

Work plan for PCB source tracking in Anne Arundel County

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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. The County has collaborated with Biohabitats to develop a Targeted Action Strategy that aims to first investigate and then address sources of PCBs within the County. The AACo TMDL Action Strategy (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, among which Sawmill Creek catchment (PT7) 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 to use a traceback strategy to identify and eventually eliminate ongoing sources.

UMBC, MDE, and AACo collectively developed a PCB monitoring plan in the catchment PT7 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 (U.S. EPA/SERDP/ESTCP. 2017) following recent work performed by UMBC to track ongoing pollutant sources in the Anacostia River (Ghosh et al. 2020). Objectives of the study are to:

- 1) Measure freely dissolved PCBs in the water column at each location using passive samplers deployed for a 2-3 month period. Passive sampling is recommended because it provides a time-averaged concentration and when implemented correctly, is able to

provide very low detection limits in the water phase ranging from 0.01- 0.001 ng/L (ppt) for each PCB congener.

- 2) Compare surface water total PCB concentrations with the water quality criteria for Human Health protection (0.64 ng/L), and the water column TMDL endpoint (0.27 ng/L).
- 3) Assess if the catchment PT7 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.
- 4) [Measure PCB concentration in sediment at the sampling locations to identify any dominant PCB source in surface sediments in the study area.](#)
- 5) Based on the results of the study (Phase 1), provide a recommendation for additional sampling (Phase 2) to further identify the source(s) of PCBs within the watershed, as appropriate and replicate the effort at other catchments.

2. Sampling Plan

AACo would like to perform trackback identification of PCB sources in the Sawmill Creek watershed, as specified in the TMDL Action Strategy (AA 2019). For the Phase 1 of monitoring, sampling is planned in the catchment PT7. The sampling locations are shown in Figures 1a-c and listed in Table 1. In addition, two reference sites were selected. The site selection was based on initial discussions with AACo and MDE followed by a site visit to determine the logistical feasibility of performing the sampling operations. Key considerations included locations of potential sources, and other tributary inputs, availability of a deeper section of the tributary that would not likely run dry during low flow periods, location away from high traffic areas to reduce chances of vandalism and loss of samplers, and safe public access to the locations by personnel.

3. Material and Methods

Water column measurements. The freely dissolved concentrations of PCBs in surface water 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 as shown in **Figure 2**, 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 four 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 °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.

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 exist 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 stream, 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 °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).

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 to 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).

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 μ m 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.

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 (C_w), will be estimated using the approach as described in the Appendix B.

Data Analysis. The water column concentrations will be compared with the USEPA water quality criteria (WQC) protective of human health for the consumption of water and organisms. Criteria for total PCBs are available online at the following website <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-human-health-criteria-table>. Locations with concentrations above EPA WQC will require further analysis to identify the source of contamination using the traceback approach. Water concentrations will also be compared between catchment PT7 and measurements performed in the Harbor and assess whether the catchment is releasing water that has higher PCB concentrations than what exists within the Harbor.

Sediment concentration will be normalized by organic carbon content and compared among the different locations to identify potential hot spot source of contamination.

4. Scheduling and deliverables

A tentative project schedule is provided as a Gantt Chart in Figure 3. The Gantt Chart was based on the seven major tasks that are identified in the Scope of work. Processing time is shown in yellow and deliverables deadlines in orange. All deliverables would be within 12 months after the notice to proceed. Note that lab analysis for the sample will take about a month under normal circumstances, but restricted access to the lab during the COVID-19 pandemic requires extended timeline for processing samples. The draft of the report was requested within 8 weeks after data reception. So, the draft report will be submitted about 3 months after completion of the Phase 1 sampling. Several conference calls and in-person meetings in the field are scheduled at critical point of the project steps, i.e. decision on sampling site, retrieval of the sampler, data analysis completion, draft report completion.

