

Washington State Department of Ecology

Environmental Assessment Program

Standard Operating Procedures for the Collection, Processing, and Analysis of Stream Samples

Version 1.3

Author - William J. Ward

Date -

Reviewer - Dave Hallock

Date -

QA Approval - William R. Kammin, Ecology Quality Assurance Officer

Date -

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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)
2/9/2007	1.1	Editorial; formatting	All	Bill Ward
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Environmental Assessment Program

Standard Operating Procedure for the Collection and Processing of Stream Samples

1.0 Purpose and Scope

- 1.1 This document is the Environmental Assessment Program (EAP), Standard Operating Procedure (SOP) used to collect, preserve, measure, and analyze water quality at Freshwater Ambient Monitoring stations.
- 1.2 It describes the general stream monitoring procedures used for run preparation, sample collection, measurement, processing, preservation, and shipment. The document also addresses quality assurance and quality control procedures.
- 1.3 The standard set of samples collected, measured, or processed include: temperature, pH, conductivity, dissolved oxygen, turbidity, total suspended solids, fecal coliform bacteria, ammonia, nitrate plus nitrite, total nitrogen, total phosphorus, soluble reactive phosphorus, metals, and stage height.
- 1.4 Other samples that may also be collected and processed on a special study request basis include: alkalinity, dissolved organic carbon (DOC), total organic carbon (TOC), filtered total phosphorus, filtered total nitrogen, and suspended sediment concentration (SSC).
- 1.5 All Ambient stations are typically monitored once a month and dissolved metals are also monitored every other month at only a few stations.

2.0 Applicability

- 2.1 This SOP is intended for long term ambient stream monitoring.

3.0 Definitions

- 3.1 Dissolved Oxygen (DO) – The concentration of dissolved oxygen (mg/L) in a water sample.
- 3.2 Conductivity –A measure of the ability of water to carry an electrical current. It is dependent upon the concentrations and types of dissolved ions and the water temperature. In general, a greater concentration of ions in the water will lead to a larger conductivity value.
- 3.3 Ecology – Washington State Department of Ecology.
- 3.4 EAP – Environmental Assessment Program.

- 3.5 EIM – Environmental Information Management System. A searchable database developed and maintained by the Washington State Department of Ecology.
- 3.6 Fecal coliform – A group of bacteria that inhabit the intestinal tract of warm-blooded animals and remain viable in freshwater for a variable period of time. The presence of fecal coliform bacteria in water indicates fecal contamination of the water by a warm-blooded animal; harmful bacteria and viruses associated with fecal contamination may also be present.
- 3.7 FEP – fluorinated ethylene propylene
- 3.8 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 sample sites.
- 3.9 μmhos – micro mhos ($\text{mho} = 1/\text{ohm} = 1 \text{ Siemen}$) per centimeter
- 3.10 MEL – Manchester Environmental Laboratory
- 3.11 MQO’s – Measurement Quality Objectives
- 3.12 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.
- 3.13 OC – Operations Center. The location of the program field equipment, boats, walk-in cooler and shop (where technicians repair or fabricate the equipment).
- 3.14 pH – A measure of the acidity or alkalinity of a solution, numerically equal to 7 for neutral solutions, increasing with increasing alkalinity and decreasing with increasing acidity. The pH scale ranges from 0 to 14.
- 3.15 Run – Scheduled sampling event (usually lasting 2-4 days).
- 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 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 includes 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 (see Attachment D for all MSDS sheets)

- 5.1 DO Sampler (based on design presented in Figure 4500-0:1 of the 20th Edition of Standard Methods), 1 L Funnel, or Kemmerer/Van Dorn samplers
- 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 Field Logbook or Field Data Report Form
- 5.5 Meter Calibration Log Form
- 5.6 Ambient Run checklist
- 5.7 Sample tags
- 5.8 Sample coolers
- 5.9 Sample bottles
- 5.10 Cube ice
- 5.11 Gel-Ice (Blue Ice)
- 5.12 250 mL 10% HCl
- 5.13 Bacteria sampler
- 5.14 Long-line thermistor
- 5.15 Red-liquid thermometer
- 5.16 Weighted measuring tape
- 5.17 USGS gage keys
- 5.18 pH meter with a two point calibration capability.
- 5.19 Refillable Star or Ross Electrode.
- 5.20 pH 6.97 & 9.15 Low Ionic Strength Buffers.
- 5.21 pH probe filling solution.
- 5.22 pH probe storage solution.
- 5.23 Conductivity meter and a 4-cell probe
- 5.24 2 – one-shot 100 µmhos/cm conductivity standards
- 5.25 2 – 1 L nutrient grab sample bottles¹ (marked up with black permanent ink)
- 5.26 1 – 1 L pH and conductivity grab sample bottle (marked with red permanent ink)
- 5.27 DO box that has the following supplies:
 - 5.27.1 300 mL BOD bottles (enough for the Run plus two)
 - 5.27.2 Glass BOD stoppers
 - 5.27.3 Plastic BOD bottle caps
 - 5.27.4 250 mL plastic wash bottle
 - 5.27.5 3 mL graduated disposable transfer pipettes (one dedicated to each reagent)
 - 5.27.6 250 mL Manganous sulfate monohydrate reagent
 - 5.27.7 250 mL Alkali-iodine-azide reagent



