

December 21, 2018

Mr. Erich Weissbart Remedial Project Manager Land and Chemicals Division US EPA Region III 1650 Arch Street Philadelphia, PA 19103-2029

> Re: RWM Interim Measure Supplemental Investigation Work Plan (Revision 0) Tradepoint Atlantic Sparrows Point, MD 21219 EPA ID No. MDD053945432

Dear Mr. Weissbart:

ARM Group Inc. (ARM), on behalf of EnviroAnalytics Group (EAG), has prepared this Pre-Design Investigation (PDI) Supplemental Work Plan for a portion of the Tradepoint Atlantic Property that has been designated as Parcel A3 – Rod and Wire Mill (RWM) Area. The proposed activities presented in this PDI Supplemental Work Plan are based on the findings and recommendations from the Rod and Wire Mill Interim Measures Progress Report – August 2018, and the United States Environmental Protection Agency (USEPA) comments received in an email dated November 28, 2018.

1.0 BACKGROUND

The RWM Area is located in the northwestern portion of the Tradepoint Atlantic Property and has also been given the designation of Parcel A3, as the entire facility has been divided into several separate parcels. In 1986, a soil and groundwater remediation program was initiated to address groundwater exhibiting elevated levels of cadmium and zinc, and residual soil contamination in the Sludge Bin Storage Area. Remediation initially consisted of a soil flushing program and associated pumping and treatment of groundwater from shallow and intermediate wells. This pump and treat system was reconfigured in 2001 to provide groundwater recovery from two intermediate zone recovery wells in 2001 and remained active until September 2016.

The current remedial approach for addressing the elevated dissolved cadmium and zinc in the intermediate groundwater zone was to precipitate the dissolved metals in-situ by raising the

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groundwater pH from approximately 4 to approximately 9.5 to 10. The design and oversight of this remedial technique was completed by Advanced GeoServices (AGS) and is discussed in greater detail in the AGS Work Plan, *Interim Measure Work Plan In-Situ Groundwater Treatment* dated August 22, 2016. Alkaline reagents (TerrabondMG – 40% by weight in conjunction with limestone aggregate – 60% by weight) were added into the intermediate groundwater zone at select high concentration areas. The construction of the trenches was completed in January 2017.

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Since the completion of the trench installation, groundwater monitoring (monthly through 2017 and quarterly in 2018) has been performed at upgradient, performance and perimeter wells to assess the performance of the installed interim measure. A "Rod and Wire Mill Interim Measures Progress Report – August 2018" was submitted to EPA on November 4th, 2018, summarizing the results of the quarterly monitoring as of August 2018. The progress report showed that there have been substantial reductions in zinc and cadmium concentrations in the groundwater in the wells near the treatment trenches. In a November 28 email, the EPA provided comments on the progress report and noted several concerns with respect to the quarterly monitoring data. The EPA comments identified elevated zinc levels and possible increasing concentrations in some perimeter monitoring wells as a potential concern with respect to discharges to surface water.

Tradepoint Atlantic and EnviroAnalytics Group recognize the agency's desire to perform additional interim or final corrective measures to address this potential risk from the RWM Area and have received your request to provide additional data and also begin pumping groundwater from two former recovery wells. We have reviewed this request and respectively request that we delay implementation of further corrective actions including pump and treat methods until further assessment and data collection can be completed in the area. This data collection is necessary to determine the most relevant and effective further corrective actions that may be necessary based on the potential presence of risk.

This work plan presents a proposed scope and methodology for additional data collection necessary to improve the understanding of groundwater conditions in the RWM Area. As discussed in the reporting section, this additional data will improve and support the evaluation of the effectiveness of the existing interim measures in the next semiannual progress report that will be submitted in February 2019, and will provide the data to prepare a supplement evaluation to determine the most relevant and effective further corrective actions that may be necessary based on the potential for risk to the off-shore environment due to the discharge of groundwater.





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2.0 ADDITIONAL INVESTIGATION

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2.1 Well Redevelopment and Potentiometric Surface

Some of the monitoring wells in the RWM Interim Measure Area were converted to flush-mount completions or were abandoned to facilitate installation of the trenches or redevelopment of Parcel A3 and later re-installed. As a result, reference top-of-casing elevations needed to be re-established to facilitate the development of potentiometric surface maps to indicate groundwater flow directions following the installation of the treatment trenches. Reference elevations for the monitoring wells were determined on December 13, 2018.

In comparing the measured total depth to the recorded original depth of the existing wells, it was determined that some of the wells were installed as early as the 1980s and had significant thicknesses of accumulated sediment. This accumulated sediment could affect the response of water levels in the wells to changes in the surrounding water table, as well as affecting the turbidity and total metals concentrations in samples collected from these wells. Therefore, all of the wells for which there were no recent records of development were redeveloped in accordance with the procedures referenced in the QAPP Worksheet 21 – Field SOPs, SOP No. 15 – Well Development.

Potentiometric surface maps were created for the intermediate and shallow groundwater zones (**Figures 1 and 2**) based on the recent well survey and water level measurements. A synoptic round of water level measurements for the RWM Interim Measure monitoring wells was completed on December 17, 2018.

