCB concentrations in suspended sediments collected during storm events at outfalls located and/or connected to suspected land sources. PCB concentrations in the sediments transported during storm events will be compared to those in riverbed. Similar to higher PCB concentration in suspended sediments compared to that in riverbed sediment would indicate ongoing PCB sources from stormwater runoffs to the downstream waterbody. Freely dissolved PCB concentrations during storm events will also be monitored at selected locations using a novel passive sampling approach. Information collected will be used to further track potential on going PCB sources from land.

2. Sampling Plan

Sampling locations are shown in Table 1 and Figures 1-3

North Glen tributary. PCB sources were tracked back to sediments located at the most upstream station PT7-RW-01. The tributary is connected to an upstream PCB era building through storm pipes.

Sediments located downstream, at station NG-01, showed very low PCB concentrations, suggesting depositional between the two stations. Possible depositional area include the NHD waterbody located about 130 m downstream, or at the lowest elevation point located about 250 m downstream.

We propose to:

1. Repeat the sampling the water column passive sampling (WC) at PT7-RW-01 to confirm the findings of the phase 1, and check for any change (increase or decrease) of PCB levels.
2. Repeat bed sediment sampling and perform porewater passive sampling (PW) at PT7-RW-01 to compare measured concentrations to the predicted concentrations from sediment and confirm PCB diffusive fluxes from bed sediment to water column.
3. Collect and measure PCB concentration in suspended sediments at the outfalls NG-OF1 (most downstream location of the storm pipe) and NG-OF2 (connected to PCB era building). The PCB concentrations in suspended sediments will be compared to that in bed sediment collected at PT7-RW-01 to verify presence of ongoing PCB sources from land sources.
4. Identify possible depositional area between PT7-RW-01 and NG-01 that could act as significant PCB source to overlying water by deploying PW and /or collecting bed sediments at NG-02 and NG-03.

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, but PCB flux at PT7-RW-03 were inconclusive due to low fraction of organic carbon in sediments collected at this site. A PCB era building and a NRC Potential Spill site were identified connected through storm pipes to the station PT7-RW-04. An industrial site was identified near PT7-RW-03. Due to stream restoration projects starting in June/July 2022 (Figure 4), the sampling plan was modified to avoid sampling in sections of the Ferndale Branch and sub-tributary being restored.

We propose to:

1. Repeat WC at PT7-RW-04 to confirm the findings of the phase 1, and check for any change (increase or decrease) of PCB levels. As PT7-RW-03 is within section of the stream being restored, WC will be performed about 180 meters downstream of PT7-RW-03, at PT7-RW-03bis. WC will also be repeated at the downstream site FD-01-17 to truly compare freely dissolved PCB concentration between phase 1 and phase 2 and verify how the ongoing restoration project is impacting PCB levels in water column.
2. Perform PW sampling at PT7-RW-04 and PT7-RW-03bis to confirm PCB diffusive fluxes from bed sediment to water column at PT7-RW-04 and verify PCB diffusive flux status at PT7-RW-03bis.
3. Add a WC and PW sampling location at OD-1 to capture inputs from the "Olen drive" (OD) tributary into Ferndale Branch, and determine if the OD tributary is a potential ongoing PCB source that could explain the elevated PCB concentration observed in the water column of PT7-RW-03 during phase 1 of the study. Bed sediment sampling is also proposed in the OD tributary (OD-02) before stream restoration project begins, in order to determine if the OD sediment could have acted as a PCB source to the water column.
4. Collect suspended sediments at/ or downstream stormwater outfalls connected to suspected PCB land sources. This include the following stormwater outfalls: FD-OF0 (NRC Potential Spill Site), FD-OF1 (PCB era building), FD-OF2 and OF3 (DC power batteries, Arundel Metal Products Corporation, NAPA Auto parts). The last 3 outfalls are within section of the stream being restored, suspended sediments will therefore be collected in stream at OD-1 (downstream of FD-OF1) and PT7-RW-03bis (downstream of FD-OF2 and OF3) to capture soil/sediments potential land sources during storm events. For FD-OF0, suspended sediments will directly be collected outside of the outfall. PCB concentration measured in suspended sediments will be compared to those measured in riverbed at PT7-RW-04, PT7-RW-03bis and other downstream locations measured during phase 1 of the study to identify sections of Ferndale Branch with ongoing PCB sediments sources during storm events.
5. Implement short time (24h) passive sampling during baseline and storm events at OD-1 and PT7-RW-03bis to confirm (or not) that stormwater runoffs contribute to the elevated freely dissolved PCB concentrations measured at PT7-RW-03 compared to PT7-RW-04.

Table 1: Proposed sampling locations

Waterbody	Site ID	x	y	WC	PW	Sh. WC	SS	Sed	TOC	Comments
North Glen Tributary	NG-OF1	-76.62512149	39.18422365				1		1	Outfall connected to PCB era building
	NG-OF2	-76.62871623	39.18457371				1		1	Outfall downstream
	PT7-RW-01	-76.6248363	39.1837608	1	1			1	1	High PCB concentration in water column and sediment
	NG-02	-76.62352	39.182759	1	1			1	1	Depositional area?
	NG-03	-76.62327311	39.1825872	1	1			1	1	Depositional area?
Ferndale Branch	FD-OF0	-76.638396	39.182932				1		1	Outfall connected to PCB era building
	PT7-RW-04	-76.632838	39.178922	1	1			1	1	Elevated PCB concentration sediment (above TMDL endpoint)
Olen drive tributary	OD-02	-76.633476	39.17885					1	1	Olen drive tributary section with high organic matter based on visual inspection
Ferndale Branch/ Olen drive	OD-01	-76.6321085	39.1786677	1	1	2	1	1	2	Confluence "Olen drive" tributary
Ferndale Branch	PT7-RW-03 bis	-76.6252889	39.1784334	1	1	2	1	1	2	Elevated PCB concentration in water column, downstream from outfall connected to industrial sites
	FD-01-17	-76.623773	39.17876	1						Ferndale Branch PCB water concentration reference phase 1 vs phase 2
Sum	40			6	6	4	5	7	12	

PW: Porewater, SS: Suspended Sediments, Sh. WC: Short time water column passive sampling, WC: Water column

