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# SOP: SEDIMENT PORE WATER SAMPLING AND ANALYSIS

## HERRINGTON LAKE, KENTUCKY

RAMBOLL ENVIRON

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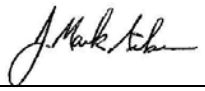
| **Approved by** | Mark Nielsen:  | 9/14/2017 |
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# ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| CAP | Corrective Action Plan |
| cm | centimeter |
| DUP | Duplicate |
| GPS | Global Positioning System |
| NSPDS | Nylon-screen passive diffusion samplers |
| ml | milliliter |
| PPE | Personal Protective Equipment |
| PW | Pore water |
| QAPP | Quality Assurance Project Plan |
| SOP | Standard operating procedure |

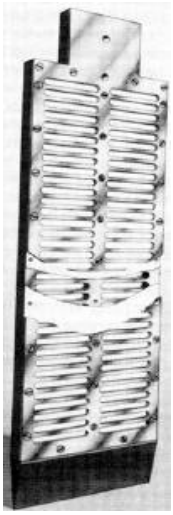
# 1. OVERVIEW

This standard operating procedure (SOP) describes the use of small volume peepers and passive diffusion samplers to collect sediment pore water consistent with the sampling plan outlined in the E.W. Brown Corrective Action Plan (CAP; Ramboll Environ 2017a). The aquatic invertebrate community lives in constant and direct contact with surface water and/or sediment and sediment pore water (i.e., the interstitial water within the sediment). These organisms are potentially exposed to chemicals in sediment through direct contact between sediment pore water and structures, such as gills and setae, and ingestion of sediment. Sediment pore water will be collected using small volume peeper samplers or nylon-screen passive diffusion samplers. The approaches outlined herein are consistent with US EPA guidance provided by US EPA (2016), Peijnenburg et al. (2014) and Ghosh et al. (2014).

The deionized water filled diffusion samplers allow dissolved metals to diffuse into the sampler, providing an estimate of the time-averaged concentration of metals in sediment pore water. Given enough time, a volume of water contained in the sampler will equilibrate with the surrounding pore water as pore water solutes diffuse through the sampler membrane. Only dissolved constituents are collected using these devices and for the Herrington Lake field sampling program will include selenium, arsenic, total mercury, methyl mercury, cadmium, lead, zinc, iron, boron, and magnesium. Sediment pore water sampling locations target Curds Inlet, HQ Inlet, and Hardin Inlet. The pore water sampling will also evaluate the species of selenium present which will provide insight into whether or not the sediments are a source of selenium to the geochemical cycle of selenium into biological tissues. Where practical, sediment pore water samples will be collected at the same locations as sediment. However, final sampling locations will be determined in the field, based on field conditions, and at the discretion of the field team leader.

# 2. SMALL VOLUME PEEPER PORE WATER SAMPLING

Pore water samples will be collected from 14 locations using a Modified Hesslein In-Situ Pore Water Sampler, also known as a "small volume peeper". These samplers consist of small compartments with membrane or mesh walls that are buried in the sediments, where interstitial waters are allowed to infiltrate. These require deployment by hand and an equilibration period.



**Modified Hesslein In-Situ Pore Water Sampler (small volume peeper)**

The small volume peepers that will be used during the Herrington Lake study consists of three parts: a 1.3-centimeter (cm)-thick acrylic body, a 0.3-cm-thick acrylic cover, and a 0.45-micrometer Teflon® dialysis membrane. The 6- by 18-inch sampler body is equipped with a series of approximately 10-milliliter (mL) sample chambers spaced at 1 cm. This sampler is capable of collecting approximately 200 mL of water over 15 inches of sediment depth.

The small-volume peepers will be deployed during the same sampling event as the sediment sampling. Peepers will be pushing directly into the sediments to a depth of approximately 12 inches. Peepers will be left in place to equilibrate for at least 28 days. This equilibration period allows some flexibility in planning following the implementation of the field effort. Each peeper will be secured to a line at the sediment surface that is tied to a clump-weight anchor. At nearshore locations, a second line will be run from the anchor to the shore where it will be tied to a rebar (or similar) pole driven into the bank. This will facilitate locating the peeper during the retrieval phase. At deeper water locations, a surface buoy will be attached to the clump anchor, so that the peeper can be readily located during the recovery effort.

