UPPER COLUMBIA RIVER

Quality Assurance Project Plan
Methods Development for the White Sturgeon Sediment Toxicity Study - Amendment No. 1

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SECTION A: PROJECT MANAGEMENT

A1 TITLE AND APPROVAL SHEET

QUALITY ASSURANCE PROJECT PLAN
METHODS DEVELOPMENT FOR WHITE STURGEON
AMENDMENT NO. 1

Approvals

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A3 DISTRIBUTION LIST

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A4 INTRODUCTION

A4.1 Introduction

This amendment outlines a proposed modification to sediments for use in methods development work as outlined within the April 2010 *Methods Development for the White Sturgeon Sediment Toxicity Study* quality assurance project plan (QAPP). The modification outlined herein is limited to substituted sediments for methods development work and the inclusion of a diffusive sampling technique (peepers).

All other aspects associated with field sampling and handling procedures, laboratory analysis, and Quality Assurance/Quality Control (QA/QC) measures remain unchanged from the approved QAPP (April 2010).

A4.2 Modifications

Because sediments from the gravel bar at Deadman's Eddy are presently not available, aquarium grade silica sand as produced by GEOsystems substrates[1] will be added to the methods development work described in the approved QAPP (April 2010).

In conjunction with the testing and evaluation of suction devices, pore water sampling will also be evaluated using a diffusive sampling technique (i.e., peepers[2]). Typical peeper design and implementation procedures to be evaluated are presented within Appendix A.

[1] http://www.geosystemaquarium.com/geoeng/products/substrate.php?link=4
[2] When sediments from the gravel bar at Deadman's Eddy become available other diffusive sampling techniques such as DGTs (Diffusive Gradients in Thin-Films) will also be evaluated.

SECTION B: REFERENCES

Teck American Incorporated. 2010. Upper Columbia River: Quality Assurance Project Plan for the Methods Development for the White Sturgeon Sediment Toxicity Study. Prepared for Teck American Incorporated. April, 2010. ENTRIX Inc., Saskatoon, SK

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APPENDIX A

TYPICAL PEEPER METHODOLOGY

USGS CERC peeper method for in-situ sampling of sediment pore water

Prepared by B. Brumbaugh; revised 9-30-09.

Overview: Peepers (equilibrium diffusion samplers) are used for in-situ sampling of sediment pore water for dissolved metals and other ions. They are constructed from a plastic snap-cap vial that is filled with de-ionized water and fitted with a micro-porous membrane. The peeper volume is kept small relative to that of the surrounding sediment so as to minimize disturbance to the sediment/pore-water equilibrium and depletion of dissolved metals in the surrounding pore water. For laboratory sediment toxicity tests, "mini" peepers are prepared from a 2.9-mL (2.5 mL nominal), low-density polyethylene snap-cap vial (Fisher Sci cat. no. 03-338-1B) and a 0.45 µm pore-size, 25 mm diameter polyether-sulfone (PES) filter membrane (VWR Sci cat no 28147-617). Field peepers are prepared using the 50-mL vial and 47 mm diameter membrane counterparts.

Preparation: Using a hole-punch tool (e.g., Roper-Whitney hand punch model 5JR), punch out a single 6-mm diameter hole in the center of each vial cap (with the cap still attached to the vial) for the mini peeper, or five 6-mm holes for the field peeper. A suitable number of punched vials are cleaned by soaking overnight (with occasional agitation to wet all vial surfaces) in a suitable plastic bottle containing 4M HNO_3, 2M HCl. The vials are triple rinsed with DI water then stored in DI water until further preparation. To prepare the peepers, a small acid-cleaned plastic tub is half-filled with freshly de-oxygenated, de-ionized water (DODI water) and up to 20 cleaned and punched vials (caps in the open position) are submerged in it (use a fresh batch of DODI water for each 20 vials). Wearing suitably clean waterproof gloves, a submerged vial is grasped with the cap open and held with its top edge just at the water surface. A PES filter membrane is then placed over it (aligned with minimal overlap near the hinged area of the vial) and the perforated cap is carefully closed to seal the membrane. Excess membrane material on the outside is torn away and discarded, but a small portion opposite the hinge is left to facilitate grasping both the membrane and cap when opening. Once seated, the membrane is inspected for rupture and the peeper is inverted above the water to check for leaks. The peeper should be inverted only momentarily, otherwise water droplets may begin to seep through the membrane. A correctly filled and sealed peeper will have no air bubbles inside. A small nylon cable tie (10-cm long for the min-peeper) is strapped around the vial for aid in gauging depth when inserting in the sediment and to facilitate retrieval. The finished peeper is transferred to a wide-mouth 1-L or 2-L acid-cleaned HDPE or PP bottle containing DODI water and a few hundred mg of metal-chelating resin (e.g., Chelex-100™). After 20 vials are prepared the storage bottle is "topped off" with DODI water, then capped tightly and placed in a refrigerator. Peepers can be stored in this manner for several weeks before use, but the surrounding water must be de-oxygenated once again at least 24 hours in advance if they are to be stored for more than 48 hours before use (note that this is somewhat of an arbitrary guideline for minimizing DO inside the peeper).

