DEPARTMENT OF ECOLOGY
State of Washington

Standard Operating Procedure EAP029, Version 1.7

Collection and Field Processing of Metals Samples

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Purpose of this Document

The Washington State Department of Ecology develops Standard Operating Procedures (SOPs) to document agency practices related to sampling, field and laboratory analysis, and other aspects of the agency's technical operations.

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Washington State Department of Ecology
Environmental Assessment Program
Standard Operating Procedure for the Collection and Field Processing of Metals Samples
EAP029, Version 1.7

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The Washington State Department of Ecology's (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 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	Revision number	Summary of changes	Sections	Revisers
2/1/2007		Editorial; formatting	All	Bill Ward
		Comments	All	Dave Hallock
2/2/2007 3/21/2007	1.1 1.1	Edits based on comments Editorial Review	All All	Bill Ward Bill Kammin
4/2/2007 4/16/2007	1.2 1.2	Edits based on comments Final Review	All All	Bill Ward Jim Ross
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10/14/2010 10/15/2010	1.4 1.4	Minor revisions to blank samples Recertified	5 & 8 All	Bill Ward Bill Kammin
4/9/2013	1.5	Added new chemical awareness language. Attached the MSDS sheet	5	Bill Ward
12/30/2014		Added new Hg methods	All	Bill Ward
1/7/2015 1/9/2015		Edits Review Recertified	2, 6 All	Howard Christensen and Casey Clishe Bill Kammin
12/27/2017 1/09/2018	1.6 1.6	Updated with clarifying edits Recertified	1 - 8 All	Bill Ward and Terri Hoselton Bill Kammin
04/05/2021	1.7	Accessibility updates	All	Joan LeTourneau

1.0 Purpose and Scope

1.1 This document is the Environmental Assessment Program (EAP)'s Western Operations Section Freshwater Monitoring Unit's 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 and field processing 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 Metals Method – Prep Method EPA 200.2 (Hot Block Assisted Digestion) and a modified version of EPA 200.8 Method (ICP-MS).

2.4 Total Mercury Method –EPA 1631 (Cold Vapor Atomic Florescent Spectroscopy (CVAFS))

2.5 Hardness Method - SM2340B

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 waterproof writing paper used to document field activities, sample data, methods, and observations that are not noted on the field data sheet.

3.6 Field Data Report - Form used to document field activities, sample data, methods, and observations.

3.7 MQOs – Measurement Quality Objectives

3.8 MSDS – Material Safety Data Sheets provides both workers and emergency personnel with the proper procedures for handling or working with a particular substance. The MSDS 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.

3.9 QA – Quality Assurance

4.0 Personnel Qualifications/Responsibilities

4.1 Field operations require training specified in EAP's Field Safety Manual (Ecology, 2016), 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, 2015), 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

5.1 Metals sampler

5.2 Sampling ropes 1 @ 10 ft., 1 @ 35 ft., and 2 @ 55 ft.

5.3 Extension pole with bottle clamp

5.4 Cooler containing ice

5.5 Hand vacuum pump with hose

5.6 4 - 500mL Teflon FEP bottles pre-filled with DI water by the lab

5.7 125 mL narrow-mouth poly bottle containing Sulfuric acid (H_2SO_4) preservative for hardness sample

5.8 Lab provided disposable 0.45 micron cellulose nitrate filter unit (pre-cleaned Nalgene #450-0045, type S)

5.9 Lab provided small Teflon vials containing 5 ml concentrated nitric acid (HNO_3) preservative (see Quality Assurance SharePoint for MSDS). *Danger* this acid causes severe burns by all exposure routes.

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, by hand or with a pole sampler. 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.

6.2 All samples, except for mercury, need to be preserved with acid and then placed in ice in a cooler as soon as possible after collection. The holding time for mercury is 28 days. The holding time all other metals is six months.

6.3 **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.

6.3.1 Remove the cap, invert the Teflon sample bottle, and rinse the sampler with the deionized water that empties out of the bottle.

6.3.2 Replace the bottle cap after the bottle empties, and set the sampler down.

6.3.3 Fit the sample bottle into the base of the stainless steel metals sampler.

6.3.4 Completely loosen the bottle cap while it is kept on the bottle opening. Gently lower the sampler lifting-arm hose clamp over the cap, tighten the clamp to it, and then make sure the lifting-arm may easily lift it off the bottle opening.

6.3.5 Attach the sampling rope.

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

6.3.7 Put on a pair of work gloves.

6.3.8 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, 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.*

6.3.9 Lower the sampler about 15 cm (6 inches) into the water. Allow the current to reorient it 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 to minimize 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 or multiple drops to get the bottle to fill.*

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

6.3.11 Hold the bottle cap down on the bottle opening, carefully loosen the lifting arm hose-clamp, screw on the cap until it is tight, remove the filled sample bottle from the sampler, and place the bottle back in the Ziploc bags that it shipped in.

6.3.12 Repeat the procedures to obtain the second metals sample.

6.3.13 Put on two pairs of the disposable gloves from the special Hg metals bottle bag, and repeat procedures 6.3.1 – 6.3.10 to collect the sample.