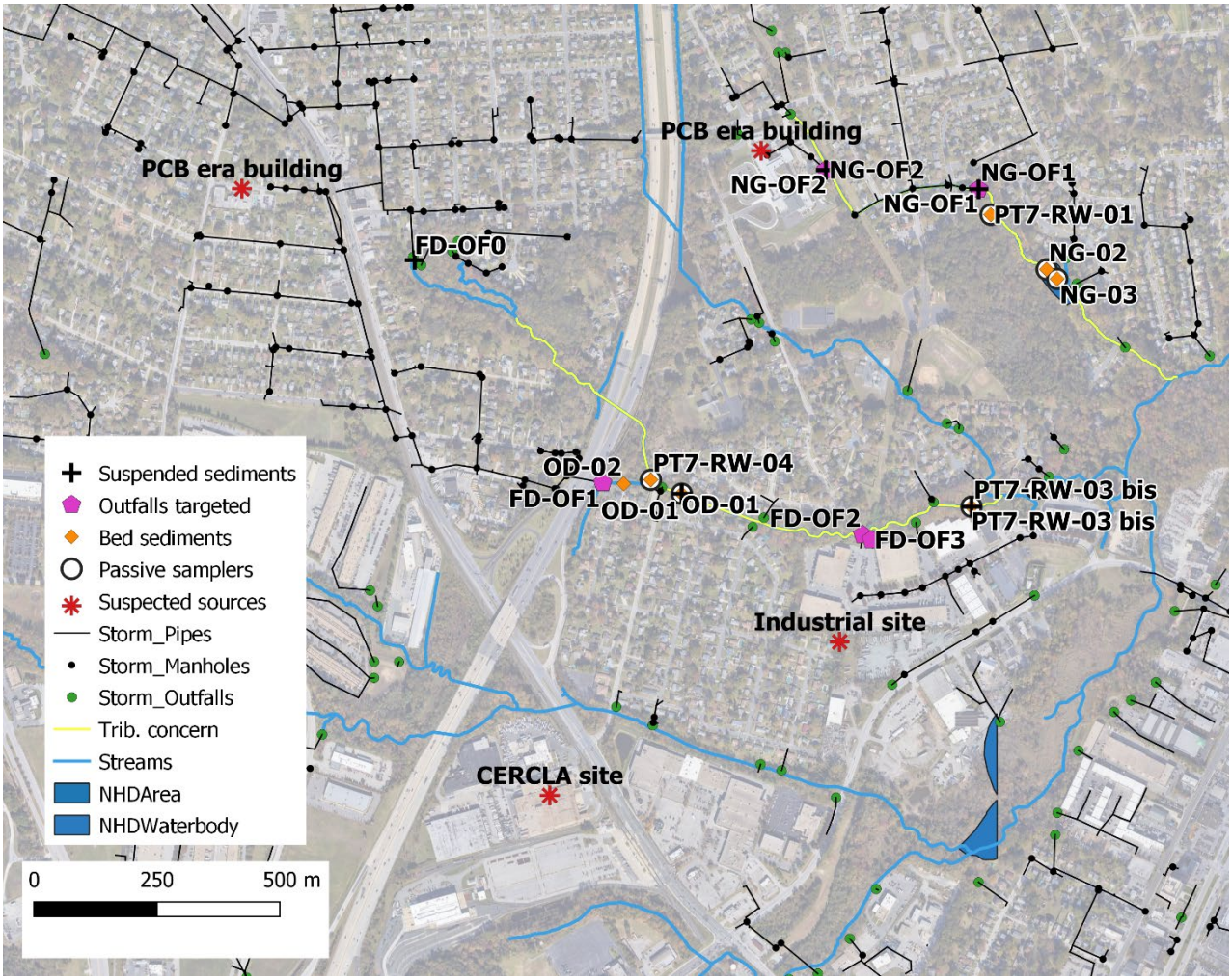

Figure 1: Sampling map of Ferndale Branch and North Glen tributary

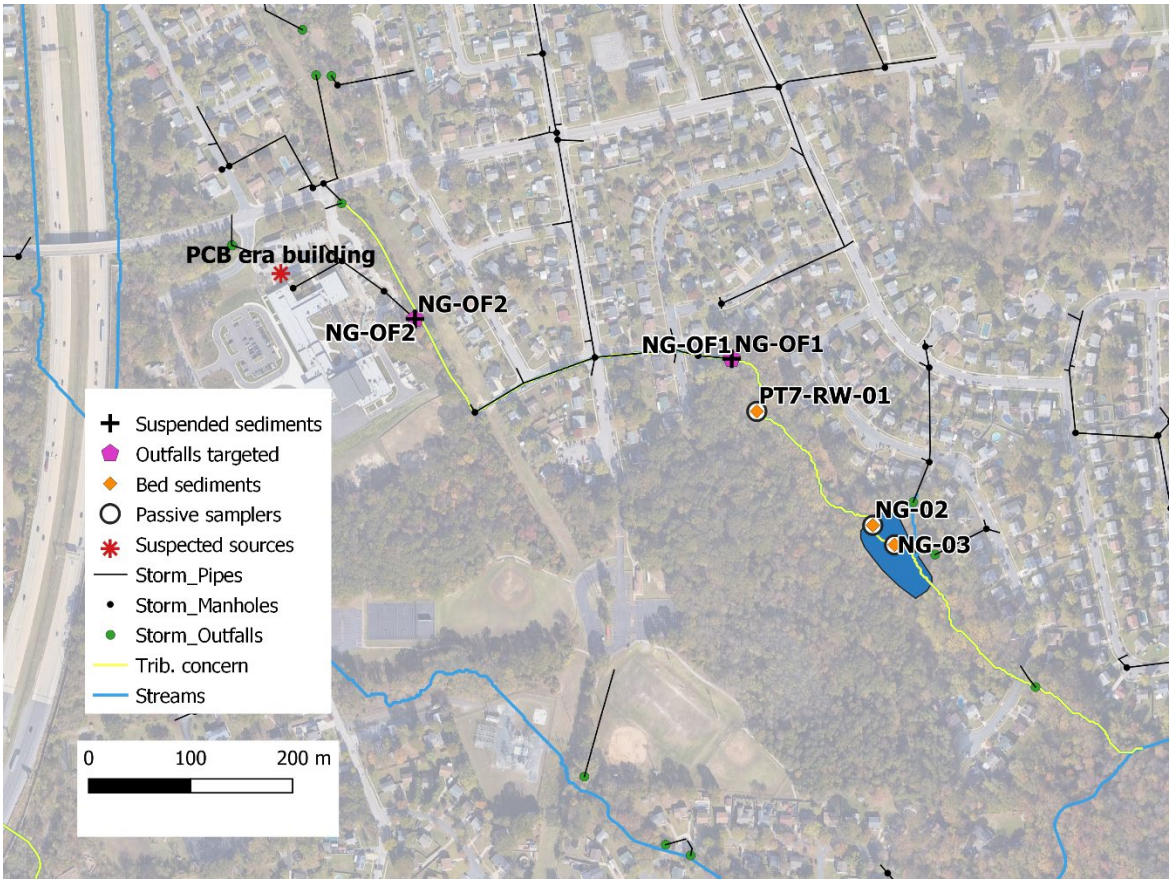

Figure 2: Sampling map zoom-in of North Glen tributary

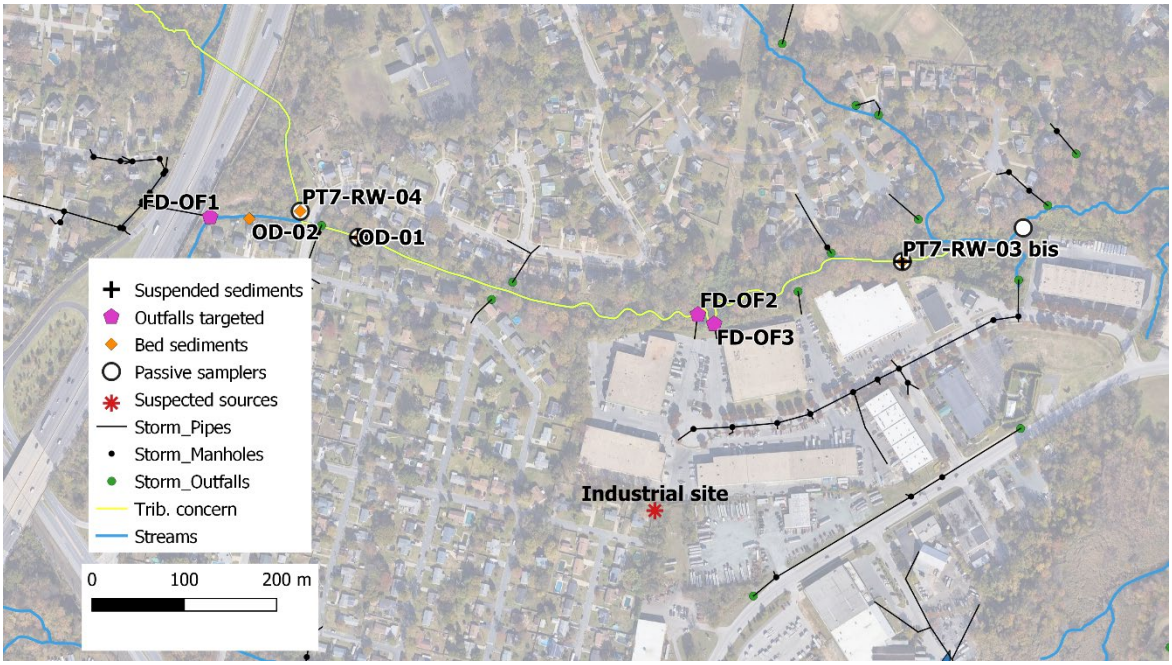

Figure 3: Sampling map zoom-in of Ferndale Branch

Figure 4: Stream restoration project of the Ferndale Branch. Yellow polygons indicate sections of the stream being restored. Red circles show sampling locations impacted by the restoration project. Map provided by AACo.

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 µm 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 ^{o}C 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 time 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 3month 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. 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 will provide an assessment of whether high concentration regions exists within the study area that may need further evaluation.

Stream channel sediments will be sampled using a petite ponar stainless steel sampler that measures 6” W x 6” L. Three grab samples will be 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 will be mixed to create a composite sample for each sampling