The intermediate zone groundwater contour map (**Figure 1**) shows the flow to be to radial from RW16-MW(I) to the southwest and northwest, although there are no wells to the north or northeast of RW16-MW(I) to determine direction of flow in that direction. The water level in RW19-MW(I) would indicate that the flow through the eastern treatment trench is to the east. In general, the groundwater elevations in all the wells are very similar, with only slight gradients indicated. As are result, groundwater flow velocities in the intermediate zone are expected to be very low. As noted, the water level in RW05-MW(I), was not used in the development of the contour map. The water level in this well was anomalously high. In addition, an obstruction prevented measurement to the bottom of the well, indicating that the casing may be compromised.

The shallow groundwater contour map (**Figure 2**) shows relative high elevations in the eastern wells with flow generally to the southwest. The higher shallow zone water levels in the center of the RWM treatment area indicate a downward gradient to the intermediate zone. However, the comparison of the water levels in the perimeter wells to the southwest nearest the shore, show little downward gradient to slight upward gradients, indicating the intermediate zone likely discharges close to the shoreline.



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2.2 Well Data Evaluation

Groundwater samples collected during December 2018 will be analyzed for both total and dissolved metals (zinc and cadmium). Dissolved analyses will serve as a check on the sampling method and laboratory analysis, but will also provide information on the form of the metal in the groundwater and the potential for migration. In addition, pH will be run in the laboratory as a check on the field measurements.

The groundwater data collected for the next quarterly sampling event will be subjected to 100% data validation to assess the potential for any issues or bias in the laboratory analyses. In addition, the data for the August and October 2018 sampling events will be subjected to data validation.

2.3 Additional Groundwater Investigation

A supplemental groundwater investigation will be completed to support the characterization of the subsurface conditions within and around the RWM IM area. During this investigation, new intermediate zone monitoring wells will be installed at the locations identified on **Figure 3** in accordance with the procedures referenced in the QAPP Worksheet 21 – Field SOPs, SOP No. 13 – Drilling and SOP No. 14 – Monitoring Well Construction.

Several locations for new wells are proposed along the western boundary of the Site. These new locations would serve to further define the nature and extent of metals concentrations in groundwater near RW22-MW(I) and serve as sentinel wells along the property boundary for monitoring metal concentrations in intermediate groundwater near the western shoreline of Bear Creek.

New wells are also proposed as replacements for existing wells RW05-MW(I) and RW22-MW(I). These are old, historically-installed wells that have been observed to have very poor recharge. One additional proposed well is located to the north of the RW19 well pair. As shown on **Figure 1**, groundwater in the intermediate zone is mounded in the northern-central portion of the site, and there may be a portion of groundwater flow in the north/northeast direction. The new intermediate zone monitoring well proposed to the north of the RW19 cluster will help to better define the groundwater gradient in the northern portion of the Site.

The monitoring well installation activities will include the use of a drilling rig that is suitable for the site conditions and proposed work. Final depths and screen intervals will correspond to the current on-site intermediate zone wells. The newly installed wells will be developed in accordance with QAPP Worksheet 21 – Field SOPs, SOP No. 15 – Well Development

Groundwater samples will be collected from the newly installed and existing wells in accordance with the procedures referenced in the QAPP Worksheet 21 – Field SOPs, SOP No. 6 – Groundwater Sampling. All groundwater samples will be analyzed for total and dissolved metals (Zinc and Cadmium only), hardness, and pH. Analytical methods, sample containers,



preservatives, and holding times for the sample analyses are listed in the QAPP Worksheet 19 & 30 – Sample Containers, Preservation, and Holding Times.

Groundwater sampling points will be evaluated for the presence of NAPL (non-aqueous phase liquid) using an oil-water interface probe, in accordance with methods referenced in the QAPP Worksheet 21 – Field SOPs, SOP No. 19 – Depth to Groundwater and NAPL Measurements. The proposed new monitoring wells will also be surveyed and depth to water will be collected to obtain groundwater elevation data. The elevation data from these piezometers and wells will be used to create a groundwater contour map indicating groundwater flow direction.

2.3 **Pore Water Investigation**

Sediment and pore water were previously collected by EA in 2015 in off-shore locations generally proximate to the Rod and Wire Mill Area. The Ecological Risk Assessment for the Northeast/Near Shore grouping found that benthic organisms are potentially at risk from chromium and zinc (not cadmium) in sediment. Cadmium was not identified as being of concern. The sediment data (see **Attachment 1**) indicated that the zinc concentrations were relatively low off the shore of the northern portion of the former Rod and Wire Mill, in the area of the RWM Interim Measure. Samples SD-D01 and SD-D02 had zinc concentrations of 510 and 670 mg/kg, respectively. The sediment samples slightly exceed the benchmark criteria for potential toxicity, but were low compared to concentrations greater than 2,200 mg/kg further out in Bear Creek, indicating the most significant zinc impacts appear to be associated with past discharges or other sources unrelated to groundwater discharge from the Interim Measure area. This also corresponds with where EA noted a change in the river bottom from sandy (silty) (as indicated by the yellow line on Figure 5-2 in Attachment 1) to more fine-grained sediments, so the higher zinc levels could be associated with deposition of suspended sediment.

A single pore water sample was collected from this area, PW-D02 at the location of sediment sample SD-D02. The result from this sample $(22 \ \mu g/L)$, reported as an estimated value below the quantitation limit, was below the National Recommended Water Quality Criteria (NRQWC) of 81 ug/L. Although this pore water sample indicates that groundwater discharges were not causing an adverse impact to sediment, additional pore water sampling will be conducted to support this assessment and existing limited data.