6.3.14 Remove the work gloves and one pair of the disposable gloves, hold the bottle cap down on the bottle opening, carefully loosen the lifting arm hose-clamp, screw on the cap until it is tight, remove the bottle from sampler, tag it with the Hg tag, and place it back in the Ziploc bags that it shipped in. ***Note: Do not acidify this sample.***

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

6.4 **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.

6.4.1 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 has been waded.*

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

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

6.4.4 Allow the bottle to fill, then take it out of the water.

6.4.5 Replace the cap in a way that avoids contamination to the inside of the bottle, and place the bottle in the Ziploc bags that it shipped in.

6.4.6 Repeat the procedure to obtain the second metals sample.

6.4.7 Put on a pair of gloves from the special metals bottle bag, repeat procedures 6.4.1 – 6.4.5 to collect the Hg metals sample, tag the bottle with the Hg tag, and place it back in the Ziploc bags that it shipped in. ***Note: Do not acidify this sample.***

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

6.5 **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.

6.5.1 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.*

6.5.2 Remove the metals bottle cap, rinse the extension pole clamp with the DI water from the metals bottle, and replace the cap.

6.5.3 Secure the metals sample bottle in the extension pole clamp, remove the cap, 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.

6.5.4 Position the bottle over the desired sample location.

6.5.5 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.

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

6.5.7 Repeat the procedure to obtain the second metals sample.

6.5.8 Put on two pair of gloves from the special metals bottle bag and repeat procedures 6.5.1 – 6.5.5 to collect the Hg metals sample.

6.5.9 Then remove one pair of gloves, replace the bottle cap in a way that avoids contamination to the inside of the cap, loosen the extension pole clamp, take the filled bottle out of the pole sampler water, tag the bottle with the Hg tag, and place it back in the Ziploc bags that it shipped in. ***Note: Do not acidify this sample or set the cap down.***

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

6.6 Field Processing - Total Recoverable Metals

6.6.1 Put on the vinyl gloves.

6.6.2 Remove the cap from the first sample bottle. Do not set the cap down.

6.6.3 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.

6.6.4 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.

6.6.5 Attach the Total Metals sample tag to the sample bottle.

6.6.6 Place the tagged sample in the original Ziploc bags that it shipped in, along with the empty (capped) Teflon vial, eliminate air from the Ziploc bags, seal them, and set them aside.

6.7 Field Processing - Dissolved Metals

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

6.7.2 Attach the hand-pump hose to the disposable filter unit.

6.7.3 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. Occasionally the tubing for the hand*

pumps can cause the filter apparatus to tip over. Make sure that the filter apparatus is in a secure position so that it does not tip over while attached to the hand-pump.

6.7.4 Cap the empty sample bottle, put it into the large Ziploc bag that contained the tagged total metals sample. Also place the already processed and bagged total metals sample into the bag.

6.7.5 Hold on to 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.

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

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

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

6.7.9 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 recap the nitric acid vial.

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

6.7.11 Place the tagged sample in the original Ziploc bags along with the empty (capped) Teflon vial.

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

6.8 Field Processing – Hg Metals

6.8.1 Tag the sample, eliminate air from the Ziploc bags, seal the bags, and put them in the large Ziploc bag that contains the total metals sample, dissolved metals sample, and the empty Teflon bottle.

6.8.2 Eliminate air from the large Ziploc bag and place it on ice in a cooler.

6.9 Field Processing – Hardness

6.9.1 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 SOP034). The collected 1 L total suspended solids (TSS) or 0.5 L general chemistry samples may also be used if those other samples are unavailable.

6.9.2 Pour approximately 100 mL of the field grab sample into the 125 mL hardness sample bottle (small-mouth poly bottle containing H_2SO_4 preservative).

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

6.9.4 Label the hardness sample, and place the sample in ice in a cooler. ***Do not put this bottle in with the metals samples***.

6.10 **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 indicate that sample contamination may have occurred during field processing or laboratory analysis.

6.10.1 Load the sampler with a metals bottle (do not empty the special DI water out of the bottle). Go to the sample site and follow the normal Metals sample collection method specified in section 6.3 for the station, except do not immerse anything into the stream, and recap the bottle.

6.10.2 Return to the van, and follow the Dissolved Metals filter processing procedure (see procedure 6.7), except pour the filtered sample into the original sample bottle (do not do procedure 6.7.6) and attach a dissolved metals QA_-1 tag.

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 a database, reviewed and verified following the Quality Control and Quality Assurance procedures (see 8.1 below), uploaded into EIM, and posted on our webpage: www.ecology.wa.gov/Ambient.

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).

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.

9.2 Material Safety Data Sheets (MSDSs) for all chemicals used in EAP field sampling or analytical procedures can be found at the following SharePoint link: http://teams/sites/EAP/QualityAssurance/ChemicalSafetyDataSheets/Forms/AllItems.aspx

Also, binders containing MSDSs can be found in all field vehicles, vessels, Ecology buildings, or other locations where potentially hazardous chemicals may be handled. EAP staff following Ecology SOPs are required to familiarize themselves with these MSDSs and take the appropriate safety measures for these chemicals.

10.0 References

10.1 Ecology, 2016. Environmental Assessment Program Safety Manual. Olympia, WA.

10.2 Ecology, 2015. Chemical hygiene plan and hazardous material handling plan. Olympia, WA.

10.3 Ecology, 2016. 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 03-03-200. https://fortress.wa.gov/ecy/publications/summarypages/0303200.html