STANDARD OPERATING PROCEDURE FOR:

SEDIMENT SAMPLING FOR AVS/SEM ANALYSIS

TVA-KIF-SOP-09

Prepared by

Environmental Standards, Inc.

for

Tennessee Valley Authority

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Environmental Resources and Services

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1.0 PURPOSE

This standard operating procedure (SOP) provides the technical requirements and operational guidelines for sampling and handling of sediments and sub-aqueous ash being analyzed for Acid Volatile Sulfide (AVS) and Simultaneously Extracted Metals (SEM) at Kingston Fossil Plant (KIF). The term AVS represents the amount of sulfide in sediments available for binding heavy metals, and the term SEM represents the amount of heavy metals in sediment that could be available to plants and animals. The term "heavy metals" in this scenario generally refers to cadmium, copper, lead, nickel, silver and zinc although additional metals (such as arsenic) can also be requested for analysis. The exact list of metals must be specified on the Chain-of-Custody (COC) records.

The following is a simplified summary of the AVS/SEM evaluation.

- If AVS > ΣSEM, a non-bioavailability of metals in the sediment investigation area is indicated.
- If AVS ≤ ΣSEM, the potential for bioavailability of heavy metals into the aquatic biota system is indicated.
- If there are low values of ΣSEM (< 1 μmole/g), little potential for bioavailability is indicated (McGrath *et al.,* 2002).

These calculated concentrations of metal mixtures in sediment are protective of the presence of benthic organisms. The requirements of this SOP are applicable to sampling of sediments for AVS/SEM analysis in streams, rivers, lakes, and ponds in the KIF area.

2.0 GENERAL CONSIDERATIONS

General guidelines and sediment sampling techniques can be found in the *Sediment Sampling* SOP (TVA-KIF-SOP-05).

Potential hazards associated with the planned tasks shall be thoroughly evaluated prior to conducting field activities. The site-specific Health and Safety Plan (HASP) provides a description of potential hazards and associated safety and control measures.

Additionally, a Float Plan shall be completed prior to traveling anywhere on a water vessel. A Float Plan includes a description of the water vessel, specifies who is on board, provides a description of the safety equipment being carried, and indicates destination and expected time of return.

3.0 SEDIMENT SAMPLING PROCEDURES FOR AVS/SEM ANALYSIS

The following sections describe the procedures for sampling sediment. In the event these procedures cannot be performed as written in this SOP, field personnel must contact the Project Manager to get approval for the deviation to the procedure prior to conducting sampling activities. If the Project Manager cannot rectify the circumstances leading to the deviation, then the Project Manager shall contact the Quality Assurance/Quality Control (QA/QC) Lead to-determine if the deviation is acceptable from the standpoint of effecting data reliability. If the deviation is not acceptable to the QA/QC lead, then the field team must cease sampling activities until the issue associated with the deviation is resolved. Documentation of approved deviations will be recorded in the field logbook.

The sampling equipment and selected methodology depend on the depth and velocity of the water, the consistency of the bottom sediments (such as soft, hard, or rocky), and the project-specific quality control (QC) sample volume requirements. Care must be taken when selecting equipment and designing the sampling approach to ensure that representative samples are collected. Accurate prediction of exposure of benthic organisms to metals is critically dependent on sampling appropriate sediment horizons at appropriate times.

It will be necessary to use a sampling vessel (boat or barge) to collect sediment samples. Navigate the sampling vessel to the coordinates stored in a GPS unit. Use an anchor (or spuds, if available) in a manner that will hold the sampling vessel within 10 feet of the target coordinates. If anchors or spuds are used, allow five minutes to elapse before commencing sampling to allow any suspended solids to settle downstream. Field conditions may be such that anchoring or using spuds is not effective (such as rock bottom, high flow velocity). At these locations, the vessel's engine should be used to maintain position over the sampling location.

