

UPPER COLUMBIA RIVER

Quality Assurance Project Plan Methods Development for the White Sturgeon Sediment Toxicity Study - Amendment No. 2

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SECTION A: PROJECT MANAGEMENT

A1 TITLE AND APPROVAL SHEET

QUALITY ASSURANCE PROJECT PLAN
METHODS DEVELOPMENT FOR WHITE STURGEON
AMENDMENT NO. 2

Approvals

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A3 DISTRIBUTION LIST

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A4 INTRODUCTION

A4.1 Background Information

As detailed within the April 2010 Quality Assurance Project Plan (QAPP) for *Methods Development for the White Sturgeon Sediment Toxicity Study* and its amendment (i.e., No. 1), a number of laboratory based tests have been identified to evaluate the flow-through, fluvial simulation systems for sediment toxicity testing outlined within the May 2010 *Assessment of Sediment Toxicity to White Sturgeon (Acipenser transmontanus)* QAPP. An integral component of the methods development work is to evaluate a number of sampling techniques and methods to select those that accurately and precisely record chemical concentrations at the points of exposure for early life stages (ELS) of white sturgeon. Based on the experience of the Principal Investigator and researchers at the University of Saskatchewan (U of S) Aquatic Exposure Laboratory, potential points of exposure for ELS of white sturgeon to dissolved constituents¹ within flow-through exposure chambers are defined as follows:

- Overlying water – water located in the water column of the exposure chamber;
- Sediment interface water – surface water which is located within the water column approximately 0 to 0.5 inches (in.) above the sediment surface and water found within the interstices of sediment located approximately 0 to 0.5 in. below the sediment surface in the exposure chamber².

In addition to obtaining samples at the appropriate points of exposure, porewater³ will also be collected. It is critical that the recorded concentrations be accurate, precise, complete, and readily interpretable in regard to exposure of ELS white sturgeon.

As outlined within the April 2010 QAPP, there are a number of sampling techniques (e.g., suction and diffusion) that can be used to quantify dissolved chemical concentrations at the above-listed points of exposure and medium. This amendment outlines a proposed modification to that QAPP that evaluates the accuracy and precision

¹ Dissolved constituents (e.g., metals) are operationally defined as that fraction which passes through a 0.45 µm (micron) filter.

² Based on visual observations from researches at the U of S Aquatic Exposure Laboratory, sturgeon fry/larvae have been observed to ‘burrow’ into sediment interstices at depths of up to approximately 1 centimeter below the sediment surface layer.

³ For the purposes herein, water found within the interstices of sediment at depths greater than approximately 0.5 inches will be considered as ‘porewater’.

of suction (e.g., airstones), diffusion-equilibrium (e.g., peepers⁴) and diffusion-kinetic (e.g., Diffusion Gradients in Thin-Film [DGT]) sampling techniques within flow-through exposure chambers. Minor modifications intended to optimize operations of the flow-through exposure chambers with natural sediments are also described herein.

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 and its amendment.

A4.2 Additional Flow-Through Fluvial Exposure Chamber Testing

A flow-through fluvial exposure chamber has been developed and is routinely employed to evaluate surface water chronic exposures to fish including white sturgeon at the U of S Aquatic Exposure Laboratory. These chambers were modified and extended such that they allow testing of sediments under chronic fluvial exposure conditions. To ensure that these modified exposure chambers are operating optimally prior to the introduction of test organisms per the May 2010 *Assessment of Sediment Toxicity to White Sturgeon (Acipenser transmontanus)* QAPP; a number of experimental tests are being conducted (refer to the April 2010 QAPP). This amendment identifies and presents additional testing to be included as part of the methods development work. Specifically, it outlines approaches to: 1) evaluate sediment homogenization procedures; 2) evaluate exposure chamber conditions with the introduction of site-specific sediments⁵; and 3) evaluate the accuracy and precision of sampling techniques at defined points of exposure.

A4.2.1 Sediment Homogenization

Objective: Confirm the effectiveness and reliability of sediment homogenization procedures outlined within Standard Operating Procedure Number 8 (SOP-8) of the May 2010 QAPP *Assessment of Sediment Toxicity to White Sturgeon (Acipenser transmontanus)*.