Another pore water sample was also collected in 2015 at location SD-DE01 south of the RWM interim measure area. The pore water zinc concentration at this location was 160 ug/L, which is above the NRWQL of 81 ug/L, indicating a potential for impact to benthic organisms. Therefore, additional pore water sampling is also proposed for this area as well.

Additional pore water samples are proposed to be collected in six transects with sample locations at approximately 50 feet and 200 feet off-shore, as depicted on **Figure 3**. This proposed pore water sampling includes repeating the sampling at PW-D02 and PW-DE01 to determine if levels have



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changed since 2015 and collecting samples further to the north and south of the previous sample locations to provide full coverage of the RWM interim measure area. The criteria outlined in the 2015 off-shore report were considered in selecting the additional pore water sample locations. These criteria included the following:

- Off-shore locations near onshore monitoring wells where groundwater COPCs exceeded the BTAG surface water screening criteria by at least five-fold (or consistently exceeded the criteria by two-fold). The proposed transect locations extend north to the 695 bridge and south of the existing well monitoring well network.
- Sandy (or silty) locations within approximately 200 ft of the shoreline, where pore water upwelling is thought to be likely. Upwelling is thought to be most likely in the near-shore area because the underlying geology does not include prominent shallow confining layers, and because sandy sediment lithology had been observed in the near-shore area. Therefore, proposed sample locations were placed 50 feet and 200 feet from shore, subject to access constraints with the boat.
- Locations without highly impacted sediments, such that any inputs from groundwater in the pore water would not be overshadowed by impacts from sediment. As indicated on Figure 5-2 in Attachment 1, zinc concentrations in sediment increase by and order of magnitude further off shore, possibly corresponding to the edge of the observed sandy bottom and the deposition of more fine-grained sediment. Therefore, pore water sampling locations were limited to 300 feet from shore to avoid these areas.

At each of the proposed pore water sampling locations, push-point samplers (see **Attachment 2**) will be advanced 1-foot below and 3-feet below the sediment-water interface. This will facilitate the determination of temperature and concentration gradients in the sediment pore water to allow assessment of whether the sample is located within a discharge or recharge area. Each push-point sampler will be equipped with a sampling flange to gauge the proper depth of to the sampler below the sediment surface and to serve as a surface seal to prevent intrusion of surface water into the sampler. In addition, tubing will be attached to the push-point sampler open at approximately 2 feet above the flange to allow simultaneous measurement of surface water and pore water conditions during pore water sample collection.

Pore water samples will be collected in accordance with the procedures referenced in the QAPP Worksheet 21 – Field SOPs, SOP No. 6 – Groundwater Sampling. Samples will be collected by connecting peristaltic pumps to tubing leading to the push-point sampler as well as to the surface water tubing. During sampling from each push-point sampler, two water quality multi-meters (temperature, pH, dissolved oxygen, conductivity, oxidation-reduction potential) will monitor the water conditions of the surface water and of the pore water simultaneously to verify the push-point sampler is sealed and isolated from the surface water.

All porewater samples will be analyzed for total and dissolved metals (zinc and cadmium only), hardness, and pH. Analytical methods, sample containers, preservatives, and holding times for the





sample analyses are listed in the QAPP Worksheet 19 & 30 – Sample Containers, Preservation, and Holding Times.

2.4 Laboratory Analysis

EAG has contracted PACE of Greensburg, Pennsylvania to perform the laboratory analysis for this project. The samples will be submitted for analysis with a standard turnaround time (approximately 5 work days). The specific list of compounds and analytes that the soil and groundwater samples will be analyzed for, as well as the quantitation limits and project action limits, is provided in QAPP Worksheet 15 – Project Action Limits and Laboratory-Specific Detection/Quantitation Limits.

3.0 **REPORTING**

The next semi-annual report, to be provided in February 2019, will include a thorough evaluation of data quality based on the re-development of existing wells, dissolved analyses and data validation. The report will include an assessment of trends using Mann-Kendall statistical trend tests for individual wells grouped by upgradient, treatment zone, and sentinel well areas. The trend analysis will include pre-trench data for those wells that have a record before the trench installation. In addition, the report will include isoconcentration plots and a quantitative mass analysis using the Thiessen Polygon method. These evaluations will be used to assess the effectiveness of the treatment trenches based on the existing monitoring well network.

A supplemental investigation report will be prepared to summarize the findings of the proposed additional groundwater and pore water investigation. The pore water sample results will be compared to relevant criteria for marine aquatic life. The pore water results and the data from the proposed new wells will be evaluated, along with the data from existing wells, to assess the migration of contaminants in groundwater and evaluate the potential need for enhancements to the current RWM Interim Measure.

4.0 SCHEDULE

Well surveying, development and re-sampling of existing wells has been completed. The RWM semi-annual report including an evaluation of this data and other collected information will be submitted in February 2019.

Assuming approval of this supplemental work plan in January 2019, it is anticipated that the additional well installation can be completed in February 2019. Sampling of the wells and pore water sampling can occur concurrently with the planned first quarterly monitoring event in early March 2019. Data should be available by the end of March and the supplemental investigation report will be provided by the end of April 2019.



5.0 CLOSING

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If you have questions regarding any information covered in this document, please feel free to contact ARM Group Inc. at (410) 290-7775.

Respectfully Submitted, ARM Group Inc.