After the equilibration period, the peepers will be retrieved and brought to the surface for immediate processing on the sampling vessel or at the bank. Upon retrieval, two water samples will be collected from each peeper:

- The first sample will be collected from chambers in the upper portion of the peeper and these samples will reflect pore water from the biologically active zone (i.e., the upper 6 inches of the sediment column).
- The second sample will be collected from the bottom portion of the peeper. These samples will be from a portion of the sediment column below the biologically active zone.

## 2.1 Equipment and Supplies

The following is a list of equipment that may be necessary to carry out the procedures contained in this SOP. Additional equipment may be required, pending field conditions.

- Small volume peeper sampling device
- Appropriate membrane material
- 0.45-micron polypropylene
- Deionized water
- Waterproof marker
- Sampling vessel
- Diving gear
- Differential global positioning system
- Watch
- Waterproof sample tags, waterproof marker, and cable ties
- Sufficient line to extend from peeper to shore or floating buoy
- Buoys and tags (if unable to affix peeper line on the shore)
- Anchors to fix peeper samplers
- Personal protective equipment (PPE) for field team (e.g., rain gear, steel-toed boots,
- nitrile gloves)
- First aid kit
- Cell phone
- Logbooks, indelible black-ink pens, and field forms
- Sample coolers and ice
- 20-mL glass syringe
- Disposable stainless-steel needles

## 2.2 Procedures

The following general guidelines will be followed in all the procedures and in all studies with peepers:

- Always wear clean nitrile gloves to handle the sampling device.
- Sampling and sample processing staff will endeavor to minimize the amount of time peepers are exposed to air to minimize the chance of cross contamination.
- As stated in the CAP, field collection will be opportunistic and will be based on field conditions at the time of sampling.

### 2.2.1 Pre-Deployment Preparation

- Prior to deployment, the sampler body is laid flat and the chambers overfilled with deionized oxygen-free water that is held in the chambers by the porous membrane and the overlays.

- Care must be taken during assembly to avoid trapping air bubbles under the membrane in the sample chambers.
- The membrane is then placed atop the sampler body and overlain by the sampler cover.
- Screws are used to secure the cover to the sampler body and to seal the membrane against the sampler body such that there is will be no air entrained in the sample chambers.
    - The cover contains elongated openings spaced exactly opposite the compartments of the peeper body
- Following construction, peepers are degassed to remove any oxygen present in the chambers that could markedly impact the concentration of reduction-oxidation sensitive constituents within the peeper chamber after deployment.
- The oxygen is removed from the chambers and from the plastic by aerating the entire peeper assembly with nitrogen or argon gas for 24 hours in a large water bath prior to installation (Lorah et al. 2005).
- Peepers are carried into the field in the degassed water bath and removed just prior to installation.

### 2.2.2 Deployment

- Load all precleaned sampling equipment on the boat, including decontamination fluids/equipment and investigation-derived waste (IDW) containers.
    - The sampling boat should be of sufficient size to accommodate the required sample containers, a support boat will be used to transport containers and collected samples as necessary.
- Navigate the boat to the target stations.
- Data will be obtained with an external global positioning system (GPS) receiver capable of sub-meter accuracy.
- Confirm that the vessel is well anchored during sampler deployment.
- Record approximate water depth in the field data sheets.
- All material from processed samples, decontamination fluids, and used PPE will be disposed of as described in the Herrington Lake Quality Assurance Project Plan (QAPP: Ramboll Environ 2017b).
- All field activities will be documented as detailed in the Herrington Lake QAPP (Ramboll Environ 2017b).
- For all stations, two divers will be used to place the sampling devices.
- The sampling device will be deployed by inserting it into the sediment to a depth of 15 cm below the mudline or as deep as possible to allow the surrounding interstitial water to infiltrate the sampler.
    - If multiple peeper assemblies are needed to provide adequate sample volume, each assembly will be spaced approximately 1 foot apart.
- If the sediment is soft, the peepers will be pressed into the sediment by hand (if wadeable or divers are used) or with a weighted frame.

- An underwater camera can potentially be used to verify that the peepers are placed appropriately.
- The peepers will be connected with leader lines attached to the shoreline, if possible, to facilitate locating/retrieving.
- If attachment to the shoreline is not possible, the leader lines will be attached to floating buoys to identify their locations.
- GPS coordinates will be recorded.
- The sampling device location will be marked to facilitate retrieval by divers. With the expected low visibility in the surface water, one method of marking will consist of attaching to each sampling device a nylon line. This line will be run along the bottom to the nearest point along the shoreline, brought to the surface, and secured. The line will be weighted sufficiently to not float into the water column and pose a threat to navigation.
- The sampling device will be deployed for a minimum of 28 days prior to retrieval.

