Washington State Department of Ecology

Environmental Assessment Program

Standard Operating Procedure for the Collection and Field Processing of Metals Samples

Version 1.4

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Signatures on File

Please note that the Washington State Department of Ecology's Standard Operating Procedures (SOPs) are adapted from published methods, or developed by in-house technical and administrative experts. Their primary purpose is for internal Ecology use, although sampling and administrative SOPs may have a wider utility. Our SOPs do not supplant official published methods. Distribution of these SOPs does not constitute an endorsement of a particular procedure or method.

Any reference to specific equipment, manufacturer, or supplies is for descriptive purposes only and does not constitute an endorsement of a particular product or service by the author or by the Department of Ecology.

Although Ecology follows the SOP in most instances, there may be instances in which Ecology uses an alternative methodology, procedure, or process.

SOP Revision History

Revision Date	Rev number	Summary of changes	Sections	Reviser(s)
2/1/2007		Editorial; formatting	All	Bill Ward
		Comments	All	Dave Hallock
2/2/2007	1.1	Edits based on comments	All	Bill Ward
3/21/2007	1.1	Editorial Review	All	Bill Kammin
4/2/2007	1.2	Edits based on comments	All	Bill Ward
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10/14/2010	1.4	Minor revisions to blank samples	5 & 8	Bill Ward
10/15/10	1.4	Recertified	All	Bill Kammin

Environmental Assessment Program

Standard Operating Procedure for the Collection and Field Processing of Metals Samples

1.0 Purpose and Scope

1.1 This document is the Environmental Assessment Program (EAP), Environmental Monitoring and Trends Section, Freshwater Monitoring Unit, Standard Operating Procedure (SOP) for collecting freshwater metals samples for laboratory analysis. The sample collection and field processing methods generally follow those under Method 1669 (EPA, 1996).

2.0 Applicability

2.1 This SOP is intended for the collection of freshwater metals samples to be analyzed by one or more of the following methods:

2.2 Dissolved Metals Method – Modified version of EPA Method 200.8 (Using inductively coupled plasma - mass spectrometry (ICP-MS))

2.3 Total Recoverable Metals Method – Method EPA 202.2 (Hotplate Assisted Digestion) and a modified version of EPA 200.7 Method (ICP).

2.4 Total Mercury Method – Method EPA 245.7 (Free Bromide Digestion) and EPA Method 245.1 (Cold Vapor Absorbance)

3.0 Definitions

3.1 EAP – Environmental Assessment Program.

3.2 Ecology – Washington State Department of Ecology.

3.3 EIM – Environmental Information Management System. A searchable database developed and maintained by the Washington State Department of Ecology.

3.4 FEP – fluorinated ethylene propylene resin

3.5 Field Logbook – A weather resistant logbook containing “Rite in the Rain” ® writing paper used to document any and all field activities, sample data, methods and observations for each and all collection sites.

3.6 MQO’s – Measurement Quality Objectives

3.7 MSDS – Material Safety Data Sheets provides both workers and emergency personnel with the proper procedures for handling or working with a particular substance. MSDS’s include information such as physical data (melting point, boiling point, flash point, etc.), toxicity, health effects, first aid, reactivity, storage, disposal, protective equipment and spill/leak procedures.

3.8 QA – Quality Assurance

4.0 Personnel Qualifications/Responsibilities

4.1 Field operations require training specified in EAP's Field Safety Manual (Ecology, 2006) such as First Aid, CPR, and Defensive Driving.

4.2 Boat operations require that staff meet specific training requirements as described in EAP's Field Safety Manual, such as an EAP Boating Course and an approved Boating Safety Course.

4.3 Because the procedure requires the use of hazardous materials, training is required as per the Ecology Chemical Hygiene Plan and Hazardous Material Handling Plan (Section 1) (WA State Department of Ecology 2006), which include Laboratory Safety Orientation, Job-Specific Orientation and Chemical Safety Procedures. The Standard Operating Procedures in Section 16 of the Chemical Hygiene Plan and Hazardous Material Handling Plan for handling chemicals must also be followed.