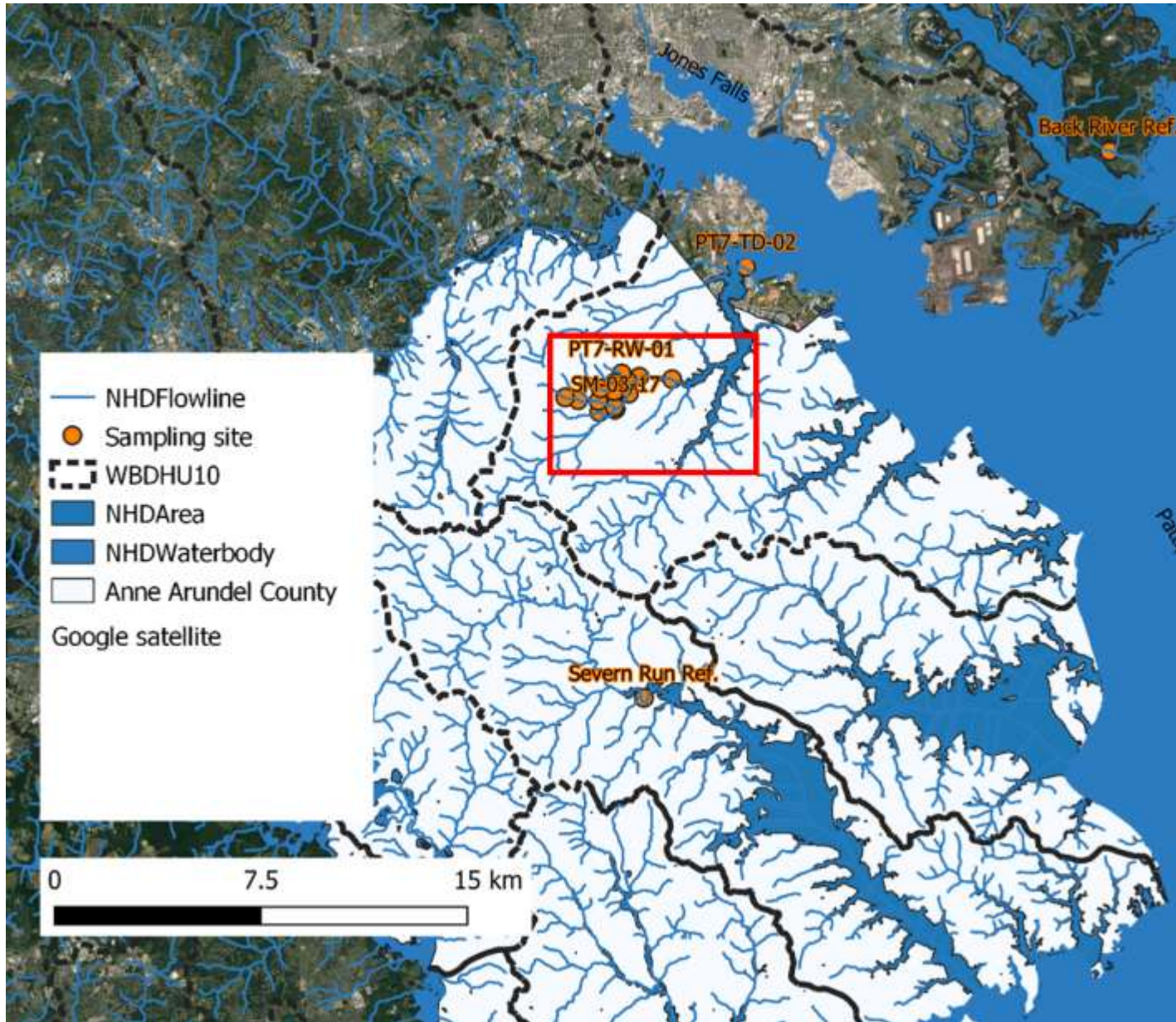


Figure 1a: Sampling locations. Map showing sampling watershed and reference sites in Back River and Severn Run. Red rectangle area shown in more detail in Figure 1b. NHD: National Hydrography Dataset, WBD: Watershed Boundary line.