### 2.2.3 Retrieval

- The sampling device will be retrieved via the same method as deployment (i.e., by hand via nylon line with the aid of divers).
- The line attached to the sampling devices during deployment will be identified and divers will use them to follow back to the deployed sampling devices.
- Once the sampling device is removed from the sediment, it will be brought to the surface and transferred to staff on the sampling vessel as quickly as possible.
- Recovered peepers will be lightly rinsed with deionized water to remove any trapped sediment.
- Porewater is removed from the chamber using a 20-mL glass syringe and sterile, one-time use stainless-steel needles.
- The syringes will be used to fill laboratory-provided sample containers.
- While collecting porewater to fill laboratory-provided containers, the porewater pH, temperature, and conductivity will be measured from additional sample volume. Following porewater collection into the laboratory-supplied containers, the porewater samples will be placed in a cooler at 4 degrees Celsius for transport to the field facility where they will be packaged for shipment.
- All field activities will be documented, including sampling and field measurement activities as summarized in the Herrington Lake QAPP (Ramboll Environ 2017b).
- Survey data and field records/forms will be reviewed by the Field Team Leader, scanned, and sent to the Data Management Task Manager as soon as possible. Electronic data collection records will be downloaded at the end of each day they are collected and saved to the project files.
- At the end of the day and between sample intervals, the instruments will be decontaminated as described in the Herrington Lake QAPP (Ramboll Environ 2017b).

# 3. NYLON-SCREEN PASSIVE DIFFUSION SAMPLERS

In the event that the substrate in Herrington Lake preclude the use of peepers. A nylon-screen diffusion sampler may be used. Field collection will be opportunistic and will be based on field conditions at the time of sampling.

Nylon-screen passive diffusion samplers (NSPDS) are diffusion based samplers developed to sample for a broad range of analytes including metals. A NSPDS typically consists of a 175 mL polypropylene wide mouth bottle (diameter of 62 mm at top, 58 mm at bottom and a height of 58 mm) filled with analyte-free water, with a 125µ-mesh nylon screen placed across opening and covered with a cap that has an opening of about 58 mm in diameter (see figure below).

NSDS units are assembled in water that is purged of dissolved oxygen by sparging with nitrogen for at least 1 hour.

Place samplers in a 19-L bucket and continuously bubble nitrogen through the water filled 19-L buckets. The samplers can be transported to the field sites in buckets under a nitrogen atmosphere that was maintained by keeping the buckets covered except during the removal of a sampler.

## 3.1 Deployment

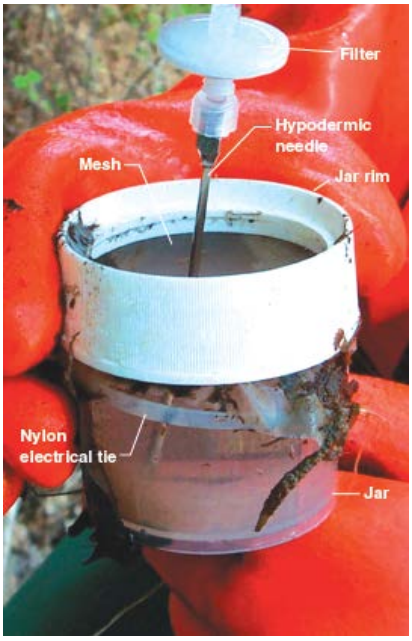
- To deploy, or insert, the NSDSs into the sediment, push a PVC shovel into the sediment to create a hole that would allow the sampler to be buried approximately 20 cm below the sediment surface. Each NSDS can then be covered with sediment after the shovel is removed.
- Place samplers on their sides to decrease the danger of puncturing the mesh during insertion and retrieval.

## 3.2 Retrieval

- To locate the samplers for retrieval, wrap each NSDS unit tightly with a nylon electrical tie attached to nylon monofilament and a brightly colored fishing bobber.
- Remove samplers by gently gripping its sides.

## 3.3 Sample Collection

- Collect NSDS samples by using a 60-mL disposable syringe with a 13-gage, 8.9-cm hypodermic needle and a 25-mm, 0.45-µm filter unit (Millipore HPF Millex- HN) mounted between the syringe and hypodermic.
- Thrust the sharp tip of the hypodermic through the nylon mesh to extract the sample (see Figure right). Two withdrawals may be required to retrieve a volume sufficient for analysis.