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Stewart Kabis, G.I.T. Project Geologist

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T. Neil Peters, P.E. Senior Vice President

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Attachments:

Figures

- Figure 1 Intermediate Zone Groundwater Contour Map
- Figure 2 Shallow Zone Groundwater Contour Map
- Figure 3 Proposed Sample Locations

Attachments

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Attachment 1 – Off-shore Sample Data from Previous Investigations Attachment 2 – Push-Point Pore Water Sampling SOP



FIGURES







ATTACHMENT 1 Off-shore Sample Data from Previous Investigations



TABLE 5-20 METALS, CYANIDE, ORGANIC CARBON, POLYCYCLIC AROMATIC HYDROCARBON, AND PHTHALATE CONCENTRATIONS IN PORE WATER SAMPLES. SPARROWS POINT PHASE I OFFSHORE INVESTIGATION

ANALYTE	Units	AVG RL	BTAG ¹	Aquatic Life NRWQC ²	Human Health NRWQC ³	PW-A01	PW-B01	PW-C01	PW-C02	PW-D02	PW-DE01	PW-E01	PW-F05
METALS													
CADMIUM		7.75	0.12	8.8						10 U	10 U	10 U	
CHROMIUM	UG/L	14.9	57.5**	50			20 U						
COPPER	UG/L	16.4	3.1	3.1		20 U	20 U			2.6 J	20 U	20 U	20 U
LEAD	UG/L	8.20	8.1	8.1						0.74 J	10	10 U	10 U
MERCURY	UG/L	0.20	0.016	0.94				0.2 U	0.095 J				
NICKEL	UG/L	8.20	8.2	8.2	4600	2.9 J	2 J	2.1 J	3.5 J	10 U	20	10 U	
SILVER		6.40	0.23				10 U	10 U					
ZINC	UG/L	41	81	81	26000	50 U	50 U	12 J	210	22 J	160	50 U	
GENERAL CHEMISTRY													
CYANIDE, TOTAL	UG/L	10	1	1	140					4.4 J	2.5 J	3.5 J	24
HARDNESS AS CALCIUM CARBONATE	MG/L	56.9				1700	2100	1300	920	1400	1800	1700	1400
TOTAL ORGANIC CARBON	MG/L	1				0.96 J	1	1.2	1.7	1.8	2.8	2.1	6.7
POLYCYCLIC AROMATIC HYDROCARBO	DNS												
ACENAPHTHENE	UG/L	0.19	6.6		990					0.19 U	0.19 U	0.19 U	0.19 U
ACENAPHTHYLENE		0.19								0.19 U	0.19 U	0.19 U	0.19 U
ANTHRACENE	UG/L	0.19	0.18		40000					0.19 U	0.19 U	0.19 U	0.19 U
BENZO[A]ANTHRACENE		0.19	0.018*		0.018					0.19 U	0.19 U	0.19 U	0.19 U
BENZO[A]PYRENE		0.19	0.015*		0.018					0.19 U	0.19 U	0.19 U	0.19 U
BENZO[B]FLUORANTHENE		0.19			0.018					0.19 U	0.19 U	0.19 U	0.19 U
BENZO[G,H,I]PERYLENE		0.19								0.19 U	0.19 U	0.19 U	0.19 U
BENZO[K]FLUORANTHENE		0.19			0.018					0.19 U	0.19 U	0.19 U	0.19 U
CHRYSENE		0.19			0.018					0.19 U	0.19 U	0.19 U	0.19 U
DIBENZ(A,H)ANTHRACENE		0.19			0.018					0.19 U	0.19 U	0.19 U	0.19 U
FLUORANTHENE		0.19	1.6		140					0.19 U	0.19 U	0.19 U	0.19 U
FLUORENE	UG/L	0.19	2.5		5300					0.19 U	0.19 U	0.19 U	0.19 U
INDENO[1,2,3-CD]PYRENE	UG/L	0.19								0.19 U	0.19 U	0.19 U	0.19 U
NAPHTHALENE	UG/L	0.19	1.4							0.19 U	0.15 J	0.19 U	0.19 U
PHENANTHRENE		0.19	1.5							0.19 U	0.19 U	0.19 U	0.19 U
PYRENE		0.19	0.24		4000					0.19 U	0.19 U	0.19 U	0.19 U
TOTAL PAHs (ND=0)										0	0.15	0	0
SEMIVOLATILE ORGANIC COMPOUNDS													
BIS(2-ETHYLHEXYL) PHTHALATE	UG/L	1.92	16*		2.2	2 U	1.9 U	0.73 J		1.9 U	0.24 J	1.9 U	1.1 J
NOTES: Bold values represent detected concentrations. RL is reported for non-detected constituents													

¹ Surface Water Benchmarks from the U.S. Environmental Protection Agency Biological Technical Assistance Group. Marine values unless marked with asterisk.

*BTAG freshwater surface water benchmark

² National Recommended Water Quality Criteria for Saltwater Aquatic Life, Chronic

³ National Recommended Water Quality Criteria for Human Health, Consumption of Organism Only, prior to June 2015 update. Pre-2015 values were used in identification of Site-Related COPCs and screening pore water, due to project timing and consistent with the Work Plan.