site. Sediment samples will be collected by MDE, placed in a cooler, transported back to the UMBC laboratory and stored at 4 ^{o}C. Sediment samples will first be manually homogenized in the sample bottle before taking an aliquot out. The aliquot will be freeze dried and stored in a freezer until analysis (Details are provided in Appendix C).

Suspended sediments will be collected 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.

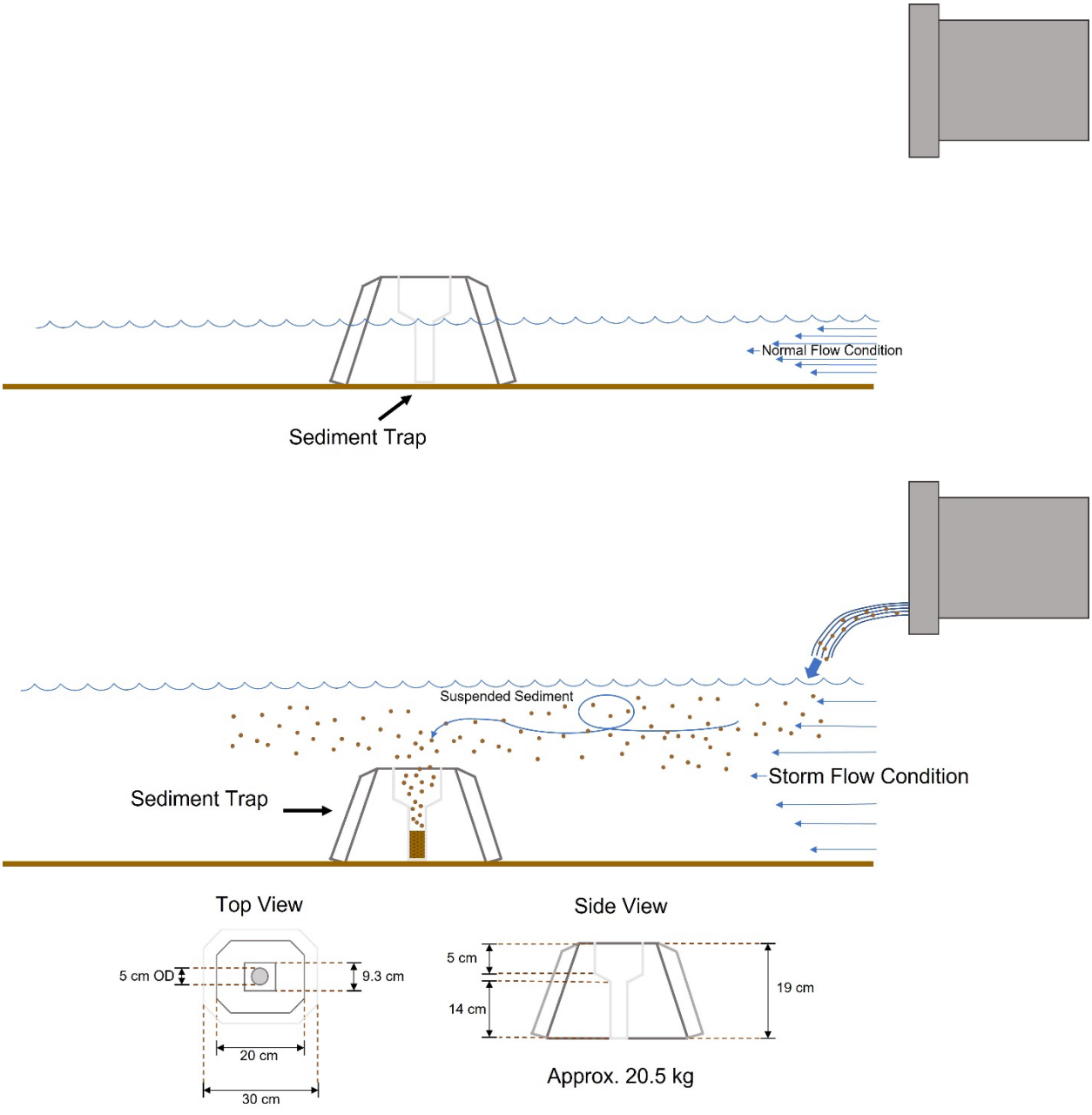

Figure 5: Sediment trap design. Top: normal flow condition, bottom: stormflow conditions.

4. REFERENCES

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.

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Sanders JP, Andrade NA, Ghosh U. 2018. Evaluation of passive sampling polymers and non-equilibrium adjustment methods in a multi-year surveillance of sediment porewater PCBs. *Environ. Toxicol. Chem*. 37: 2487–2495

U.S. EPA/SERDP/ESTCP. 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.

5. BUDGET

The tasks outlined above will be carried out by a team of personnel from UMBC including a post-doctoral associate and an undergraduate student. The team will be supervised by PI, Dr. Upal Ghosh. A rough breakdown of the costs are provided below.