Approach: In addition to off-site reference sediment samples (refer to the April 2010 QAPP); samples collected from the gravel bar at Deadman's Eddy will be mixed and homogenized in a specially designed 'concrete mixer.' The large rotating drum of the mixer contains a plastic liner that has been tested and confirmed to not leach measurable

⁴ Details associated with the use of peepers are outlined and presented within the QAPP for *Methods Development for the White Sturgeon Sediment Toxicity Study - Amendment No 1* (April 2010).

⁵ Samples from the gravel bar at Deadman's Eddy were collected on May 27, 2010 per the April 2010 QAPP.

amounts of metals (cadmium [Cd], copper [Cu], lead [Pb], and zinc [Zn]) into a water rinsate. Compositated sediment will be tumbled for a period long enough (e.g., hours) to create a visual appearance of complete mixing. Two sediment samples each taken from the top, middle, and bottom layers of the drum for a total of six samples, will be analyzed for Cu, Cd, Pb and Zn to verify the visual determination/approach of a homogenized sediment. If analyses are greater than ± 20 percent of the mean of the six samples, then the sediment will be tumbled for another period, and the analysis repeated. Methods for sample collection and storage will be as stated in the April 2010 QAPP; analysis will be conducted by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at the U of S to provide rapid response (refer to Table 3).

Decision criteria: Sediments will be determined to be completely homogenized when the maximum from all measurements on all six samples are within ± 20 percent of the mean. Photographs of homogenized sediment will be taken to document the visual appearance of samples at homogeneity.

A4.2.2 Time to 'steady-state' after introduction of test sediments into the test chambers

Objective: Characterize changes in water quality, if any, in overlying water upon the introduction of natural sediments into the exposure chamber under optimized hydrological flow conditions as determined during methods development work detailed within the April 2010 QAPP. The primary objective is to identify the minimum period of time needed for the exposure chamber to attain a 'steady-state' for the basic water quality parameters. It is important to note that the objective of this work is not to attain steady-state conditions for chemicals of potential concern (COPCs) such as the metals; but rather, to ensure that non-COPCs do not adversely affect test results (i.e., introduce uncertainty) when organisms are introduced.

Approach: Basic water quality parameters will be monitored at 0, 12, 24, and 48 h, and every 48 h thereafter until steady state. Measurements will be made of conductivity, dissolved oxygen (DO), DOC, ammonia, nitrate, color, total dissolved solids (TDS), and pH at the inflow and outflow of the exposure chamber. All measurements will be made at the U of S according to methods in the April 2010 QAPP (and as shown here in Tables 4 and 5).

Decision criteria: 'Steady state' is attained when measured water quality parameters do not vary more than 10 percent from one measurement time to the next.

A4.2.3 Exposure Point Concentrations – Accuracy and Precision

An integral component of methods development work is to evaluate sampling techniques and methods that accurately and precisely record chemical concentrations and provide readily interpretable data at potential points of exposure for ELS of white sturgeon. Potential points of exposure will include overlying water and sediment interface water. In addition, porewater (i.e., located below the sediment water interface layer) will also be measured. This measurement in conjunction with the overlying surface water may provide data to help determine if concentrations at the sediment water interface can be reasonably estimated with sufficient accuracy (i.e., bounded) by surface water and porewater concentration measurements. The precision in estimating sediment interface water exposure point concentrations may also be increased if the difference between surface water and porewater concentrations is relatively small.

Exposure point concentrations for COPCs such as metals, are operationally defined as the dissolved fraction (i.e., that fraction which passes through a 0.45 µm filter), as detailed within the May 2010 QAPP. For metals, the dissolved concentration provides the most relevant measure of exposure concentration because:

- Ambient Water Quality Criterion (AWQC) for metals are based on the dissolved concentration;
- Interstitial Water Toxicity Unit (IWTU) methods are calculated by normalization of porewater concentrations by the AWQC (USEPA 2005); and
- Dissolved concentrations can be adjusted to bioavailable concentrations using the Biotic Ligand Model (BLM).

Sampling techniques to quantify dissolved concentrations at the aforementioned points of exposure (see Section A4.1) and underlying porewater; and to be evaluated as part of methods development work will include: suction (e.g., airstones and a modified pipette⁶), diffusion (e.g., peepers and DGTs). The following sections are intended to outline how the accuracy and precision of these techniques will be evaluated.