** total chromium screening level

Value exceeds BTAG criteria

Value exceeds NRWQC criteria

 \mathbf{J} = compound was detected, but below the reporting limit (value is estimated)

U = compound was analyzed, but not detected

NA = not analyzed

RL = reporting limit

ATTACHMENT 2 Push-Point Pore Water Sampling SOP

U.S. Environmental Protection Agency Region 4, Science and Ecosystem Support Division Athens, Georgia							
OPERATING PROCEDURE							
Title: Pore Water Sampling							
Effective Date: February 28, 2013	Number: SESDPROC-513-R2						
Author							
Name: Mel Parsons							
Signature: Scientist Date: 2/20/13							
Approval							
Name: John Deatrick	-						
Title: Chief, Ecological Assessment Branch							
Signature: the Death, is	Date: 2/20/13						
Name: Bobby Lewis							
Title: Field Quality Manager, Science and Ecosystem Support Division							
Signature: MADL.	Date: 2/20/13						

Revision History

The top row of this table shows the most recent changes to this controlled document. For previous revision history information, archived versions of this document are maintained by the SESD Document Control Coordinator on the SESD local area network (LAN).

History	Effective Date		
SESDPROC-513-R2, Pore Water Sampling, replaces SESDPROC-513-R1.	February 28, 2013		
General: Corrected any typographical, grammatical and/or editorial errors.			
Revision History: Changes were made to reflect the current practice of only including the most recent changes in the revision history.			
Section 3.4 : Item 4 was revised to reflect practice of using individual single-use preservative vials instead of preservatives prepared by ASB.			
SESDPROC-513-R1, Pore Water Sampling, replaces SESDPROC-513-R0.	January 29, 2013		
SESDPROC-513-R0, Pore Water Sampling, Original Issue	February 05, 2007		

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1 General Information

1.1 Purpose

The purpose of this operating procedure is to describe the procedures, methods and considerations to be used when obtaining a sediment pore water sample.

1.2 Scope/Application

This document describes procedures generic to all pore water sampling methods to be used by field personnel when collecting and handling samples in the field. On the occasion that Science and Ecosystem Support Division (SESD) personnel determine that any of the procedures described in this section are inappropriate, inadequate or impractical and that another procedure must be used to obtain a pore water sample, the variant procedure will be documented in the field logbook, along with a description of the circumstances requiring its use. Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use.

1.3 Documentation/Verification

This procedure was prepared by persons deemed technically competent by SESD management, based on their knowledge, skills and abilities and has been tested in practice and reviewed in print by a subject matter expert. The official copy of this procedure resides on the SESD local area network (LAN). The Document Control Coordinator is responsible for ensuring the most recent version of the procedure is placed on the LAN and for maintaining records of review conducted prior to its issuance.

1.4 References

International Air Transport Authority (IATA). Dangerous Goods Regulations, Most Recent Version.

M.H.E. Products. 2003. PushPoint Sampler (US Pat. # 6,470,967) Operators Manual and Applications Guide, Version 2.01. East Tawas, MI. <u>http://www.mheproducts.com</u>

SESD Operating Procedure for Control of Records, SESDPROC-002, Most Recent Version.

SESD Operating Procedure for Sample and Evidence Management, SESDPROC-005, Most Recent Version.

SESD Operating Procedure for Logbooks, SESDPROC-010, Most Recent Version.

SESD Operating Procedure for Surface Water Sampling, SESDPROC-201, Most Recent Version.

SESD Operating Procedure for Pump Operation, SESDPROC-203, Most Recent Version.

SESD Operating Procedure for Field Equipment Cleaning and Decontamination, SESDPROC-205, Most Recent Version.

SESD Operating Procedure for Field Equipment Cleaning and Decontamination at the FEC, SESDPROC-206, Most Recent Version.

SESD Operating Procedure for Groundwater Sampling, SESDPROC-301, Most Recent Version.

SESD Operating Procedure for Potable Water Supply Sampling, SESDPROC-305, Most Recent Version.

Title 49 Code of Federal Regulations, Pts. 171 to 179, Most Recent Version.

USEPA. ASBLOQAM. Analytical Support Branch Laboratory Operations and Quality Assurance Manual. Region 4, Science and Ecosystem Support Division, Athens, GA. Most Recent Version.

USEPA. SHEMP. Safety, Health and Environmental Management Program Procedures and Policy Manual. Science and Ecosystem Support Division, Region 4, Athens, GA. Most Recent Version.

SESD Operating Procedure for Field Sampling Quality Control, SESDPROC-011, Most Recent Version.

1.5 General Precautions

1.5.1 Safety

Proper safety precautions must be observed when collecting pore water samples. Refer to the SESD Safety, Health and Environmental Management Program Procedures and Policy Manual (most recent version) and any pertinent site-specific Health and Safety Plans (HASP) for guidelines on safety precautions. These guidelines, however, should only be used to complement the judgment of an experienced professional. When using this procedure, minimize exposure to potential health hazards through the use of protective clothing, eye wear and gloves. Address chemicals that pose specific toxicity or safety concerns and follow any other relevant requirements, as appropriate.

1.5.2 Procedural Precautions

The following precautions should be considered when collecting pore water samples:

• Special care must be taken not to contaminate samples. This includes storing samples in a secure location to preclude conditions which could alter the

properties of the sample. Samples shall be custody sealed during long-term storage or shipment.