3.1 AVS/SEM Mechanical Sampling Techniques

Sampling devices used to collect undisturbed sediment samples should be selected by considering the depth and flow of the water above the sample and the bed characteristics of the bottom. Usually, manual equipment (scoops and trowels) cannot be used for off-shore sampling—box- core samplers or core samplers are more appropriate. The goal of this sampling is to collect an undisturbed sample from the top several inches of sediment or sub-aqueous ash. An example checklist of equipment and materials needed for sampling is provided in Table 1.

a. Locate sediment sampling locations in accordance with the project guidance documents. Locate sediment sampling locations using a portable Global Positioning System (GPS) unit, if possible, and document in the field logbook and with photographs. When possible, sampling should proceed from downstream to upstream locations so that disturbance related to sampling does not affect the sample quality.

b. Identify the physical characteristics of the sediment before sampling since stones and gravel may prevent a box corer from penetrating the sediment or sealing the sampler in some instances.

c. Use a properly decontaminated sampler to collect sediment samples. Decontaminate sampler following procedures described in *Decontamination of Equipment* SOP (TVA-KIF-SOP-08) for organic and inorganic analysis.

d. Sample the undisturbed sediments using box cores, grabs, or coring. Coring is generally less disruptive, facilitates sampling of sediment horizons, and limits potential metal contamination and oxidation if sealed PVC core liners are used (U.S. Environmental Protection Agency [EPA]).

e. When using a coring sampler, simply drive the core sampler into the sediment and retract the sampler so that the sediment is recovered. If recovery of surface sediment is difficult, drive the core sampler deeper into more competent sediment and section off the surface sediment for sampling.

f. Immediately cap samples on both ends.

g. At a minimum, sample the surface 2.0 centimeters (cm) (or 0.75 inches) of sediment between November and early May (EPA). A sample depth of 2.0 cm is appropriate for monitoring; however, for instances such as dredging or in risk assessments where depths greater than 2.0 cm are important, sample depths should be planned based on particular study needs.

h. Avoid mixing of aerobic and anaerobic sediments because the trace metal speciation in the sediments will be altered (Bufflap and Allen, 1995). Visual differentiation (such as color change) will determine if aerobic and anaerobic sediments are present in the sample.

i. Measure Oxidation Reduction Potential (ORP) and pH using a hand-held field measuring device. Collect sediment samples needed for the measurement of ORP

and pH from co-located samples so that the investigative sample remains undisturbed. Combine 10 grams of sediment with 10 grams of deionized water in a small, clean container. Gently mix into a slurry with a disposable sampling scoop and let slurry settle. Repeat mixing every minute for five minutes. Record the measurements for subsequent use to determine the integrity of the sample. Use care to *gently* insert the pH or combination pH/ORP probe into slurry to avoid breaking the thin glass bulb of the pH sensor.

j. Transfer collected sample to the processing area in an upright position while minimizing disturbances. Care should be given to protect the sample through transport back to land.

3.2 AVS/SEM Manual Sampling Techniques

The techniques described below may be employed to manually collect sediment without the use of a mechanical sampling device typically in shallow waters.

a. Locate sediment sampling locations in accordance with the project guidance documents. Locate sediment sampling locations using a portable Global Positioning System (GPS) unit, if possible, and document in the field logbook and with photographs. When possible, sampling should proceed from downstream to upstream locations so that disturbance related to sampling does not affect the sample quality.

b. Identify the physical characteristics of the sediment before sampling since stones and gravel may prevent a box corer from penetrating the sediment or sealing the sampler in some instances.

c. Utilizing clean Nitrile gloves, place a clean core liner in a vertical position and slowly advance the open (top and bottom) core liner through the water and to the top of the ash located under the water at the ash/water interval.

d. Using a very slow push and twist method, advance the core through the ash approximately 12 inches to 18 inches and then stop.

e. Taking care not to disturb the ash within the core tube (limiting up/down or side to side motions), place a core liner end cap or rubber stopper into the top of the core liner in an attempt to create sufficient vacuum in the liner to hold contained ash/water during removal of the core liner.

f. Remove the core liner utilizing a very slow pull and twist method taking care not to fully remove the core liner from the core location until ready to cap the in-water end of the core liner.

g. Using a free hand, place hand under water as close to the core bottom and prepare to cap in-water core end as core liner is extracted from core location.