Accuracy – Exposure Point Concentrations

To assess the accuracy of the above-mentioned sampling techniques, the following assessment will be performed using de-chlorinated water from the U of S laboratory,

⁶ The modified pipette is applicable and will only be evaluated in the extraction of overlying surface water and sediment interface water, and may for simplicity be referred to as a grab sample.

spiked with a mixture of four primary metals of interest (i.e., Cd, Cu, Pb, and Zn); under two separate dissolved organic carbon (DOC) regimes (i.e., ~2.0 mg/L and ~5.0 mg/L)⁷.

The following metal mixture will be evaluated under the above-mentioned DOC regimes:

- Cd = 0.5 µg /L; (introduced as cadmium chloride hemi-pentahydrate; purity 99.999%)
- Cu = 10 µg /L; (introduced as copper (II) sulfate pentahydrate; purity 99.995 %)
- Pb = 5 µg /L; (introduced as lead (II) nitrate; purity 99.99%); and
- Zn = 20 µg/L; (introduced as zinc chloride; purity 98%).

The preceding concentrations are approximately equal to the maximum (rounded-up) dissolved porewater concentrations reported by the U.S. Geological Survey (2006), see Table 24 of the report.

Additional water quality characteristics to be maintained during the work include: water hardness (~70 mg/L as CaCO₃), pH (~7.9 s.u.), and temperature (15°C)⁸. Triplicate samples will be collected from each of the four above-mentioned devices (modified pipette, airstone, peeper and DGT) at four distinct times over the course of 16 days (i.e., days 2, 4, 8, and 16). A summary of the total number of samples to be collected per device, per DOC level is presented within Table 1. Sample collection, shipping, storage and analysis will be as described in the April 2010 QAPP and are shown here in Tables 2 and 3.

It is important to note that, unlike airstones that can be sampled throughout the exposure period (i.e., 16 days); both diffusion sampling techniques (peepers and DGTs) are designed for a one-time sampling event (i.e., disposable use). Therefore, to ensure that samples can be collected throughout the duration of the time-series (i.e., 16 days), dedicated diffusion samplers will be installed at the beginning of the evaluation and three samplers of each type will be removed at each of the appropriate discrete time steps. It is also important to note that DGT samplers do not directly measure exposure point concentrations (of labile metal), but rather, record the mass of accumulated metal

⁷ These DOC regimes were selected to be representative of the UCR water (~2 mg/L) and a slightly higher concentration (5 mg/L) to determine if DOC will affect the accuracy and precision of measuring the dissolved metals or of DOC itself. The slightly elevated DOC concentration as identified for the purposes of this amendment is equal to the 'unadjusted' laboratory water at the U of S Aquatic Exposure Laboratory and as such, will not require any modification.

⁸ Water quality characteristics listed and proposed herein are consistent with those outlined within the May 2010 QAPP *Assessment of Sediment Toxicity to White Sturgeon (Acipenser transmontanus)* and are designed to simulate river water characteristics.

within the device. Therefore, to obtain an estimate of the exposure point concentration, the mass of accumulated metals within the DGT will be translated using the following relationship⁹:

$$C_{DGT} = \frac{M \times \Delta g}{D \times t \times A}$$

Where:

C_{DGT} = Concentration of metal measured by DGT

M = Mass of metal accumulated on the resin as determined by ICP-MS

Δg = Thickness of the diffusive gel plus the thickness of the filter membrane (cm)

D = Diffusion coefficient of the metal in the gel (cm²/cm)

T = Deployment time (s)

A = Exposure area (cm²)

Typical processing of DGTs will be carried out per the Standard Operating Procedure as provided by Dr. Brumbaugh (Appendix A).

Precision – Exposure Points

For this work, two potential points of exposure have been identified (Section A4.1). They include: 1) overlying water and 2) sediment interface water. In addition and as previously discussed porewater concentrations will also be measured.

Of the above-listed measurement locations, overlying water is by far the easiest to measure, while sediment interface water and porewater measurements inherently present unique challenges. One of the primary factors that will influence the precision of any one of the sampling devices (i.e., suction and diffusion samplers) is its actual placement within the exposure chamber. Therefore, to test the precision of the sampling devices, procedures detailed above for evaluating their accuracy will be repeated under the regime where DOC concentrations are approximately 2 mg/L¹⁰; but with sediments

⁹ The relationship is based on the theory of DGTs. Based on personal communication (April 27, 2010 electronic mail message) with Dr. William (Bill) Brumbaugh of the USGS however; an Excel spreadsheet will be made available to Dr. Markus Hecker of the U of S which can be used to facilitate the conversion of DGT results to average porewater metal concentrations.