- Collected samples are in the custody of the sampler or sample custodian until the samples are relinquished to another party.
- If samples are transported by the sampler, they will remain under his/her custody or be secured until they are relinquished.
- Shipped samples shall conform to all U.S. Department of Transportation (DOT) rules of shipment found in Title 49 of the Code of Federal Regulations (49 CFR parts 171 to 179), and/or International Air Transportation Association (IATA) hazardous materials shipping requirements found in the current edition of IATA's Dangerous Goods Regulations.
- Documentation of field sampling is done in a bound logbook. Chain-of-custody documents shall be filled out and remain with the samples until custody is relinquished.
- All shipping documents, such as bills of lading, will be retained by the project leader and stored in a secure place.

1.5.3 Records

Information generated or obtained by SESD personnel will be organized and accounted for in accordance with SESD records management procedures found in SESD Operating Procedure for Control of Records, SESDPROC-002 (most recent version). Field notes, recorded in a bound field logbook, will be generated, as well as chain-of-custody documentation, in accordance with SESD Operating Procedure for Logbooks, SESDPROC-010 (most recent version), and SESD Operating Procedure for Sample and Evidence Management, SESDPROC-005 (most recent version).

2 Sampling Methodology

2.1 General

The pore water sampling techniques and equipment described in this procedure are designed to minimize effects on the chemical and physical integrity of the sample. If the procedures in this section are followed, a representative sample of the pore water should be obtained.

2.2 Collection Considerations

The physical location of the investigator when collecting a sample may dictate the equipment to be used. Wading is the preferred method for reaching the sampling location, particularly if the stream has a noticeable current (i.e., is not impounded). However, wading may disrupt bottom sediments causing biased results; therefore, the sampler should enter the area downstream of the sampling location and collect sample facing upstream. If the stream is too deep to wade, the pore water sample may be collected from a platform such as a boat or by SCUBA diving. If sampling from a boat or in water deeper than the length of the sampler, extensions may be utilized. The device is suitable for use only in fine-grained material (no gravel or cobble).

2.3 Summary of Procedure

Sediment pore water is collected using a pore water extracting device (Figure 1). The most common type used is the PushPointTM sampler (M.H.E. Products 2003), made out of stainless steel tubing. The sampling end of the pore water device is inserted into the sediment to the desired depth, and pore water is extracted using a syringe or peristaltic pump. Other similar devices may be used providing that the integrity of the sample is maintained and no ambient surface water is allowed in contact with the sample.

2.4 Sampling Equipment

A PushPointTM or similar sampler typically consists of a pointed tubular stainless steel tube with a screened zone at one end and a sampling port at the other. The pointed end with the screened zone consists of a series of very fine interlaced machined slots to allow pore water to enter the sampler. A removable guard rod adds rigidity to the sampler during sediment insertion. The length of the screened zone will depend on the site specific study design. Depending on the data quality objectives (DQO) of the study, filters may be placed over the screened zone if additional screening is needed. Pore water is collected through the opposite end of the device by connecting flexible tubing and using a syringe or peristaltic pump to extract the sample. Teflon® tubing is the preferred tubing to be used for collecting pore water samples. However, other tubing may be used, depending upon the DQOs for the specific application.

There are many modifications that can be incorporated into the procedure to satisfy data quality objectives for a specific application. The procedures discussed in the following

sections provide guidance on the basic operation of pore water sampling devices and issues to consider when collecting pore water.

An alternative system is available in SESD inventory for use in soft sediments in water deeper than wading depth. A well screen and short riser approximately ³/₄" in diameter has external threads to fasten to the bottom of a custom flange and internal threads to accept a tubing compression adapter. The accompanying rimmed flange has a coupling with both top and bottom threads. The well screen is screwed into the bottom of the flange coupling and Teflon® tubing is attached to the tubing compression adapter which is threaded into the well screen. The tubing is then inserted through the pipe or well casing which is then screwed into the upper coupling threads. The entire assembly can be deployed in water up to ten feet of depth from a well anchored boat.

2.5 **Pore Water Sampler Deployment Considerations**

It is critical in the collection of pore water to avoid surface water intrusion. Water will flow in a path of least resistance. If space is created around the sides of the sampling end of the pore water device during deployment, surface water may flow down the outside of the device to the screened area and into the intended sample. Therefore, the pore water device should be used with a sampling flange (Figure 2), especially when collecting pore water near the sediment-surface water interface. If pore water is collected from deep in the sediments, a flange may not be necessary. When inserted though the sampling platform, or flange, the body of the pore water device should form a water tight seal to eliminate surface water intrusion during sample collection. Flanges should include a cutting ring to enhance sealing. Flange systems can be augmented by flexible plastic sheeting of appropriate material. The sheeting can be weighted to conform to the stream bottom by sediments obtained from other areas of the stream or banks away from the sampling location.

The flange can be made of any material that will not cross contaminate the intended sample. If both inorganic and organic analyses are required, the flange should be made of inert material such as stainless steel or Teflon®. The size of the flange depends on the volume of pore water to be collected. If large volumes of pore water are to be collected, use a large flange size. A useful estimate can be made for planning by taking the entire required water volume, tripling it to assume 33% porosity, and then calculating the dimensions of a sphere or cylinder of this volume. The flange should cover at least this estimated volume. If it is not practical to use a large flange, then multiple devices may be deployed and smaller volumes can be collected from several devices for a composite sample. If multiple devices are deployed, they should be spaced an appropriate distance apart so they will not interfere with one another.

For irregular surfaces a flange can be improvised from polyethylene sheeting weighted by shovelled nearby stream sediments. Several of the flanges in SESD inventory have a threaded nut and washer to facilitate sealing the flange to a polyethylene sheet for this purpose.