Salary + fringe	$32,796
Supplies	$4,000
Travel	$1,000
Student tuition and insurance	$0
Total Direct	$37,796
Total Indirect (UMBC indirect rate of 54%)	$20,410
TOTAL	**$58,206**

Appendices

UMBC Department of Chemical, Biochemical and Environmental Engineering

STANDARD OPERATING PROCEDURES A

2021. DEPLOYMENT, MONITORING AND RETRIEVAL OF PASSIVE SAMPLERS

Prepared by N. Lombard 3/2021; Version 2.0

A. Objective

This SOP has been prepared to document procedures for the deployment of passive samplers in water column of streams and rivers. The passive samplers are enveloped in stainless steel meshes and attached inside cinder block holes or attached to U-post, and left to equilibrate with ambient water column concentration for 2-3 months before retrieval.

B. Equipment list:

- Hexane
- Methanol
- Acetone
- Fumehood
- DI water
- LDPE sheets 2mil (Husky)
- Performance Reference Compounds (PRCs) (cf section C)
- Wide mouth jar
- Tweezers
- Waders and 18 inch nitrile gloves
- Disposable nitrile gloves
- Precut stainless steel mesh (to envelop PE sheets)
- Aluminum foil
- 18 inch Gloves and nitrile disposable gloves
- Scissors to cut ropes, Scissors to cut meshes
- Ropes
- Waders
- Cinder blocks
- U-posts
- Shovel
- Metal hammer
- Staplers
- Tape to secure ropes (optional)
- DI water squeezer and Kim wipes
- 40 mL certified vials
- Folding table

- Cooler to transport the passive samplers
- Ice packs
- Water, detergent and hand sanitizer
- Labnote, 2 pens, 2 sharpies
- Printed COC
- Trash bags
- Camera
- Car, GPS and sites coordinates
- Masks

C. Pre cleaning of passive samplers

Low density polyethylene (LDPE) sheet is purchased from hardware/painting stores in large sheets with thickness of 2 mil (50.8 µm).

PE sheets are cut into 6 by 6 inch, then pre cleaned to remove residual monomers and any target and non-target contaminants in acetone/hexane (50/50 v/v) for 24 hours as described in Jonker and Koelmans, 2001.

After cleaning, the passive sampling strips are dried under the fumehood, and then kept in a clean glass bottle at -4˚C in the dark to prevent recontamination from exposure to laboratory air and other sources.

D. Impregnation of PE sheets with PRCs compounds

The choice is based on the need to have Performance Reference Compounds (PRCs) covering a wide range of K_{ow} values, PRCs that do not interfere with the analysis of the target compounds, and compounds that are not already used as analytical internal standards or surrogates.

PCB-PRCs:
PCB29 - 2,4,5-Trichlorobiphenyl
PCB34 - 2,3',5'-Trichlorobiphenyl
PCB69 - 2,3',4,6-Tetrachlorobiphenyl
PCB121 - 2,3',4,5',6-Pentachlorobiphenyl
PCB150 - 2,2',3,4',6,6'-Hexachlorobiphenyl
PCB155 - 2,2',4,4',6,6'-Hexachlorobiphenyl

PCB192 - 2,3,3',4,5,5',6-Heptachlorobiphenyl

Labelled PCB-PRCs

^{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

Clean passive samplers are impregnated in a mixture of methanol/water by volume (80/20 v/v) spiked with the PRCs. The system is left on a shaker until equilibrium is reached between the mixture and passive samplers. After impregnation, the samplers are soaked in DI water overnight to remove the methanol.

1. Calculate mass of PRC that should be injected to the mixture by the following equation (Booij et al., 2002):
   $N_t = N_m \frac{V_s + n * m_m * K_{ms}}{m_m * K_{ms}}$

   Where N_t is mass of PRC that needs to be added to the system (µg), N_m is the target amount of PRC per sampler (µg), V_s is volume of incubation solution (mL), n is number of samplers in solution, m_m is mass of each sampler (g), and K_{ms} is the membrane-solution partition coefficient (mL/g)

2. Add methanol with the volume of $0.8V_s$ to a wide mouth jar.
3. Add PRC with the mass of N_t (calculated in step 1) to methanol by spiking appropriate volume of PRC stock solution into the mixture.
4. Add DI water with the volume of $0.2V_s$ to the jar and stir the solution
5. Envelop the jar in aluminum foil to protect from photodegradation
6. Place the jar on a shaker and let equilibrate at least 2 weeks
7. Check the concentration of PRCs before use (extraction,(clean-up not required) and analysis on GC-ECD as described in SOP B)

E. Preparation of the passive sampler

One day before deployment, the passive samplers are taken out from PRCs mixture, rinsed in deionized water, then mounted into frames for the sediment pore water passive sampler or enveloped in meshes for the water column passive sampler.

1. Take out the strips from PRC solution with tweezers and rinse them with DI water
2. Transfer samplers to a clean jar and add DI water until water surface is right above the samplers. Adding too much water will result in losing PRCs from the samplers.
3. Let the passive samplers soak for 8h to eliminate any residual of methanol
4. Take out the strips from water solution and rinse them with DI water.
5. Dry the PE sheets with kim-wipes

6. On a bench covered with aluminum foil, place 1 PE sheet per mesh envelop and staple the edge of the mesh envelop. These PE sheets will be used for water column measurement
7. Envelop all passive samplers into aluminum foil and place them into zip lock bags
8. Keep them in the freezer and avoid contact with water to avoid PRCs loss
9. Put aside passive samplers in clean glass vials for initial PRC measurement

F. Passive sampler deployment

The passive samplers are transported to the deployment site in a cooler. All passive samplers are attached to the cinder blocks or U-post with ropes. The choice deployment device depends on the stream configuration (depth, width, flow rate) and is decided during recon.

1. Transport the passive sampler in a cooler containing ice pack.
2. On site, put on waders, gloves and masks.
3. Attach the passive sampler enveloped in mesh to the deployment device (cinder block or U-post).
    - The cinder block is attached to riparian tree with rope, then placed in the stream/river
    - The U-post is hammered down in the bed sediment of the stream/river
4. Record date, time and location, and take photo.
5. Clean waders and gloves with water, wash hands with soap and water. If soap is not available, use hand sanitizers.

G. Passive sampler retrieval

After 2-months of deployment, the passive samplers are retrieved from sites, rinsed with DI water to remove any sediment, transferred in vials and transported back to the lab in cooler. Alternate (shorter) procedure will be sent if the retrieval is planned during the colder months of the year to minimize time spent on site.

1. On site, put on waders, long gloves and masks.
2. Take out the deployment device from the stream
3. Disassemble the deployment device on the bank of the stream
4. Collect the passive sampler enveloped in stainless steel mesh and pre-clean the sampler in the stream to remove majority of mud and debris
5. Prepare the folding table with aluminum foil on top and put on single use nitrile gloves
6. Take out the passive sampler from mesh and place it on the aluminum foil
7. Clean it thoroughly with water and Kim wipes
8. Place them into certified clean 40mL vials
9. Add 2 drops of water to avoid the desiccation of sampler

10. Label the vial adequately with name of site, sampler ID, type of sampler, date of retrieval and fill the printed COC
11. Place the vial in a cooler with ice pack
12. Remove the deployment device from the stream and bring it back to the lab/office
13. Clean the wader as necessary between sites and at the end of the day
14. Store the vials in a fridge at 4 ºC as necessary until sent to UMBC lab
15. Send the cooler to UMBC with the printed and filled COC
16. Proceed with step 1 and 2 of extraction (cf SOP B) when back to the lab (addition of 30 ml of hexane, and add surrogates)
17. An additional vial will be used for blank procedures (addition of 30 mL hexane)
18. Store at 4°C until extraction is completed

H. Reference

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.