5.0 Equipment, Reagents, and Supplies

Metals Sampler W/sample bottle

5.1 Metals sampler
5.2 Sampling ropes 1 @ 10 ft., 1 @ 35 ft. and 2 @ 55 ft.
5.3 Extension pole with three prong **stainless** clamp
5.4 Cooler containing ice
5.5 Hand vacuum pump with hose
5.6 500mL Teflon FEP bottles pre-filled with DI water by the lab
5.7 125 mL narrow mouth poly bottle containing H2S04 preservative for hardness sample
5.8 Disposable 0.45 micron cellulose nitrate filter unit (pre-cleaned Nalgene #450-0045, type S)
5.9 Small Teflon vials containing 5 ml concentrated nitric acid preservative
5.10 Powder free vinyl disposable gloves

6.0 Summary of Procedure

6.1 Sampling procedures generally follow EPA Method 1669. Samples are collected as single grabs in a 500ml Teflon FEP bottle using the stainless steel metals sampler or by hand. Care must be used at all times when collecting and processing metals samples to avoid contaminating the inside of the sample bottle or cap with debris or ambient air. Also, samples need to be preserved with acid and placed in ice in a cooler as soon as possible after collection. The holding time prior to analysis for all metals, except mercury, is six months. The holding time for mercury is 28 days.

6.2 Metals Sampler Method. This method is typically used to collect samples from a bridge or from the stream bank through the use of a rope.

6.2.1 Invert the Teflon sample bottle, remove the cap, pick up the metals sampler, and rinse the sampler with the deionized water that empties out of the bottle.

6.2.2 After the bottle empties, set the sampler down and replace the bottle cap.

6.2.3 Then fit the sample bottle into the base of the stainless steel metals sampler.

6.2.4 Remove the bottle cap and place it in the clean plastic bag it shipped in.

6.2.5 Lower the sampler bottle cap lifting arm until the sampler cap covers the bottle opening (make sure the lifting arm can move up freely).

6.2.6 Attach the sampling rope.

6.2.7 Move to a well mixed location such as the deepest part of the active channel where a representative sample may be collected.

6.2.8 Carefully lower the sampler to the water surface, taking care to not dislodge bridge debris onto it. Allow the bottom of the sampler to touch the water surface, and then raise the sampler off the water for a few moments to allow any debris from the bottom of the sampler to drop off and float away. Note: This minimizes the sampling of any debris from the bottom of the sampler.

6.2.9 Lower the sampler about 15 cm (6 inches) into the water. Allow the current to re-orient the sampler so the sample bottle is on the upstream side of the sampler. Then rapidly lower the sampler about 0.5 meters to completely submerge it. This minimizes the sampling of surface film. Note: At about 25 cm under the water surface, the sampler should automatically raise the bottle cap and allow the bottle to fill. Also, it may take more than 45 seconds for the bottle to fill.

6.2.10 Retrieve the filled bottle taking care to not dislodge bridge debris onto it or the sampler.

6.2.11 Remove the filled sample bottle from the sampler, cap it with the original cap from the clean plastic bag, and place the bottle in the Ziploc bag it shipped in.

6.2.12 Repeat the procedure to obtain a second metals sample.

6.2.13 Return to the van with the samples and sampling gear.

6.3 Hand Dip Method. This method is typically used to collect samples from a small or shallow stream, or near the bank of a large stream.

6.3.1 Move to a well mixed location such as the deepest part of the active channel or another location where a representative sample may be collected. *Note: Do not contaminate the sample location by wading upstream of it or collect a sample from an eddy that had been waded.*

6.3.2 Grab the base of the sample bottle with one hand, invert the Teflon sample bottle, remove the cap, and let the deionized water empty out of the bottle.