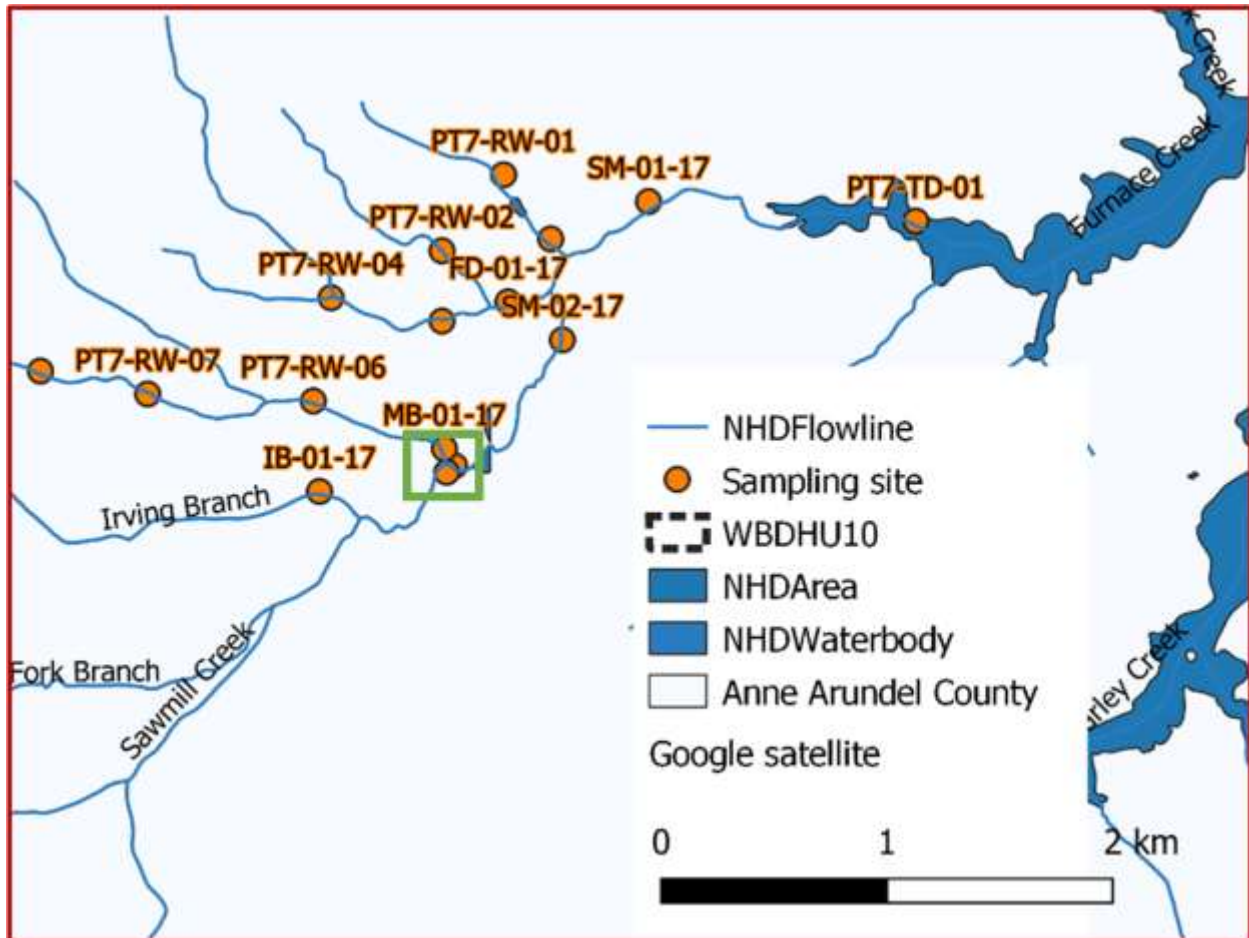


Figure 1b: Sampling locations (continued). Map showing main sampling locations. Detail of area marked in green rectangle shown in Figure 1c. NHD: National Hydrography Dataset, WBD: Watershed Boundary line.