¹⁰ Other water quality characteristics to be maintained during this portion of the work will remain unchanged from previous tests (i.e., hardness @ ~70 mg/L as CaCO₃, pH @ ~7.9 s.u., and temperature @ 15°C).

placed at the bottom of the exposure chambers. Each device will be strategically placed to measure the desired exposure points.

To aid in the evaluation, two types of sediments will be used: 1) laboratory control sediments as outlined within the April 2010 QAPP amendment spiked with the same metal concentrations as described above in the accuracy measurement section; and 2) site-specific sediments collected from the gravel bar at Deadman's Eddy under simulated river conditions (without being spiked with metals). These two experimental 'treatments' are intended to allow comparisons of the precision of sampling devices under different ranges of COPC concentrations.

A brief description of how each of the sampling devices will be deployed within the exposure chambers is described below.

Sediment Interface Water: It is anticipated that both suction and diffusion sampling techniques can be used to evaluate this exposure point (i.e., the layer of water located within approximately 0.5 in. above and below the sediment surface in the exposure chamber). The suction technique will be limited to slow suction with a pipette or needle and syringe positioned approximately at the sediment surface. Peepers will be placed vertically (i.e., membrane facing upward) within the sediment such that the top of the peeper membrane is located approximately 0.5 inches below the sediment surface (see footnote 4). Similarly, DGTs will be deployed vertically within sediments until the tip of the probe contacts the bottom of the exposure chamber, and the cover plate is oriented perpendicular to the sediment surface and parallel to the flow. To quantify this exposure point, the DGT probe will protrude above the plane of the sediment surface layer approximately 0.5 in. as well. These same DGT samplers will also measure concentrations in porewater that is up to 0.5 in below the sediment surface, as the resin gel can be sectioned such that the portion just below the sediment plane can be analyzed separately from the portion above the sediment plane. As with tests designed to evaluate the accuracy of suction and diffusion samplers, triplicate samples will be collected from all three devices at four distinct times over the course of 16 days (i.e., days 2, 4, 8, and 16) and analyzed for dissolved metals. Sample collection, storage and analysis will be as described in the April 2010 QAPP and are shown here in Tables 2 and 3.

Porewater: As with the sediment interface water, both suction and diffusion sampling techniques will be assessed for this medium (i.e., the water found within the interstices of sediment located greater than 0.5 in below the sediment surface in the exposure chamber). Airstones will be positioned within the sediment such that the top of the

airstone is covered by at least 1.5 in. of sediment. Similarly, peepers will be vertically inserted in the sediment such that the top of the peeper is located at least 1.5 in. below the plane of the sediment surface. The same DGT samplers employed in the above-mentioned sediment interface water sampling would also be employed to evaluate porewaters, as the resin gel will be sectioned such that the portion extending down into the sediment below the sediment water interface and analyzed separately. Again triplicate samples (requiring placement of three each of the DGT, peeper, and airstone devices) will be collected at four distinct times over the course of 16 days (i.e., days 2, 4, 8, and 16). Sample collection, shipping, storage and analysis will be as described in the April 2010 QAPP and are shown here in Tables 2 and 3.

Data Analysis

Accuracy -- For the purposes of this work, concentrations in the "source water" (refer to Table 1) are considered the actual or true concentration of elements and DOC at the point of exposure. Therefore, accuracy of the sampling devices from both the water only and sediment exposure chambers will be assessed and expressed in terms of percent error from the "source water" (analyses of grab samples). Percent error will be calculated as follows:

$$\% \text{ Error} = \frac{|C_{\text{Device}} - C_{\text{Source}}|}{C_{\text{Source}}} \times 100$$

Where:

C_{Device} = Concentration of metal measured by sampling device

C_{Source} = Concentration of metal measured in grab samples of "source water"

Comparisons among the results for all elements obtained with the different sampling technologies may also be compared using parametric (e.g., Analysis of Variance followed by Student's t-test), or non-parametric (e.g., Kruskal-Wallis followed by the Mann Whitney U-test) statistics, as appropriate based on the distribution of the data.