Department of Chemical, Biochemical and Environmental Engineering

STANDARD OPERATING PROCEDURES B

2021. PCB EXTRACTION FROM PASSIVE SAMPLERS

Prepared by N. Lombard 3/2021; Version 2.0

A. Objective

This SOP has been prepared to document procedures for the extraction from passive samplers and the extract clean-up for PCB. The extraction procedure is based on hexane extraction on orbital shaker. PCB extracts are cleaned up on a 3.3% deactivated silica gel column.

B. Equipment list:

- PCB surrogate mix at 500 µg/L (PCB#14, PCB#65)
- PCB internal standard (ISD) mix at 400 mg/L (PCB#30, PCB#204)
- PCB surrogate and PCB ISD syringes
- Hexane (pesticide residue grade solvent)
- Acetone (pesticide residue grade solvent)
- Methanol
- Deionised (DI) water
- Oven at 100ºC
- Orbital shaker
- Fume hood
- Aluminum foil
- 60 mL vials with polytetrafluoroethylene (PTFE) lined screw caps
- 40 mL vials with polytetrafluoroethylene (PTFE) lined screw caps
- Glass Pasteur pipettes, disposable (5 3/4" and 9" length)
- Graduated cylinder
- 2 mL autosampler vials for GC with PTFE septa.
- Analytical balance
- N-evap (Organomation) and nitrogen gas tank
- Copper
- Sulfuric acid
- Silica gel
- Sodium sulfate baked at 400°C for 4 hours
- Column and PFTE stopcock
- Glass wool
- Agilent 6890N gas chromatograph
- Helium, Argon/methane gas tanks
- Hewlett Packard gas chromatograph (Model 6890)

C. Preparation of glassware

All glassware are cleaned with a non-corrosive detergent and rinsed with tap water, then rinsed with deionized (DI) water, followed by a final rinse with methanol under fume hood. They are then dried in an oven maintained at 100°C. The glassware is rinsed with hexane before use.

D. Copper preparation

Copper is used to remove any trace of sulfur that might interfere with PCBs and Pesticide analysis. It is activated with hydrochloric acid (HCl), then thoroughly rinse with water to remove any trace of acid. The copper is further rinse with methanol, acetone/hexane, hexane, and then finally stored in hexane. The copper must be used within 48hours.

1. Transfer few scoops of copper in small vial (on paper towel under fume hood)
2. Add DI water and 3 drops of HCl with glass pipet/bulb. Cap with Teflon cap. Agitate and let settle down. Remove supernatant.
3. Rinse with DI water (x3): add DI water, agitate and let settle down, remove supernatant
4. Rinse with methanol (x4)
5. Rinse with acetone/hexane (x3)
6. Rinse with hexane (x3)
7. Add hexane and leave it in the vial

E. Silica gel preparation

Silica gel of chromatographic grade 923, 100-200 mesh (Fisher Scientific, Fair Lawn, NJ) is activated at least 16h at 130C in a shallow glass tray, loosely covered with foil and used for PAHs clean up.

For PCBs and pesticide clean up, activated silica gel is further processed by deactivation with 3.3% water in a 500 mL glass jar for 6 hours on a roller at approximatively 2rpm.

F. Extraction of PCBs from passive samplers

PCBs are extracted from passive samplers with hexane on orbital shaker for 24h. The extraction is repeated 3 times. Surrogates are added to estimate extraction efficiency. The surrogate recovery is reported but not used for correcting final concentration unless specified. The PE is kept after extraction, dried, and weighted. Its mass is used to calculate the final target contaminant concentrations measured on the sampler in units of contaminant mass per PE mass (e.g., ng/g PE)

1. Add 20 mL of hexane

2. Add 30 µL of the PCB surrogate mixture (15 ng) with the syringe. The syringe is immediately rinsed with hexane after use.
3. Place the vials on orbital shaker 30 rpm for 24 h, protected from light to avoid photodegradation
4. Collect the extract and transfer it in a 60 mL vial (keep in fridge)
5. Add 20 mL of new hexane in the 40 mL vial containing passive sampler
   And repeat the extraction step 3 to 5 two additional times (total of 3 extractions)
6. Allow the extracted PE strips to air dry and record their weights using an analytical balance.
7. Store the solvent extracts at -4˚C in the dark until further processing

G. Nitrogen blow down evaporation of the extract

The volume of solvent (hexane) is reduced down to 1-2 mL under nitrogen. The method used follows EPA publication SW-846, method 3550B.

10. Clean a needle from the N-evap unit thoroughly with hexane, wrap needle in aluminum foil and place in oven at 100°C for about 10-20 minutes.
11. Return cleaned needle to organomation unit, and place the 40 ml vial containing the extracted sample on the N-evap stand below the cleaned needle.
12. Lower the needle into the flask until the needle is about 3-5 cm above the level of the solvent.
13. Start nitrogen gas by first opening the valves on the needles, and then opening the pressure control, and last turning the regulator on the nitrogen gas tank.
14. Use the vertical regulator dial (in hood next to water bath) to change the flow rate of nitrogen.
15. Blow nitrogen on sample so that a small divot is visible in the water, but no splashing should occur.
16. Reduce sample to about 1 mL

H. PCB clean up and analysis

After hexane evaporation down to 1-2ml, the extract is treated with copper (EPA SW-846 method 3660B) to remove any sulfur trace that might interfere with PCBs and Pesticides analysis, and finally cleaned on silica gel deactivated column (EPA SW-846 , method 3630C). PCB analysis is performed on Agilent 6890N gas chromatograph) with an electron capture detector. Carrier gas used is helium (ultrapure grade) and the make-up gas is argon-methane mixture P5 (ECD grade). Pesticides are analyzed using an Agilent Gas Chromatograph (6890N) with a mass spectrometer detector.

(Optional pre-clean up)

1. Remove 1-2 mL sample from N-evap unit and add 4ml of hexane.
2. Add 2 mL of concentrated sulfuric acid dropwise.

3. Cap the vial and vortex the sample. A vortex must be visible in the vial.
4. Allow the phases to separate, so that the acid settles out and the hexane forms a layer on top.
5. Using a glass Pasteur pipette, siphon out the hexane and transfer to a clean 40mL vial. Add 2 mL of hexane to the 40 mL vial with the acid and shake vigorously. Allow sample to separate and again remove the hexane layer and add to 40 mL vial.
6. Repeat the previous liquid-liquid extraction step with hexane at least one more time, and add all hexane to the 40 mL vial.
7. Next treat sample with anhydrous sodium sulfate to remove any remaining water. Return sample to N-evap unit and reduce to 1 mL.
8. Lastly, treat the 1 mL sample with copper by adding a few mg of activated copper powder to the 40 mL vial. Shake vigorously and allow sample to sit for at least 30 minutes.