**Nylon-screen passive diffusion samplers (NSPDS)**

# 4. SAMPLE VOLUMES, CONTAINERS, AND HOLD TIMES

The table below provides information on the metals that will be measured in pore water, the analytical methods, minimum sample volumes needed for the analysis, the required containers and preservatives and the sample hold times. All samples need to be cooled and stored at 4ºC.

Where quality control samples are collected, sample volume requirements will be proportionally greater (e.g., approximately double volume for sample duplicates).

| Chemicals of Interest | Analytical Methods | Minimum Volumes Required(a) | Container | Hold Times (b) |
|---|---|---|---|---|
| Metals selenium, arsenic, cadmium, lead, zinc, iron, boron, and magnesium | USEPA 200.8<br>USEPA 6010/6020 | 50 ml | Glass or plastic<br>HNO3 preservative | 6 months |
| Mercury | USEPA 7471 | 30 ml | Glass, plastic, or polytetrafluoroethylene | 28 days |
| Methylmercury | USEPA 1630 and USEPA 1631E | 50 ml | Fluoropolymer bottle with HCl preservative | 6 months |
| Speciated selenium | IC-ICP-CRC-MS | 50 ml | Field-filtration with 0.45um syringe filter | 1 year |
| Speciated arsenic | USEPA 1632 | 100 ml | Glass with HCl preservative | 28 days |
| Sulfate | EPA 300.0 | 10 ml | Glass or plastic | 28 days |
| Total Organic Carbon | USEPA 9060 | 25 ml | Glass with H2SO4 preservative | 28 days |
| Hardness | SM 2340C | 50 ml | Glass or plastic with HNO3 preservative | 6 months |

(a) The listed volumes are minimum requested. Extra mass is needed for QC samples and reruns.

(b) Assumes samples received on ice and frozen upon receipt by laboratory

# 5. SAMPLE NOMENCLATURE

The CAP identifies the transect numbering protocols planned for the Herrington Lake sample locations, as follows:

- LHL – lower Herrington Lake
- UHL – upper Herrington Lake
- MHL – mid-Herrington Lake
- DR – Dix River
- CI – Curds Inlet
- HQ – HQ Inlet
- HI – Hardin Inlet

Within the CAP, the LHL, UHL, and MHL transects are further numbered as Transect 1, 2, 3, for each portion of the lake (e.g., LHL-1, LHL-2).

Quality assurance samples for pore water samples will be labeled as follows:

- "EB" – for equipment blanks;
- "DUP" – for field duplicate samples; and
- "MS/MSD" or "M" – for matrix spike/matrix spike duplicates.

The following sample identification convention for the discrete sediment pore water samples will be followed using the prefix "PW." Each discrete sample will use the following general identification convention:

- [sample matrix code][discrete sampling number][sample date]

An example discrete pore water sample identification number is as follows:

- **PW-001 - LHL1-170912** – indicates the pore water sample number 1 (PW-001) collected on September 12, 2017 (170912).
- The nomenclature for duplicate samples will include the matrix (PW) and transect number (LHL1) but not the exact sample location within that transect (blind duplicate) such as: **PW – LHL1—170912-DUP.**

# 6. HANDLING, PACKING, AND SHIPPING

The following identifies the procedures that will be used to handle, pack, and ship the aquatic vegetation and aquatic invertebrate samples:

- Samples will be labeled using nomenclature that follows typical nomenclature guidelines described in Section 5.
- Samples will be double wrapped and labeled with water-proof labels.
- Samples will be placed immediately on ice[1] and will be stored on ice or in a refrigerator until shipment to the laboratory.
- Samples will be maintained via Chain of Custody until shipment via overnight express to the analytical laboratory as deemed appropriate to meet hold times described in Section 3.

[1] Samples will be placed on wet ice. Dry ice may be used in place of wet ice if necessary.

# 7. DATA RECORDING AND MANAGEMENT

Field notes will be recorded during sampling activities, and at a minimum, will include the following:

- Names of field crew and oversight personnel
- Sample location (GPS of the CAP transect)
- Date, time, and duration of sampling
- General weather conditions
- Substrate characterization
- General water quality parameters
- Sample information (including matrix, sampling method, sample mass, sample ID, sample date and time)
- Habitat description where collected
- Photograph number when pictures are taken (if necessary)

# 8. QUALITY ASSURANCE/QUALITY CONTROL

One QA sample will be collected (from a location to be determined in the field based on sample availability) for a duplicate and for matrix spike/matrix spike duplicate analysis. If this is not feasible, the laboratory will analyze a lab spiked blank and spiked duplicate. Data validation will be performed in accordance with Section 2.4.1 of the CAP

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