Precision -- For the purposes of this work, the precision of the devices for measuring each of the exposure point concentrations will be determined by comparison of the coefficient of variation (CV) or standard deviation (SD) at each time period. That is, the CV (or SD) of the suction, peeper and DGT samples at each time interval and each exposure point will be determined and the one with the smallest CV or SD will be considered the most precise. Furthermore, the change in mean value over time for each device within exposure point will be plotted to determine a) how each type of device

accounts for changes over time (if any), and b) that the DGT is not saturated (which would underestimate exposure point concentrations). Corroboration that each device has collected water from the correct location (surface water, sediment interface water, porewater) will be based on comparison of metal concentrations among the three locations at the earlier collection times in the laboratory control sediments. It is presumed *a priori* that there is a gradient between sediment and surface water during initial set-up due to the spiking of the sediments. Therefore, initial measurements (time 0 and Day 2) should show higher concentrations in overlying water, lowest concentrations in porewater, and intermediate concentrations in sediment interface water. Note that inclusion of a dye as a means of verification is not necessary as it would simply act as another constituent; dye may not diffuse properly into peepers and cannot be used with DGT probes.

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.
- Teck American Incorporated. 2010. Upper Columbia River: Quality Assurance Project Plan for the Methods Development for the White Sturgeon Sediment Toxicity Study Amendment No. 1. Prepared for Teck American Incorporated. April, 2010. ENTRIX Inc., Saskatoon, SK.
- USEPA. 2005. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Metal Mixtures (Cadmium, Copper, Lead, Nickel, Silver and Zinc). EPA-600-R-02-011. Office of Research and Development. Washington, DC 20460
- U.S. Geological Survey. 2006. Concentrations of elements in sediments and selective fractions of sediments, and in natural waters in contact with sediments from Lake Roosevelt, Washington, September 2004. USGS Open File Report 2006-1350. U.S. Geological Survey, Reston, Virginia, USA.

Table 1. Total Number of Water Samples per Test Treatment.

	pH ¹				DOC ²				Hardness ¹				Dissolved Metals ³ (Cd, Cu, Pb, and Zn)				Temperature ¹				TOTAL
	Water only (DOC@2)	Water only (DOC@5)	Control Sediment ⁴	Deadman's Eddy ⁴	Water only (DOC@2)	Water only (DOC@5)	Control Sediment	Deadman's Eddy	Water only (DOC@2)	Water only (DOC@5)	Control Sediment	Deadman's Eddy	Water only (DOC@2)	Water only (DOC@5)	Control Sediment	Deadman's Eddy	Water only (DOC@2)	Water only (DOC@5)	Control Sediment	Deadman's Eddy	
Start (Day 0)																					
Source Water	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	60
Airstone/Grab	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Peeper	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DGT	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Day 2																					
Source Water	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	60
Airstone/Grab ⁵	3	3	6	6	3	3	6	6	3	3	6	6	3	3	6	6	0	0	0	0	72
Peeper ⁵	3	3	6	6	3	3	6	6	3	3	6	6	3	3	6	6	0	0	0	0	72
DGT ⁵	0	0	0	0	0	0	0	0	0	0	0	0	3	3	6	6	0	0	0	0	18
Day 4																					
Source Water	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	60
Airstone/Grab ⁵	3	3	6	6	3	3	6	6	3	3	6	6	3	3	6	6	0	0	0	0	72
Peeper ⁵	3	3	6	6	3	3	6	6	3	3	6	6	3	3	6	6	0	0	0	0	72
DGT ⁵	0	0	0	0	0	0	0	0	0	0	0	0	3	3	6	6	0	0	0	0	18
Day 8																					
Source Water	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	60
Airstone/Grab ⁵	3	3	6	6	3	3	6	6	3	3	6	6	3	3	6	6	0	0	0	0	72
Peeper ⁵	3	3	6	6	3	3	6	6	3	3	6	6	3	3	6	6	0	0	0	0	72
DGT ⁵	0	0	0	0	0	0	0	0	0	0	0	0	3	3	6	6	0	0	0	0	18
Day 16																					
Source Water	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	60
Airstone/Grab ⁵	3	3	6	6	3	3	6	6	3	3	6	6	3	3	6	6	0	0	0	0	72
Peeper ⁵	3	3	6	6	3	3	6	6	3	3	6	6	3	3	6	6	0	0	0	0	72
DGT ⁵	0	0	0	0	0	0	0	0	0	0	0	0	3	3	6	6	0	0	0	0	18
TOTAL	39	39	63	63	39	39	63	63	39	39	63	63	51	51	87	87	15	15	15	15	948