In general, the volume of pore water that can be collected at a given location is limited. Collecting large volumes of pore water will ultimately result in the collection of water from the overlying water body. Often, minimum required volumes must be negotiated with the laboratory to limit the volumes withdrawn.

Where significant differences in parameters such as pH or conductivity exist between the surface water and pore water, a check can be made at the end of sampling to assess whether surface water intrusion has occurred by measuring the pore water parameters at the beginning and conclusion of sampling.

2.6 **Pore Water Collection**

The flange is first placed at the desired sampling point with the push-point removed to allow water to escape from under the flange. The flange rim should be carefully worked into the sediment until the flange is flush with the sediment surface. The pore water device should then be inserted through the compression adapter on the flange and into the sediment as carefully as possible (Figure 2). When the sampler is inserted to the desired depth, the compression adapter should be tightened. The push-point's guard rod can then be withdrawn. Do not reinsert the guard rod into the sampler for any reason until the sampler has been cleaned (sediment particles rolled between the two metal surfaces will lock the parts together and permanently damage the sampler.)

When deploying the pore water device, care must be taken not to disturb the sampling area. If the sampler is wading in the water body, the sampler should lean out and insert the pore water device as far as possible away from where the sampler is standing to reduce potential effects of the sampler on the integrity of the pore water sample. Depth of penetration of the pore water device into the sediment depends on the objectives of the specific investigation.

After the pore water device has been successfully deployed, attach the sample tubing to the sampling port of the pore water device. Short pieces of Silastic® tubing can be used to splice Teflon® sample tubing to a push-point sampler, taking care to butt the tubing to the sampler at the center of the splice. Then attach the other end of the tubing to a sample withdrawing device, such as a syringe or a peristaltic pump (according to SESD Operating Procedure for Pump Operation, SESDPROC-203). Before collecting a pore water sample, be sure to purge out all air and surface water from the pore water device and sample tubing with the appropriate amount of pore water. If utilizing a syringe for collection, a three-way valve with a side syringe must be utilized for the surface water purge in order not to cross contaminate the sampling syringe.

2.6.1 Peristaltic Pump/Vacuum Jug Collection

The peristaltic pump/vacuum jug can be used for sample collection of organic or inorganic samples because it allows for the sample to be collected without coming in contact with the pump head tubing, maintaining the integrity of the sample. This is accomplished by placing a Teflon® transfer cap assembly onto the neck of a pre-cleaned standard 1-liter amber glass container (Figure 3). Teflon® tubing (¼-inch O.D.) connects

the container to both the pump and the sample source. The pump creates a vacuum in the container, thereby drawing the sample into the container without it coming into contact with the pump head tubing.

Because the sample is exposed to a vacuum and is agitated as it enters the vacuum jug, this method cannot be used for collection of samples for volatile organic compounds. An alternative method for collecting volatile organics involves filling the Teflon® tubing with sample by running the pump for a short period of time. Once the tubing is full of water, the tubing is removed from the pore water sampler and, then pinched off at the pump in order to maintain the vacuum and disconnected from the pump head tubing. The water is then allowed to carefully drain, by gravity, into the sample vials. Alternatively, without disconnecting the tubing from the pump head, the contained sample can be pushed out of the tubing, into the sample vials, by reversing the peristaltic pump at very low speed. Great care must still be taken with this method in order not to agitate the sample during the transfer process or transfer water that has been in contact with the Silastic® tubing into the vials.

Because pore water is typically collected from an anaerobic environment, it is preferable, especially when collecting samples for nutrient analysis, to maintain the integrity of the sample by minimizing exposure to air. This can be accomplished by purging the sample container with an inert gas such as nitrogen or argon prior to sampling. In addition, if analyzing for nutrients or metals, the container can be pre-preserved in order to minimize exposure of the sample to ambient conditions.

An alternative, when collecting samples for metals, nutrients or other sample analysis not affected by the Silastic® tubing and exposure to air is not a concern, is to collect the sample directly from the discharge of the pump head tubing after an adequate purge has been demonstrated. When collecting samples in this manner, there are several considerations to be aware of. The pump head tubing (Silastic®, etc.) must be changed after each sample and a rinsate blank must be collected from a representative piece of the pump head tubing (only one blank per investigation). Also, precautions must be taken to ensure that the end of the discharge tubing is not allowed to touch the ground or other surface to ensure the integrity of the sample collected in this manner.

2.6.2 Syringe

An alternative to using the pump and vacuum container is to use a syringe as the mechanism to draw the pore water through the sampling device. The tubing from the sampling port of the pore water device can be directly attached to a syringe with a three-way valve and a side syringe and the pore water sample can be manually withdrawn from the sediment. The valve is first switched to the side syringe, which is used for purging air and any ambient surface water in the system prior to sampling. The volume to be purged is determined by the length and diameter of the sampling device and attached tubing. Once the sampler has been purged, the valve is switched to the sampling syringe and the sample is drawn into the syringe. The syringe can be used as the final sample container or the pore water can be transferred to another container, depending on project objectives and analytical requirements.

2.7 Quality Control

If possible, a control or background sample should be collected from a location not affected by the possible contaminants of concern and submitted with the other samples. In streams or other bodies of moving water, the control sample should be collected upstream of the sampled area. For impounded bodies of water, particularly small lakes or ponds, it may be difficult or inappropriate to obtain an unbiased control from the same body of water from which the samples are collected. In these cases, it may be appropriate to collect a background sample from a similar impoundment located near the sampled body of water if there is a reasonable certainty that the background location has not been impacted. Equipment blanks should be collected if equipment is field cleaned and reused on-site or, if necessary, to document that low-level contaminants were not introduced by pumps, bailers or other sampling equipment.