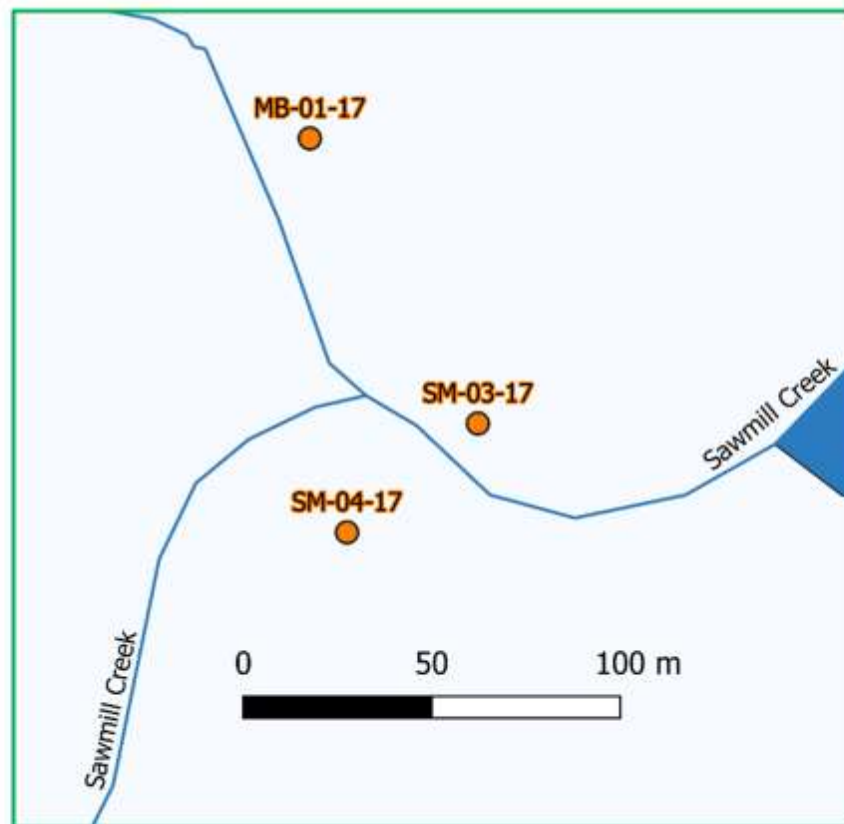


Figure 1b: Sampling locations (continued). Detail map showing sampling sites on Sawmill Creek and its tributaries. NHD: National Hydrography Dataset, WBD: Watershed Boundary line.



Figure 2: Passive sampler deployment in Anacostia River tributaries. Polyethylene (PE) sheets were enclosed in stainless steel mesh and were inserted inside a cinder block to measure water column concentration, or mounted into frames and inserted into sediments to measure sediment porewater concentration. Top left: a schematic representation of passive sampler deployment in situ. Top right: picture of passive sampler deployment in Anacostia tributaries. Bottom left: picture of water column PE inside cinder block. Bottom middle: cinder block containing water column PE is placed on the tributary bed, parallel to water flow. Bottom right: pictures of frames that are inserted into sediments to measure sediment porewater concentration.

Figure 3: Scheduling of the project and deliverables.