- Notes:**
1. The nominal source water pH, hardness, and temperature to be established during the performance of work is approximately 7.9 standard units (su), 70 mg/L as CaCO₃, and 15 degrees Celsius, respectively; and is consistent with simulated river water as outlined within the May 2010 QAPP.
 2. Two nominal dissolved organic carbon (DOC) concentrations will be evaluated in water only exposures. These include a DOC = ~2.0 mg/L (representative of simulated river water) and one at ~5.0 mg/L (unadjusted average concentration of U of S laboratory water).
 3. The nominal source water dissolved metal concentrations are intended to be as follows: Cd = 0.5 µg /L, Cu = 10 µg /L, Pb = 5 µg /L, and Zn = 20 µg/L. Only simulated river water will be employed within the Deadman's Eddy treatment/experiment.
 4. Tests using sediments will only be performed at DOC concentrations of ~2.0 mg/L (i.e., simulated river water).
 5. Samples will be collected from both pore- and sediment interface water.
 6. Treatments using Deadman's Eddy sediments will **not** be performed using spiked water samples. They will only be exposed to simulated river water consistent with the May 2010 QAPP.

Table 2. Required Sample Containers, Preservation, and Holding Times for Sediment Samples (homogenization methods development).

Container ^a		Analysis	Preservation	Holding Time	Minimum Sample Size
Type	Size				
G/P	8 oz	Grain size	4±2°C	6 months	100 g
G/P	8 oz	Metals/metalloids, and percent moisture	4±2°C	6 months	10 g
G/P	16 oz	Archive	Freeze	1 year	40 g +

Notes:

G/P = glass or plastic

TOC = total organic carbon

Table 3. Laboratory Methods for Analysis of Sediment Samples (homogenization methods development).

Analytes	Quantitative Analysis	
	Protocol	Procedure
Cadmium, copper, lead, zinc	EPA 6020	ICP/MS
Grain Size	ASTM D422	Sieving

Notes:

ASTM = American Society of Testing and Materials

EPA = U.S. Environmental Protection Agency

ICP/AES = inductively coupled plasma/atomic emission spectrometry

Table 4. Required Sample Containers, Preservation, and Holding Times for Overlying Water, Sediment-Water Interface Water, and Porewater Samples.

	Container ^a		Preservation	Holding Time	Proposed Minimum Laboratory Sample Size ^{b, c}
	Type	Size			
Conventional Parameters					
Alkalinity as CaCO ₃	HDPE	1000 mL	4±2°C	14 days	25 mL
Conductivity	HDPE	250 mL	4±2°C	28 days	25 mL
Dissolved oxygen	HDPE	250 mL	Not Applicable	None	25 mL
Dissolved organic carbon	HDPE	250 mL	H ₂ SO ₄ to pH <2; 4±2°C	28 days	10 mL
Hardness as CaCO ₃	HDPE	with metals	5 mL of 1:1 HNO ₃ ; 4±2°C	6 months	with metals ^d
Total dissolved solids	HDPE	with alkalinity	4±2°C	7 days	200 mL
Total suspended solids	HDPE	with alkalinity	4±2°C	7 days	200 mL
Nutrients					
Ammonia	HDPE	250 mL	H ₂ SO ₄ to pH <2; 4±2°C	28 days	5 mL
Nitrate + nitrite	HDPE	250 mL	H ₂ SO ₄ to pH <2; 4±2°C	28 days	5 mL
Metals					
Cadmium, copper, lead, zinc	HDPE	250 mL	5 mL of 1:1 HNO ₃ ; 4±2°C	6 months	15 to 20 mL

Notes:

HDPE = high density polyethylene bottle

H₂SO₄ = sulfuric acid

^a Sample container sizes may be modified to meet laboratory requirements

^b Extra sample volume will be collected at a frequency of 5 percent of samples to accommodate requirements for laboratory quality control samples.

^c If insufficient volume for running all analytes is collected, priority for analysis will be Metals, followed by organic carbon, alkalinity + TDS, and nutrients.

^d These analyses will be conducted from the same sample collected for metals analysis; therefore, no additional volume is required.

Table 5. Laboratory Methods for Analysis of Pore-, Interface, and Surface Water Samples.