(Required column clean up)

9. Set up clean glass column(s) in stand with PTFE stoppers in place
10. Put in a small amount of glass wool, pushing it down with flat end of a long glass pipette.
11. In a 50 mL beaker, weigh out 3 g portion of deactivated silica gel. Add hexane in the beaker and stir around with glass stirrer to form slurry
12. Pour the slurry into a 10 mm ID glass chromatographic column with the funnel on top of column and rinse funnel with hexane as necessary and
13. Top it with 2 to 3 cm of anhydrous sodium sulfate.
14. Add 10 mL of hexane to the top of the column to wet and rinse the sodium sulfate and silica gel. Just prior to exposure of the sodium sulfate layer to air, stop the hexane eluate flow by closing the stopcock on the chromatographic column. Discard the eluate.
15. Transfer the sample extract (1-2 mL in hexane) onto the column. Rinse the extract vial twice with 1 to 2 mL of hexane and add each rinse to the column.
16. Elute the column with 30 mL of hexane at a rate of about 5 mL/min.
17. Reduce to 1-2 mL through nitrogen evaporation with N-evap (cf above)
18. Transfer 1 mL sample to labeled autosampler vial with PTFE lined septa.
19. Add 10 µL internal standards mix containing PCB#30 and PCB#204
20. Make sure that there is enough solvent in the autosampler wash vials.
21. Using CHEMSTATION load the current method for analysis.
22. Go to EDIT sequence and start a new sequence table.
23. Set up the sequence table as follows:

    Vial 1: Hexane

    Vial 2: Lab reagent blank (10 µL internal standard in 1 mL hexane)

    Vial 3: PCB standard

    Vial 4: Experimental Sample

    Vial 1: Hexane

24. Place the sample vials in the correct spots in the autosampler tray.
25. Save the sequence and start the run.

26. After the run is complete make sure that all the vials have run by checking for needle puncture mark in the autosampler vial septa.
27. Analyze and tabulate the data.

J. Calculation of equilibrium concentrations

To estimate water column concentration Cw, the following equation is applied (Perron et al, 2013)

$$C_w = \frac{C_{p,t}}{(1-e^{-k_e})\times K_{pw}} \qquad \text{Equation 5}$$

Where, C_w is the water column concentration, $C_{p,t}$ 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 follow

$$k_e = ln\left(\frac{C_{prc,t}}{C_{prc,int}}\right) \times \frac{1}{t} \qquad \text{Equation 6}$$

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 will be based on published consensus values in Ghosh et al. (2014).

K. Quality assurance and quality control

- Since the polymers used for passive sampling have high partition coefficients for hydrophobic organics, there is a significant chance of contamination of the polymers from exposure to the laboratory or field atmosphere.
  Passive samplers will be protected from the laboratory and field environment through adequate containment and storage in clean glass jars (i.e., solvent washed) and adequate set of laboratory blanks will be performed to demonstrate absence of contamination at the practical quantitation limits.

  Initial measurement of PRCs will be performed on passive samplers that have been subjected to similar conditions to field deployment to verify that no significant loss of loaded PRCs occurred before sampler deployment.

- Individual batches of passive samplers loaded with PRCs should exhibit reproducible PRC concentrations (e.g., coefficient of variation <20%) in the passive sampler before

deployment.

- Blank extractions with hexane will be performed to verify the absence of contamination during the extraction and cleaning procedure.

- Target analytes with feq below 0.1 will not be reported due to uncertainty linked with low uptake and high non-equilibrium correction factor, i.e. above 10.

- All pertinent field information and chains of custody will be provided to the sample processing team. Designated laboratory personnel will review the sample information and confirm that the number of individuals, collection date(s), collection time(s), species, and porewater analyses match the chains of custody. If any questions arise, laboratory personnel will contact the Project Manager and Laboratory Project Manager to resolve.

- The laboratory logbook will be checked between steps to verify required information is completed per the next section.

L. References

Fernandez, L. A., C. F. Harvey, and P. M. Gschwend. 2009. Using performance reference compounds in polyethylene passive samplers to deduce sediment porewater concentrations for numerous target chemicals. *Environmental Science & Technology* 43:8888-8894.

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. Environ Toxicol Chem, 32: 2182–2189.

UMBC

Department of Chemical, Biochemical and Environmental Engineering

STANDARD OPERATING PROCEDURES C

2021. PCB EXTRACTION FROM SEDIMENTS

Prepared by N. Lombard 3/2021; Version 2.0

A. Objective

This SOP has been prepared to document procedures for the extraction from sediment and the extract clean-up for PCB. The extraction procedure is based on acetone:hexane extraction by ultrasonication. PCB extracts are solvent exchanged with hexane then cleaned up on a 3.3% deactivated silica gel column.

B. Equipment list:

- PCB surrogate mix at 500 µg/L (PCB#14, PCB#65)
- PCB internal standard (ISD) mix at 400 mg/L (PCB#30, PCB#204)
- PCB surrogate and PCB ISD syringes
- Hexane (pesticide residue grade solvent)
- Acetone (pesticide residue grade solvent)
- Methanol
- Deionised (DI) water
- Oven at 100ºC
- Freeze dryer
- Sieve, mesh 2mm (optional)
- Sonicator
- Fume hood
- Aluminum foil
- 60 mL vials with polytetrafluoroethylene (PTFE) lined screw caps
- 40 mL vials with polytetrafluoroethylene (PTFE) lined screw caps
- Glass filter
- Glass Pasteur pipettes, disposable (5 3/4" and 9" length)
- Stainless steel spatula
- 2 mL autosampler vials for GC with PTFE septa.
- Analytical balance
- N-evap (Organomation) and nitrogen gas tank
- Copper activated (Cf SOP B)
- Sulfuric acid
- Silica gel deactivated (Cf SOP B)
- Sodium sulfate baked at 400°C for 4 hours
- Column and PFTE stopcock

- Glass wool
- Agilent 6890N gas chromatograph
- Helium, Argon/methane gas tanks
- Hewlett Packard gas chromatograph (Model 6890)

C. Preparation of glassware

All glassware are cleaned with a non-corrosive detergent and rinsed with tap water, then rinsed with deionized (DI) water, followed by a final rinse with methanol under fume hood. They are then dried in an oven maintained at 100°C. The glassware is rinsed with hexane before use.

F. Sediments Sample Preparation

1. The sediments are visually inspected and sieved (2mm mesh), if presence of debris, pebbles and larger rocks is noticed
2. Transfer the (sieved) sediments in a 40 mL vial with a stainless steel spatula
3. Freeze dry the sediment until mass is constant
4. Store the sediment at -4 ˚C until further processing

G. Ultrasonic Extraction (follows EPA publication SW-846, method 3550B**)**

1. Weigh out about 1 g of dried sediment sample, and note down the exact mass.
2. Transfer the sediment in a 100 mL beaker and add sodium sulfate.
8. Add 1:1 hexane:acetone to the sample beaker up to about 25 mL mark.
3. Add 30 uL of the PCB surrogate mix with a syringe. The syringe is immediately rinsed with hexane after use.
4. Clean ultrasonic probe thoroughly with hexane, and wipe with a Kim-wipe.
5. Set up a 60 mL glass vial with a funnel on top, and place a GF/C filter paper in the funnel.
6. Place the sample beaker on the platform underneath the ultrasonic probe, and raise the platform up until the probe is about 2 cm below the surface of the solvent. The probe should also be about 1-2 cm above the sample in the bottom of the beaker.
7. Start ultrasonic extraction 30 sec on/off for 6 minutes, so that extraction occurred for a total of 3:00 minutes.
8. After 3:00 minutes of sonication, lower the platform, rinse probe with 1:1 hexane: acetone so that rinse solvent falls into sample beaker, and remove beaker.
9. Pour solvent only through GF/C filter paper in the funnel, and collect all filtrate in the round bottom flask. Try not to pour any solid material into the filter paper.
10. Add more 1:1 hexane: acetone to beaker with sample, up to about 70 ml and repeat the extraction two more times.
11. After the third extraction, filter the 1:1 hexane: acetone solvent from the beaker, and then pour all solids in beaker onto filter paper. Rinse beaker well with solvent and add all

rinse solvent to the beaker. Let solvent filter through and then rinse the solids in the filter paper with 1:1 hexane: acetone, collecting all solvent in the flask below.