Nb	Tasks	Responsible party	August	September	October	November	December	January	February	March	April	May	June	July
1	Project initiation	UMBC												
	Project setup and kickoff <i>deliverable: draft and final plan</i>		■	■						■				
	General coordination <i>deliverable: 4 meetings</i>			■						■			■	
2	Site verif and site recon	MDE (and UMBC)												
	finalise sampling locations and 2 ref sites		■					■						
	site recon under all flow conditions <i>deliverable: memo and map inal sampling site</i>							■						
3	PCB sampling QA/QC	UMBC												
	locations													
	methodology													
	equipment													
	measurements													
	analysis													
	data analysis													
	reporting and deliverable formats													
	QA/QC													
	project schedule													
	<i>deliverable: final sampling plan</i>									■				
4	Field sampling	MDE, UMBC												
	samplers preparation (1 month)		■											
	deployment			■										
	monitoring			■	■									
	retrieval				■	■								
	sediment grab						■							
5	PCB cleanup and analysis	UMBC												
	water column samplers								■	■				
	sediment grab									■				
	<i>deliverable: data in pdf by email</i>										■			
6	Data management	UMBC												
	Create MS Access data base										■	■		
	PCB data on MS Access										■	■		
7	Reporting	UMBC												
	technical memos			■							■			
	monitoring reports										■	■		
	comments by county												■	
	final report													■

Table 1: Sampling sites and number of analysis.

Station ID	Waterbody	PCB in Water column sampler	PCB in Sediment grab	TOC in Sediment grab	Longitude	Latitude
SM-01-17	Sawmill Creek	1	1	1	-76.6166	39.18274
SM-02-17	Sawmill Creek	1	1	1	-76.621	39.17725
SM-03-17	Sawmill Creek	1	1	1	-76.6265	39.17226
SM-04-17	Sawmill Creek	1	1	1	-76.6269	39.172
NG-01-17	Lowest tributary Sawmill Creek	1	1	1	-76.6216	39.18125
PT7-RW-01	Lowest tributary Sawmill Creek	1	1	1	-76.624	39.1838
IB-01-17	Irving Branch	1	1	1	-76.6334	39.17123
MB-01-17	Sawmill creek/Muddy Bridge Branch	1	1	1	-76.627	39.17293
PT7-RW-06	Muddy Bridge Branch	1	1	1	-76.6337	39.17482
PT7-RW-07	Muddy Bridge Branch	1	1	1	-76.6422	39.1751
PT7-RW-09	Muddy Bridge Branch	1	1	1	-76.6477	39.17601
PT7-RW-02	Tributary of Ferndale Branch	1	1	1	-76.6272	39.18078
FD-01-17	Ferndale Branch	1	1	1	-76.6238	39.17876
PT7-RW-03	Ferndale Branch	1	1	1	-76.6272	39.17799
PT7-RW-04	Ferndale Branch	1	1	1	-76.6328	39.17892
PT7-TD-01	Sawmill Creek/Furnace Creek	1	1	1	-76.6029	39.18196
PT7-TD-02	Curtis Bay	1	1	1	-76.572	39.21844
Severn Run Ref.	Severn Run	1	1	1	-76.6147	39.07821
Back River Ref.	Back river	1	1	1	-76.4195	39.25605
Number of analysis		19	19	19		

REFERENCES

AA Co. 2019. Baltimore and Curtis Creek/Bay Polychlorinated Biphenyls (PCB) TMDL Action Strategy. Final. July 2019.

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

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

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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.

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

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 °C 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 100°C
- 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 PTFE 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 approximately 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 μ L 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 μ L 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 C_w , the following equation is applied (Perron et al, 2013)

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

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

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

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 f_{eq} 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.

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 100°C
- 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 PTFE 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.
3. Add 1:1 hexane:acetone to the sample beaker up to about 25 mL mark.
4. Add 30 uL of the PCB surrogate mix with a syringe. The syringe is immediately rinsed with hexane after use.
5. Clean ultrasonic probe thoroughly with hexane, and wipe with a Kim-wipe.
6. Set up a 60 mL glass vial with a funnel on top, and place a GF/C filter paper in the funnel.
7. 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.
8. Start ultrasonic extraction 30 sec on/off for 6 minutes, so that extraction occurred for a total of 3:00 minutes.
9. 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.
10. 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.
11. Add more 1:1 hexane: acetone to beaker with sample, up to about 70 ml and repeat the extraction two more times.
12. 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 μ L 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 μ L 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:

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

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:

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

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, 65 will 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 identify 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 20 th 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 $6.24\% \pm 0.37\%$ (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.