6.3.3 Reach upstream and plunge the bottle into the water about 15 cm (6 inches) and then tip the bottle mouth up toward the water surface.

6.3.4 Allow the bottle to fill and then take it out of the water.

6.3.5 Replace the cap in a way that avoids contamination to the inside of the bottle and place the bottle in the Ziploc bag it shipped in.

6.3.6 Repeat the procedure to obtain a second metals sample.

6.3.7 Return to the van with the samples and sampling gear.

6.3.8 Extension Pole Method. This method is typically used to reach a more representative or undisturbed sample location from the stream bank or when wading in a lake or slow moving stream.

6.3.9 Secure the metals sample bottle in the extension pole clamp.

6.3.10 Move to a well mixed location where a representative sample may be reached with the pole. *Note: Do not contaminate the sample location by wading upstream of it or collect a sample from an eddy that had been waded.*

6.3.11 Invert the Teflon sample bottle, remove the cap, and let the deionized water empty out of the bottle. Also, put the cap into the Ziploc bag the bottle shipped in and put the bag in a location that will prevent contamination to the inside of the cap

6.3.12 Position the bottle over the desired sample location.

6.3.13 Invert the bottle and in one quick motion plunge the mouth of the bottle into the water about 15 cm (6 inches). Then slowly move the bottle upstream with the bottle mouth tipped toward the water surface until the bottle has filled (in lakes slowly move the tipped bottle away from the bottle entry point until it completely fills).

6.3.14 Take the filled bottle out of the water and then replace the bottle cap in a way that avoids contamination to the inside of the cap and bottle.

6.4 Field Processing - Total Recoverable Metals and Total Mercury

6.4.1 Put on vinyl gloves.

6.4.2 Remove the disposable filter unit from the large Ziploc bag and set the bag and filter unit aside.

6.4.3 Remove the cap from the first sample bottle (do not set the cap down)

6.4.4 If necessary, gently squeeze the side of the sample bottle to displace about 5 ml of sample to make room for the Nitric acid preservative.

6.4.5 Carefully uncap the small Teflon vial containing 1:1 Nitric acid and add the acid to the sample. Screw the cap on the sample and then re-cap the Nitric acid vial.

6.4.6 Attach the Total Metals and Total Recoverable Mercury sample tag to the sample bottle.

6.4.7 Place the tagged sample in its original Ziploc bag along with the empty (capped) Teflon vial, eliminate air from the Ziploc bag, seal it and then put it in the large Ziploc bag that contained the filter unit.

6.5 Field Processing - Dissolved Metals

6.5.1 Attach the hand pump hose to the filter unit.

6.5.2 Remove the cap from the second sample bottle; lift up one side of the filter unit lid about 3 cm (1 inch), and pour the sample into the top of the unit. Note: Avoid touching or contaminating the inside of the filter unit.

6.5.3 Cap the empty sample bottle and put it into the large Ziploc bag that also contains the tagged total metals sample.

6.5.4 Hold onto the filter unit with one hand and use the other hand to squeeze and release the hand pump lever to create a vacuum to filter the sample.

6.5.5 Filter as much of the sample as possible (at least half).

6.5.6 Empty deionized water from an unused Teflon bottle and put the cap on the bottle opening.

6.5.7 Unscrew the bottom of the filter apparatus, remove the cap from the top of the unused Teflon sample bottle (do not set the cap down), pour the filtered sample into the Teflon bottle, and put the cap on the bottle opening.

6.5.8 Carefully uncap the small Teflon vial containing 1:1 Nitric acid, lift the cap off the bottle containing the filtered sample, and add the acid to the sample. Screw the cap on the sample and then re-cap the Nitric acid vial.

6.5.9 Attach the Dissolved Metals sample tag to the sample bottle.

6.5.10 Place the tagged sample in its original Ziploc bag along with the empty (capped) Teflon vial.

6.5.11 Eliminate air from the Ziploc bag, seal it, and put it in the large Ziploc bag that contains the tagged total metals sample and the empty Teflon bottle.