2.8 Specific Sampling Equipment Quality Assurance Techniques

All equipment used to collect pore water samples shall be cleaned as outlined in the SESD Operating Procedure for Field Equipment Cleaning and Decontamination, SESDPROC-205 (most recent version) or SESD Operating Procedure for Field Equipment Cleaning and Decontamination at the FEC, SESDPROC-206 (most recent version) and repaired, if necessary, before being stored at the conclusion of field studies. Cleaning procedures utilized in the field or field repairs shall be thoroughly documented in field records.

3 Special Sampling Considerations

3.1 Volatile Organic Compounds (VOC)

Pore water samples for VOC analysis must be collected in 40 ml glass vials with Teflon® septa. The vial may be either preserved with concentrated hydrochloric acid or they may be unpreserved. Preserved samples have a two week holding time, whereas, unpreserved samples have only a seven day holding time. During most sampling events, preserved vials are used due to their extended holding time. In some situations, however, it may be necessary to use the unpreserved vials. For example, if the surface water sample contains a high concentration of dissolved calcium carbonate, there may be an effervescent reaction between the hydrochloric acid and the water, producing large numbers of fine bubbles. This will render the sample unacceptable. In this case, unpreserved vials should be used and arrangements must be confirmed with the laboratory to ensure that they can accept the unpreserved vials and meet the shorter sample holding times.

Samples for VOC analysis must be collected using either stainless steel or Teflon® equipment. Samples should be collected with as little agitation or disturbance as possible. The vial should be filled so that there is a meniscus at the top of the vial and absolutely no bubbles or headspace should be present in the vial after it is capped. After the cap is securely tightened, the vial should be inverted and tapped on the palm of one hand to see if any undetected bubbles are dislodged. If a bubble or bubbles are present, the vial should be refilled. Care should be taken not to flush any preservative out of the vial during topping off. If, after attempting to refill and cap the vial, bubbles are still present, a new vial should be obtained and the sample re-collected.

3.2 Dissolved Metals Sample Collection

If a dissolved metals pore water sample is to be collected, an in-line filtration should be used. The use of disposable, high-capacity filter cartridges (barrel-type) or membrane filters in an in-line filter apparatus is preferred. The high-capacity, barrel-type filter is preferred due to the higher surface area associated with this configuration.

Potential differences could result from variations in filtration procedures used to process water samples for the determination of trace element concentrations. A number of factors associated with filtration can substantially alter "dissolved" trace element concentrations; these include filter pore size, filter type, filter diameter, filtration method, volume of sample processed, suspended sediment concentration, suspended sediment grain-size distribution, concentration of colloids and colloidally-associated trace elements, and concentration of organic matter. Therefore, consistency is critical in the comparison of short-term and long-term results. Further guidance on filtration may be obtained from Section 4.7.3 of the SESD Groundwater Sampling Procedure (SESDPROC-301).

3.3 Special Precautions for Pore Water Sampling

- A clean pair of new, non-powdered, disposable latex gloves will be worn each time a different location is sampled and the gloves should be donned prior to handling sampling equipment and sampling. The gloves should not come in contact with the media being sampled and should be changed any time during sample collection when their cleanliness is compromised.
- All background or control samples shall be collected and placed in separate ice chests or shipping containers. Sample collection activities shall proceed progressively from the least suspected contaminated area to the most suspected contaminated area. Samples of waste or highly contaminated media must not be placed in the same ice chest as environmental (i.e., containing low contaminant levels) or background samples.
- If possible, one member of the field sampling team should take all the notes and photographs, fill out tags, etc., while the other members collect the samples.
- Samplers must use new, verified, certified clean disposable equipment, or precleaned non-disposable equipment. Non-disposable equipment should be precleaned according to procedures contained in SESD Operating Procedure for Field Equipment Cleaning and Decontamination (SESDPROC-205), for collection of samples for trace metals or organic compound analyses.

3.4 Sample Handling and Preservation Requirements

- 1. Pore water will typically be collected from sediments using a peristaltic pump and placed directly into the sampling containers. In some cases a syringe may be used to collect the sediment pore water and then transfer the sample into the appropriate container.
- 2. During sample collection, if transferring the sample from a collection device, make sure that the device does not come in contact with the sample containers.
- 3. Place the sample into appropriate, labeled containers. Samples collected for VOC analysis must not have any headspace (see Section 3.1).
- 4. All samples requiring preservation must be preserved as soon as practically possible, soon after sample collection. If pre-preserved VOA vials are used, these will be preserved with concentrated hydrochloric acid prior to departure for the field investigation. For all other chemical preservatives, SESD will use the appropriate chemical preservative generally stored in an individual single-use vial as described in the SESD Operating Procedure for Field Sampling Quality Control (SESDPROC-011). The adequacy of sample preservation will be checked after the addition of the preservative for all samples, except for the samples collected for VOC analysis. If it is determined that a sample is not acceptably preserved, additional preservative should be added to achieve adequate preservation. Preservation requirements for surface water samples are found in the USEPA Analytical Support Branch Laboratory Operations and Quality Assurance Manual (USEPA ASBLOQAM).