H. Nitrogen blow down evaporation of the extract and exchange (follows EPA publication SW-846, method 3550B).

17. Clean a needle from the N-evap unit thoroughly with hexane, wrap needle in aluminum foil and place in oven at 100°C for about 10-20 minutes.
18. Return cleaned needle to organomation unit, and place the 40 ml vial containing the extracted sample on the N-evap stand below the cleaned needle.
19. Lower the needle into the flask until the needle is about 3-5 cm above the level of the solvent.
20. Start nitrogen gas by first opening the valves on the needles, and then opening the pressure control, and last turning the regulator on the nitrogen gas tank.
21. Use the vertical regulator dial (in hood next to water bath) to change the flow rate of nitrogen.
22. Blow nitrogen on sample so that a small divot is visible in the water, but no splashing should occur.
23. Reduce sample to about 1 mL
24. Add 2 mL of hexane and repeat step 6-7, two times

H. PCB clean up and analysis

After hexane evaporation down to 1-2ml, the extract might be treated with sulfuric treatment (EPA SW-846 method 3665A) if required (complex baseline). The extract is then treated with copper (EPA SW-846 method 3660B) to remove any sulfur trace that might interfere with PCBs, and finally cleaned on silica gel deactivated column (EPA SW-846, method 3630C). PCB analysis is performed on Agilent 6890N gas chromatograph) with an electron capture detector. Carrier gas used is helium (ultrapure grade) and the make-up gas is argon-methane mixture P5 (ECD grade).

(Optional sulfuric treatment)

28. Remove 1-2 mL sample from N-evap unit and add 4ml of hexane.
29. Add 2 mL of concentrated sulfuric acid dropwise.
30. Cap the vial and vortex the sample. A vortex must be visible in the vial.
31. Allow the phases to separate, so that the acid settles out and the hexane forms a layer on top.
32. Using a glass Pasteur pipette, siphon out the hexane and transfer to a clean 40mL vial. Add 2 mL of hexane to the 40 mL vial with the acid and shake vigorously. Allow sample to separate and again remove the hexane layer and add to 40 mL vial.
33. Repeat the previous liquid-liquid extraction step with hexane at least one more time, and add all hexane to the 40 mL vial.

34. Next treat the sample with anhydrous sodium sulfate to remove any remaining water. Return sample to N-evap unit and reduce to 1 mL.

(Required copper treatment and column clean up)

35. Treat the 1 mL sample with copper by adding a few mg of activated copper powder to the 40 mL vial. Shake vigorously and allow sample to sit for at least 30 minutes.
36. Set up clean glass column(s) in stand with PTFE stoppers in place
37. Put in a small amount of glass wool, pushing it down with flat end of a long glass pipette.
38. In a 50 mL beaker, weigh out 3 g portion of deactivated silica gel. Add hexane in the beaker and stir around with glass stirrer to form slurry
39. Pour the slurry into a 10 mm ID glass chromatographic column with the funnel on top of column and rinse funnel with hexane as necessary and
40. Top it with 2 to 3 cm of anhydrous sodium sulfate.
41. Add 10 mL of hexane to the top of the column to wet and rinse the sodium sulfate and silica gel. Just prior to exposure of the sodium sulfate layer to air, stop the hexane eluate flow by closing the stopcock on the chromatographic column. Discard the eluate.
42. Transfer the sample extract (1-2 mL in hexane) onto the column. Rinse the extract vial twice with 1 to 2 mL of hexane and add each rinse to the column.
43. Elute the column with 30 mL of hexane at a rate of about 5 mL/min.
44. Reduce to 1-2 mL through nitrogen evaporation with N-evap (cf above)
45. Transfer 1 mL sample to labeled autosampler vial with PTFE lined septa.
46. Add 10 µL internal standards mix containing PCB#30 and PCB#204
47. Make sure that there is enough solvent in the autosampler wash vials.
48. Using CHEMSTATION load the current method for analysis.
49. Go to EDIT sequence and start a new sequence table.
50. Set up the sequence table as follows:

    Vial 1: Hexane

    Vial 2: Lab reagent blank (10 µL internal standard in 1 mL hexane)

    Vial 3: PCB standard

    Vial 4: Experimental Sample

    Vial 1: Hexane

51. Place the sample vials in the autosampler tray as indicated in the sequence.
52. Save the sequence and start the run.
53. After the run is complete make sure that all the vials have run by checking for needle puncture mark in the autosampler vial septa.
54. Analyze and tabulate the data.

K. Quality assurance and quality control

A quality control plan has been implemented to assure that PCB analyses performed on the GC-ECD are accurate. The plan consists of several assurances: initial five point-PCB calibration

using an internal standard method, continuing calibration checks, method detection limit checks, lab reagent blanks, matrix spikes, and surrogate spikes. A description of each assurance is given below and summarized in Table 1 and protocol for equipment maintenance in Table 2.

Detection Limit Determinations

The Limit of Detection is defined as the signal that is equal to three standard deviations of the baseline noise. The five-point calibration curve will be constructed and extrapolated to determine the y-axis intercept. This intercept will be considered the Instrument Detection Limit (IDL). The Method Detection Limit (MDL) for each target analyte will be determined once during an annual calibration

Seven samples spiked at the lowest level of the calibration are run, and the standard deviation of the measured concentrations (S_S) is calculated. A MDL based on spiked samples (MDL_S) is first determined by using the following equation:

$$MDL_s = t_{(n-1,1-\propto=0.99)} * S_s \quad \text{(Equation S1)}$$

Where, $t_{(n-1,\ 1-\alpha=0.99)}$ is the student's t-value appropriate for a single tailed 99th percentile t statistic and a standard deviation estimate with n-1 (here 6) degrees of freedom.

The MDL_S is either used as the "initial MDL" if none of the methods blanks (i.e. procedure blanks in this document) give numerical results, or the initial MDL is updated with the results from the method blanks if numerical value is measured for individual analytes (USEPA, 2016). Briefly, if some but not all of the methods blanks gave numerical results, the MDL for blanks (MDL_b) is set equal to the highest method blank results. If all the method blanks give numerical results, the standard deviation (S_b) of the replicates results is calculated and the MDL_b is determined as follow:

$$MDL_b = t_{(n-1,1-\propto=0.99)} * S_b \quad \text{(Equation S2)}$$

The greater of MDL_S or MDL_b is set as the "initial MDL".These MDLs will be reported along with PCB data.

Lab Reagent Blank

For every set of PCB analyses, two laboratory blanks of hexane will be analyzed at the beginning and end of sample batch to check GC for contamination from other sources. If there are peaks in the baseline above the LOD, the data obtained should be flagged and reanalyzed after the source of the contamination is eliminated.