Note: This activity should be completed quickly to avoid loss of ash as core liner is extracted from core location. It is recommended that a rubber stopper be used on the bottom end of the core liner as it can be more effectively placed quickly as compared to the core liner end cap.

h. At a minimum, sample the surface 2.0 centimeters (cm) (or 0.75 inches) of sediment between November and early May (EPA). A sample depth of 2.0 cm is appropriate for monitoring; however, for instances such as dredging or in risk assessments where depths greater than 2.0 cm are important, sample depths should be planned based on particular study needs.

i. Avoid mixing of aerobic and anaerobic sediments because the trace metal speciation in the sediments will be altered (Bufflap and Allen, 1995). Visual differentiation (such as color change) will determine if aerobic and anaerobic sediments are present in the sample.

j. Measure Oxidation Reduction Potential (ORP) and pH using a hand-held field ice. Collect sediment samples needed for the measurement of ORP and pH from co-located samples so that the investigative sample remains undisturbed. Combine 10 grams of sediment with 10 grams of deionized water in a small, clean container. Gently mix into a slurry with a disposable sampling scoop and let slurry settle. Repeat mixing every minute for five minutes. Record the measurements for subsequent use to determine the integrity of the sample. Use care to *gently* insert the pH or combination pH/ORP probe into slurry to avoid breaking the thin glass bulb of the pH sensor.

k. Transfer collected sample to the processing area in an upright position while minimizing disturbances. Care should be given to protect the sample through transport back to land.

3.3 Sample Processing, Handling, Packing, Storing, and Shipping

Samples will be marked, labeled, packaged, and shipped in accordance with the *Sample Labeling, Packing, and Shipping* SOP (TVA-KIF-SOP-07). In addition, the following procedures shall be followed.

a. Place core liner with sample in a processing stand.

b. Remove the top end cap and evacuate excess water above the ash/sediment sample using a Peristaltic pump and clean tubing. The Peristaltic pump tubing shall remain far enough away from the ash or sediment to not allow evacuation of the sediment.

c. Use a decontaminated PVC pipe cutter to cut and remove the excess core liner above and below the sample. Leave sufficient "lip" on the core liner to attach end caps.

d. Seal the sample container with zero headspace in an inert environment (such as filling headspace with oxygen-free nitrogen or argon) to minimize exposure to oxygen. If sediments are stored in this manner, there will be little oxidation of AVS even after several weeks (EPA). Capping and sealing should be done in the following manner. First, cap and seal the top end of the core; then cap and seal ¾ of the bottom end of the core. Apply the inert gas and finish sealing the bottom end of the core.

   Note: Store and use compressed gases with adequate ventilation. Secure cylinders in an upright position. Use a suitable hand truck to move the cylinders. Use a pressure reducing regulator or separate control valve to safely discharge gas from the cylinder.

e. Place sediment samples not immediately shipped for overnight delivery in sealed airtight glass jars or cores and either refrigerate or freeze them.

f. Select appropriate storage conditions: frozen at ≤ 10°C is preferred if sediments are to be used for chemical analysis while refrigeration to <6°C is preferred if sediments are to be used for biological tests.

g. Select appropriate sample containers: glass sampling containers are preferred for samples that will not be frozen while plastic containers are acceptable for samples that will be frozen.

h. If using a core sampler, make sure to label the orientation of the core sample with an up arrow. Position sample containers in an upright position if using a dredge or benthic grab sampler.

Note: Sediments experiencing oxidation of AVS during storage will become less black or grey if oxidized. The rate of metal-sulfide oxidation is markedly less than that of iron sulfide; and therefore, release of metal during storage is unlikely (EPA).