6.5.12 Eliminate air from the large Ziploc bag and place the bagged samples on ice in a cooler.

6.6 Field Processing - Hardness

6.6.1 Hardness samples are sub-sampled from the 1 L bottle used to collect nutrient samples or the 1 L bottle used to collect pH/conductivity samples (See Stream Sampling SOP). The 1 L total suspended solids (TSS) or 0.5 L general chemistry samples may also be used if the other grab samples are unavailable.

6.6.2 Pour approximately 100 mL of the field grab sample into the 125 mL hardness sample bottle (wide mouth poly bottle containing H2S04 preservative).

6.6.3 Cap and invert the hardness sample bottle to ensure that the acid gets mixed into the sample. *Note: Avoid contact with the acid.*

6.6.4 Label the hardness sample and place the sample in ice in a cooler.

7.0 Records Management

7.1 All hardcopy documentation of the data, such as completed Field Logbook and Field Data Report Forms are kept and maintained by the project lead. These documents are organized in binders or in expanding files. After about six years, hardcopies are boxed and moved to EAP archives.

7.2 Data collected for Ecology's Ambient River and Stream Monitoring Program will be entered into our Access-based database, reviewed and verified following the Quality Control and Quality Assurance procedures (see 8.1 below), uploaded into EIM, and posted on our web page http://www.ecy.wa.gov/programs/eap/fw_riv/rv_main.html .

7.3 Data collected for special project studies will be reviewed, verified, and stored based on the QAPP for the project.

8.0 Quality Control and Quality Assurance

8.1 The data QA program for field sampling consists of three parts: (1) adherence to the SOP procedures for sample/data collection and periodic evaluation of sampling personnel, (2) consistent instrument calibration methods and schedules, and (3) the collection of field quality control (QC) samples based on the study Quality Assurance Project Plan requirements. Our QA program is described in detail in Hallock and Ehinger (2003).

8.2 True Process Field Blank Samples. These field QC samples are subject to the sample site collection and dissolved metals sample processing conditions. The expected value for this analyzed result is the reporting limit. Higher results would indicate that sample contamination had occurred during field processing or laboratory analysis.

8.2.1 Load the sampler with a metals bottle (do not empty the special DI water out of the bottle). Go to the sample site, remove the bottle cap, and put the cap in a dry Ziploc bag to avoid any contamination. Lower the Metals Sampler to the water surface (do not immerse anything into the stream), retrieve the sampler, and cap the bottle.

8.2.2 Return to the van and follow the Dissolved Metals processing procedure (see procedure 6.5 above), refill the original sample bottle, and attach the dissolved metals QC tag.

9.0 Safety

9.1 Safety is the primary concern when collecting samples. Since most sample sites are located on highway bridges, road and pass conditions should always be checked before departure (especially in winter). If roadside hazards, weather, accidents, construction, etc. make sample collection dangerous, then skip that station. Note the reason on the Field Data Report Form and notify your supervisor of the hazard when you return to the office. If the hazard is a permanent condition, relocation of the station may be necessary. Review Ecology's Safety Program Manual periodically to assist with these safety determinations.

10.0 References

10.1 Ecology, 2006. Environmental Assessment Program Safety Manual. Olympia, WA.

10.2 Ecology, 2006. Chemical hygiene plan and hazardous material handling plan. Olympia, WA.

10.3 Ecology, 2007. Standard Operating Procedures for the Collection and Processing of Stream Samples. Olympia, WA.

10.4 EPA, 1996. Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. Washington, D.C.

10.5 Hallock, D. and W. Ehinger, 2003. Quality Assurance Monitoring Plan: Stream Ambient Water Quality Monitoring. Washington State Department of Ecology, Olympia, WA. 27 pp. Publication No. 03-03-200. www.ecy.wa.gov/biblio/0303200.html