Surrogate Spike (PCBs -14, -65)

A spike of the PCBs 14, 65will be added to all samples before extraction to check recovery after a given extraction/cleanup method. An appropriate spike amount will be added to produce a concentration similar to that of the internal standards in the GC vial. The acceptable recovery range is 60% - 130%.

Internal Standards (PCBs –30 and-204)

Two internal standards are used: PCB -30 (2,4,6-trichlorobiphenyl) and PCB -204 (2,2',3,4,4',5,6,6'-octachloro biphenyl), which are not present in commercial Aroclor mixtures. These are spiked into the GC vial to obtain a concentration of 4µg/L for each PCB.

Retention Times and Integration

All peaks are identified using the relative retention times of the two internal standards. Each calibration standard run at the beginning of a sample set is used to establish retention time windows. Once identified, the peaks are integrated using the HP Chemstation software. Each PCB peak is then checked manually for correct identification and integration. Any incorrect identification or integration is corrected manually.

Sample analysis sequence

Samples will be analyzed in sets that will include blank hexane and standards as follows:

Vial 1:	Hexane
Vial 2:	Lab reagent blank sample
Vial 3:	PCB standard sample
Vial 4-11:	Experimental Samples
Vial 12:	PCB matrix spike sample
Vial 13:	Lab reagent blank sample
Vial 14:	PCB standard sample
Vial 15-22:	Experimental Samples
Vial 23:	PCB matrix spike sample
Vial 24:	Lab reagent blank sample

Table 1. PCB Analysis Assurance Frequencies, Acceptance Criteria, and Actions

Assurance	Frequency	Acceptance Criteria	Failure Action
Five-Point PCB Calibration	1/year or as required	r^2>0.95 for linear regression of each analyte	redo calibration
Calibration Check	1/sample batch	% diff. < 10% (PCBs 53, 91, 153, 174, 180, 201)	1) bake column 2) redo calibration
Method Detection Limit Check	1/half year	0.1 to 0.2 ng/g	Increase sample amount, redo MDL check,
Lab Reagent Blank	2/sample batch	no peaks above LOD	flag data, bake column use fresh reagent
Surrogate PCB Spike (PCBs –14, –65, –166)	spike every sample before extraction	recovery is 60–130%	flag data, check extraction and cleanup procedures for errors.

Internal Standards (PCBs –30 and –204)	spike every sample before GC analysis	Relative ratio change < 20%	Check for contamination and fix problem
Retention Times and Manual Integration	every sample	use relative retention times of internal standards to correctly identity PCB peaks	Redo sample calibration or reinject sample after correcting problem

Table 2: Maintenance Schedule for GC and Ancillary Equipment

Equipment	Frequency	Action
GC Septa	Before each set of runs	Check for signs of deterioration, leaks, time since last replacement, and number of samples analyzed since last replacement. Replace if deterioration is obvious, more than 1 month since last replacement, or more than 50 samples have been injected.
GC inlet liner	Once/month	Replace inlet liner
Gas Traps	Every 20th cylinder	Replace trap.
Gas cylinders	Before each run	Check cylinder pressure gauge, replace if pressure is below 300 psi
GC computer	Before each run	Enter sample information in the GC logbook.
Extraction Sonicators	Once/month	Clean and examine for proper functioning
Balance	Every 1 year	Calibrate balance

L. References

USEPA. (2016). Definition and Procedure for the Determination of the Method Detection Limit, Revision 2. EPA 821-R-16-006. Office of Water. Washington DC.

Department of Chemical, Biochemical and Environmental Engineering

STANDARD OPERATING PROCEDURES D

2021. Total Organic Carbon Analysis

Prepared by J. Damond 08/2020

A. Summary

Updated protocol is based on Exhibit D of EPA Contract Laboratory Program Statement Of Work For Superfund Analytical Methods Multi-Media, Multi-Concentration SFAM01.0 May 2019. Method protocol details sediment preparation for TOC analysis, and quality control procedures.

B. Procedure

1. Thoroughly mix sediment sample in its container.
2. Dry the sediment sample via lyophilization or by baking in an oven overnight at 100 °C.
3. Sieve the dry, homogenized sediment to a particle diameter of 2-mm.
4. Weigh 200.0 ± 1.0 mg sediment in ceramic TOC combustion boat.
5. Add 1:1 phosphoric acid solution dropwise until effervescence/bubbling stops (or approx. 1 mL) for removal of inorganic carbon. Allow reaction to take place for 1 hour.
6. Heat treated sample on hotplate (at setting #3) until the acid has evaporated out. Leave samples in oven overnight at 103 – 105°C, then measure for TOC on TOC-L with SSM-5000.
7. Preparing Phosphoric Acid Solution
8. Prepare dilution using 85 wt% ACS grade phosphoric acid stock.
9. Carefully add 500 mL of Phosphoric acid stock to 400 mL of reagent water and dilute to 1 liter (L).

C. QA/QC

Calibration of the TOC-L

Weigh 5.0 mg, 12.5 mg, 25.0 mg, 37.5 mg, and 50.0 mg (± 0.5 mg) of anhydrous dextrose in a ceramic TOC combustion boat. The TOC in each of the calibration points is 40 wt% of the dextrose samples. When inputting calibration points on TOC-L, enter the expected TOC weight in mg based on the actual weight of the dextrose sample.

Test Standard

Option 1: use SRM 1944 - New York/New Jersey Waterway Sediment containing 4.4 wt% TOC to use as a standard

Option 2: use sediment of known TOC in the lab. Rhode River sediment with 4.16 wt% added AC has a TOC content of 6.24% ± 0.37% (mean ± 1 SD, n = 7, tested in BCSA BC/TOC Analysis from SERC).

Blank
Use diatomaceous earth (siliceous sedimentary rock) as a preparation blank.

Duplicate
Process one of the samples (not the standard/blank) in duplicate.

Method Detection Limit (MDL) Determination
The required quantitation limit, as per Exhibit C of SFAM01.0 May 2019 is 100 mg TOC per kg of sediment or 0.1% TOC content.

MDL should be re-determined annually. MDL determination is based on EPA 821-R-16-006. Dilute the sediment stock standard with diatomaceous earth (or with unamended sediment) so that the expected TOC concentration is 0.1%. Prepare at least 7 samples as outlined in the procedure and measure for TOC on the TOC-L. Calculate the TOC content in each of the samples. The MDL (%) is calculated as follows,

$$MDL = TOC \cdot t_{n-1,\alpha=0.01} \cdot \sigma_{sample}$$

where t is the Student's t value at $n - 1$ degrees of freedom and 99% confidence, and σ is the sample standard deviation.
Instrument Detection Limit (IDL) Determination
The IDL should be re-determined annually. Prepare at least seven 5.0 ± 0.5 mg samples of dextrose in ceramic TOC combustion boats, and measure for TOC on the TOC-L. Take the exact TOC content (%) of each of the samples and multiply by 5 mg – this is the normalized TOC. The IDL (mg) is calculated as follows,

$$IDL = TOC_{normalized} \cdot t_{n-1,\alpha=0.01} \cdot \sigma_{sample}$$

where t is the Student's t value at $n - 1$ degrees of freedom and 99% confidence, and σ is the sample standard deviation.