3.4 Field Quality Control Samples

Field QC samples may include equipment rinsate blanks, field duplicate samples, and matrix spike and matrix spike duplicate samples. A description of common field QC samples and the associated collection method are provided in the project-wide QAPP and the *Field Quality Control Sampling* SOP (TVA-KIF-SOP-11). Determine QC sample requirements before choosing a sediment sampling device.

Note: For AVS/SEM sampling, ensure that the investigative sample container/core liner has sufficient volume capacity to hold two or three aliquots for duplicates or matrix spike/ matrix spike duplicate (MS/MSD) without compromising the depth requirements of the sample. For core sampling, this can be achieved with multiple core liners being driven at co-locations. For spring-loaded sediment dredge or benthic grab samplers, the sample "bucket" should contain sufficient volume to hold two or three aliquots of sediment.

3.5 Field Logbook Documentation

Field logbooks will be maintained by the Field Team Leader to record daily activities. The minimum requirements for field logbook documentation are discussed in *Field Documentation* SOP (TVA-KIF-SOP-06).

The Field Team Leader and/or designee will review the field logbook entries for completeness and accuracy and will indicate this review by initialing each page of the logbook. The Field Team Leader is responsible for completion of the required data collection forms.

3.6 Decontamination and Cleanup

Sampling equipment decontamination will be performed in a manner consistent with the *Decontamination of Equipment* SOP (TVA-KIF-SOP-08). Wastes produced during sampling or decontamination will be managed in accordance with *Management of Investigation-Derived Waste* SOP (TVA-KIF-SOP-12).

4.0 REFERENCES

- Bufflap W.E., and H.E. Allen. *Sediment Interstitial Water Collection Methods: A Review.* Water Research 29:65-177, 1995.
- McGrath, J.A., P.R. Paquin, and D.M. DiToro. *Use of the SEM and AVS Approach in Predicting Metals Toxicity in Sediments*, Fact Sheet on Environmental Risk Assessment, International Council on Mining and Minerals, 2002
- Tennessee Valley Authoring (TVA). *Decontamination of Equipment* SOP (TVA-KIF-SOP-08), March 2009.
- TVA. *Field Documentation* SOP (TVA-KIF-SOP-06), March 2009.
- TVA. *Field Quality Control Sampling* SOP (TVA-KIF-SOP-11), April 2009.
- TVA. *Health and Safety Plan* (HASP), Kingston site-specific plan, 2009.
- TVA. *Management of Investigation-Derived Waste* SOP (TVA-KIF-SOP-12), March 2009.
- TVA. *Sample Labeling, Packing, and Shipping* SOP (TVA-KIF-SOP-07), March 2009.
- TVA. *Sediment Sampling* SOP (TVA-KIF-SOP-05), March 2009.
- United States Environmental Protection Agency (EPA). *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)*. Document # EPA-600-R-02-011, January 2005.

Table 1. Sediment Sampling Equipment and Material Checklist	
Item Description	**Check**
AVS/SEM Sediment Sampling Equipment	
GPS Device	
Vessel (boat or barge)	
Portable table	
Plastic sheeting	
Nitrile gloves	
PVC pipe cutter	
Tape measure	
Digital camera	
Sediment grab sampler or similar device that obtains an undisturbed sample	
Inert Gas	
Inert gas regulator & applicator	
pH & ORP instruments, probes and calibrants	
2" Lexan MacroCore liners or laboratory-supplied bottleware	
End caps or rubber stoppers	
Peristaltic pump and disposable tubing	
Storing equipment (bungee cords, rack)	
Sample freezer	
Chain-of-Custody forms and custody seals	
Sample labels	
Packing tape	
Permanent marker	
Field logbook	
Decontamination and Waste Management Equipment	
DOT-approved 55-gallon drums or other appropriate containers	
Drum wrench	
Duct tape	
Rinse bottle	
Potable water	
Non-phosphate detergent	
Decontamination fluids (deionized water, nitric acid, isopropyl alcohol)	
Buckets or tubs	
Brushes	
Trash bags	
Paper towels	

End of Procedure