Analytes	Sample Preparation		Quantitative Analysis	
	Protocol	Procedure	Protocol	Procedure
Conventional Parameters				
Alkalinity as CaCO ₃	--	--	SM 2320B	Titrimetric
Conductivity	--	--	SM 2510B	Instrument Probe
DO	--	--	ASTM D888-09	VWR Symphony Probe ^a
DOC	SM 5310C	Filtration, chemical oxidation	SM 5310C	Infrared detector
Hardness as CaCO ₃	--	--	SM 2340C	Titrimetric
TDS	--	--	SM 2540C	Gravimetric
TSS	--	--	SM 2540D	Gravimetric ^a
pH	EPA 150.1/SM 4500 H ⁺ B	--	EPA 150.1/SM 4500 H ⁺ B	Electrometric ^a
Nutrients				
Ammonia	SM 4500-NH3 G	Buffered to pH 9.5	SM 4500-NH3 G	Colorimetric ^a
Nitrate + nitrite	--	--	EPA 300.0	Ion chromatography ^a
Metals				
Cadmium, copper, lead, zinc	EPA 3005	Acid digestion	EPA 6020	ICP/MS

Notes:

ASTM=American Society for Testing and Materials
 CaCO₃ = calcium carbonate
 DO = dissolved oxygen
 DOC = dissolved organic carbon
 EPA = U.S. Environmental Protection Agency
 ICP/MS = inductively coupled plasma/mass spectrometry
 SM = Standard Methods for the Examination of Water and Wastewater
 TDS = total dissolved solids
 TSS = total suspended solids
^a to be measured at U of S

APPENDIX A

STANDARD OPERATING PROCEDURE FOR PROCESSING OF DGT PROBES (USGS-CERC)

Processing DGT Sediment probes for analysis of trace metals
Prepared by W. Brumbaugh, USGS-CERC, rev. April 01, 2009

Overview: DGT sediment probes are deployed for 24 to 48 hr in test sediments to assess metals fluxes from pore water and overlying water. After retrieval, the probe surface is sectioned horizontally into 1-cm or smaller components to allow spatially-resolved measurement of metals fluxes across redox boundaries. The probe is prepared according to manufacturer instructions (<http://www.dgtresearch.com/dgtresearch/dgtresearch.pdf>.) This document describes procedures for removing and processing the DGT resin for analysis by ICP-MS.

Retrieval. The sediment probe is removed and a small area of the outer edge of the plastic support frame associated with the sediment-water boundary is blotted dry with a laboratory tissue. A line is drawn with a laboratory marker to indicate the location of surface of the sediment layer. Normally, this is easily identifiable by coloration on the portion of the probe that was submerged in the sediment. Each probe is individually sealed in a pre-labeled zip-seal polyethylene bag and stored in a refrigerator until ready for processing.

Processing. For each probe, multiple 15-mL polypropylene screw-cap centrifuge tubes are used for collection of the horizontal sections of the Chelex-gel substrate. Typically, three to four 1-cm tall sections are prepared (one section to represent the overlying water just above the sediment-water interface and two or three sections below). Collection tubes are pre-cleaned by soaking overnight in 1.6 M nitric acid and then are filled with high-purity water until ready for use. The DGT probe is rinsed with a stream of high-purity water and a cotton swab is used to remove any remaining particles and moisture from the outer surface of the sampling window. The probe is then placed flat on a paper towel for marking and sectioning. Using a small ruler, marks representing the desired section heights are made with a fine-tipped lab marker on the edge of the probe housing. Using a clean scalpel, horizontal incisions are made through all 3 layers at each mark. Vertical incisions are made along the window edges just before removing each section. Starting at the top incision, the scalpel is used to peel away both the outer membrane and the outer (thicker) hydrogel layer. The inner Chelex-gel layer should remain attached to the backing plate. The scalpel is then used to scrape the desired Chelex-gel layer inward from both ends, thus forming it into a tiny roll which can be scooped up with the scalpel tip and transferred to a centrifuge tube. It may be necessary to dab it onto the inside wall of the tube to get it to release from the scalpel. The gel section is rinsed from the wall of the tube into the bottom of the tube by pipette addition of 1.5 mL 1.6 M high purity nitric acid. It is capped and allowed to soak in the dilute acid for at least 24 hours to release metals bound by the Chelex resin.

Analysis. When ready for analysis, the extract containing the Chelex is diluted to 15 mL with high-purity water, mixed, and allowed to settle briefly. The gel containing the Chelex resin should settle to near the bottom, thus allowing transfer of up to 10 mL the extract for analysis by decantation.