Deployment/retrieval: Peepers are transported to testing area in the bottle filled with DODI water (on ice if transporting to the field). Deployment is performed in one of three ways depending on the sediment density and grain size. For most sediment the peeper can be pressed into the sediment using a spatula while grasping the cable tie with plastic (hemostat

type) forceps, then "back-filled" with a small amount of sediment. If difficulty is encountered with that approach, (e.g., for dense or granulated sediments), a partial trench is first dug into the sediment using the spatula. Alternately, the peeper and the sediment can be loaded into the beaker simultaneously. For all burial methods, the bottom (closed end) of the peeper is situated next to the wall of the container and the membrane end near the center so as to maximize the sediment volume "seen" by the membrane face. After 7 to 14 days in the sediment, the peeper is pulled from the sediment by grasping the tag end of the wire tie with the plastic forceps and is carefully agitated in the overlying test water to remove loosely adhering sediment particles. It is then rinsed with a stream of DI water directed tangentially to the lid and membrane until all visible particles are displaced, then blotted dry using a laboratory tissue. The membrane and cap assembly is carefully opened with a DI-rinsed, gloved hand by grasping the protruding edge of membrane in conjunction with the edge of the cap. It is opened carefully to prevent the membrane from falling into the liquid inside the vial. Liquid is transferred to an acid-cleaned 30 mL LDPE bottle using a disposable polyethylene mini-pipette. Just before use, each mini-pipette is rinsed by drawing a small volume of high-purity 1% nitric acid, inverting, and then expelling to waste. The same sequence is then repeated with high purity water. Using the cleaned mini-pipette, the liquid from the peeper is transferred to an acid cleaned 30-mL bottle. About 2.5 mL of high purity 1.1% (v/v) HNO_3 is added to the peeper vial using a squirt bottle and with the mini-pipette this liquid is transferred to the receiving bottle in the same manner. The partially diluted sample is diluted to a final volume of 29 ml (29.2 g) with 1.1% (v/v) HNO_3 for analysis by ICP-MS (1% HNO_3 matrix, 10-fold dilution factor). For larger peepers, the liquid can be similarly transferred, but without 10-fold dilution. Once transferred, those simply can be acidified to 1% v/v HNO_3 for analysis.

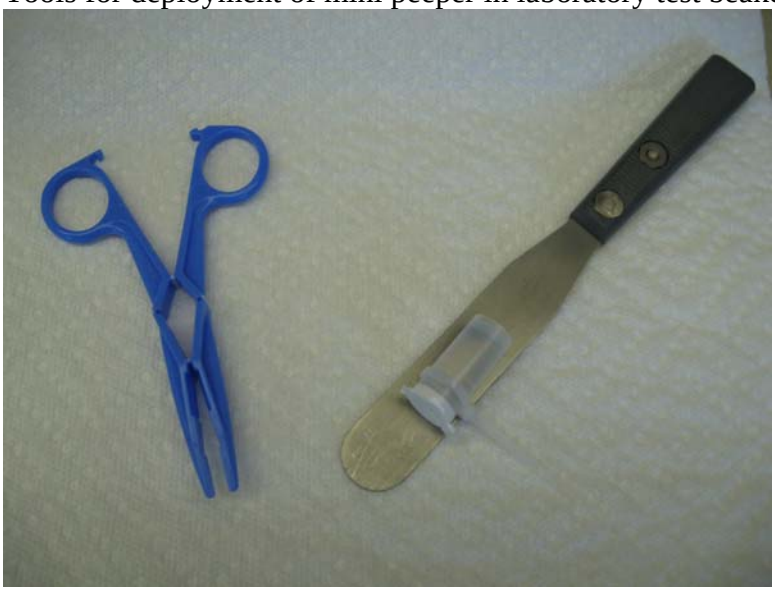
Blanks: Prepare three peepers for each 20 samples to serve as blanks. After deployment, store the bottle containing these extra peepers in the DODI water and Chelex-100 resin in a refrigerator. Process the blank peepers at the same time as those that were deployed.

Field considerations: Equilibration time depends on several factors, most notably: 1) peeper dimensions (face area vs. length); 2) sediment permeability; and 3) temperature. The conductivity in peepers deployed at increasing time intervals can be used to gage the minimum deployment time needed, but in most instances 2 weeks is sufficient. Membrane fouling, which depends on temperature and water characteristics, generally limits the maximum deployment time to about 4 weeks. For field deployments, again, depending on sediment type, preparation of a small trench might be necessary. This can be accomplished with a large spatula, a trowel, or in cobble sediments a "dibble" tool, such as that used to plant tree saplings (see Brumbaugh and others, 2007).

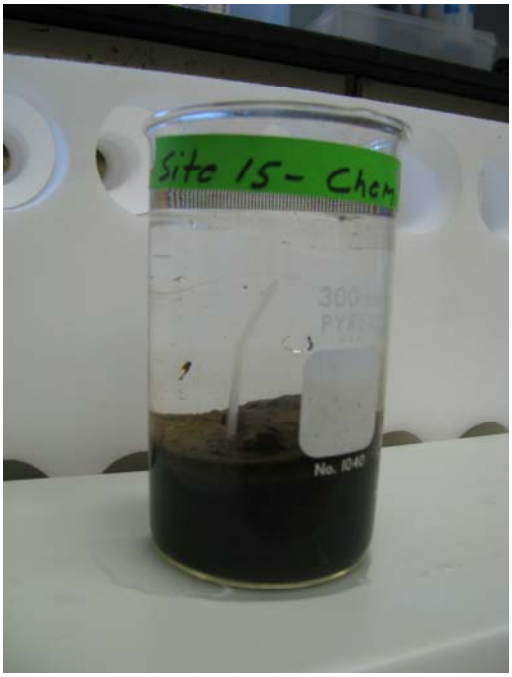
Reference: Brumbaugh, W.G., May, T.W., Besser, J.M., Allert, A.L. Schmitt, C.J., 2007, Assessment of elemental concentrations in streams of the New Lead Belt in southeastern Missouri, 2002–05: U.S. Geological Survey Scientific Investigations Report 2007–5057, 57 p. available on-line at: http://pubs.usgs.gov/sir/2007/5057/

Photos.

Tools for deployment of mini peeper in laboratory test beaker.



Mini peeper in sediment test beaker.



Preparation for transfer and dilution of mini peeper liquid to sample bottle.