DO Sampler
W/sample bottles

Bacteria Sampler
W/sample bottle



¹ These should contain about 200 mL of 10% HCL solution that is replaced every other Run

- 5.28 Deionized water (DI water)
- 5.29 Metals sampler
- 5.30 Hand vacuum pump with hose
- 5.31 500mL Teflon FEP bottles pre-filled with de-ionized water by the lab
- 5.32 125 mL narrow mouth poly bottle containing H2SO4 preservative for hardness sample
disposable 0.45 micron cellulose nitrate filter unit (pre-cleaned)
- 5.33 Small Teflon vials containing 5 ml concentrated nitric acid preservative
- 5.34 Powder-free vinyl disposable gloves

6.0 Summary of Procedure

- 6.1 Annual Run Preparation. This process typically begins in the fall (a year prior to starting a new year-long sampling schedule) and ends with the development of four documents that need to be completed in mid-September (before beginning a new Run schedule).
 - 6.1.1 The early objective is to work with the regional watershed leads to identify five new Basin Stations and three metals sample stations².
 - 6.1.2 Based on the location of the new stations, finalize and post the following two run documents on the Y drive (Y:\ambient) under the appropriate water year folder (WY__ Docs) and run name by mid-September:
 - 6.1.2.1 Run Times (details the planned daily time schedule).
 - 6.1.2.2 Run Directions (details driving and sample location directions).
 - 6.1.3 Notify the Ambient Database Administrator the finalized Run Times document has been posted and he will use the database to generate the following documents:
 - 6.1.3.1 Lab # (assigns lab numbers for each of the run stations)
 - 6.1.3.2 Bottle Order (details the sample bottle needs, delivery, and pickup schedules for each Ambient Monitoring Run).
 - 6.1.4 The administrator will then forward the finalized Lab # and Bottle Order documents to the Manchester Environmental Laboratory (MEL) and post them on the Y drive.
- 6.2 Monthly Run Preparation. This typically begins one week in advance of a run and requires the completion and posting of a Field Work Plan & Contact Person Form, making sample tags, Pre-Filling out the Field Data Report Form, and making hotel reservations.
 - 6.2.1 Samplers should always prepare for a Run by following a Run Checklist (see Attachment A for checklist) to ensure that all of the necessary tasks, sampling equipment, supplies, sample containers, and safety gear have been dealt with or loaded in the van. Note: Run sample bottles are delivered to the OC bottle storage room (or the designated regional location) by the lab courier the Wednesday before the scheduled run. The lab courier should be contacted if they are not there or the order is incorrect.

² These are sampled every other month.

- 6.2.2 Field Work Plan & Contact Person Form.
 - 6.2.2.1 Samplers must complete and post the Field Work Plan & Contact Person Form completion and posting of a Field Work Plan & Contact Person Form on Sharepoint <http://ecywblcyadxd0/sites/eap/Field%20Schedules/Forms/AllItems.aspx> along with links to the Run Directions and Run Times documents before beginning a run.
 - 6.2.2.2 The information on the Field Work Plan & Contact Person Form enables family and program staff to call a sampler in case of an emergency or conduct a search if there was a mishap.
 - 6.2.2.3 If plans change (lodging, cell phone number, etc.) the sampler must contact a supervisor or the section secretary to revise the information.
 - 6.2.2.4 If the sampler fails to check in with the contact person, then the contact person needs to notify the supervisor to begin efforts to locate the sampler. *Note: Van cell phones need to be kept on during work hours to allow the lab courier or other staff to get shipment information or to discuss other program related needs.*
- 6.2.3 Making Sample Tags
 - 6.2.3.1 Use the River and Stream Data Management Database to print the sample tag labels for the Run.
 - 6.2.3.2 Stick the labels to the Rite in the Rain sample tags provided by MEL.
 - 6.2.3.3 Rubber band the labeled tags by station and by the planned sampling order.
- 6.2.4 Pre-Filling Out Field Forms.
 - 6.2.4.1 Enter the Run, sampler, and Run date information at the top of the Field Data Report Form (see Attachment B for a sample of the form, it is a three-part carbonless form). Then enter the station number and name information for each station being sampled that day.
 - 6.2.4.2 If quality control samples will be collected at a station on that day, then put the Run QA number(s) in the station number column at the bottom of the form (e.g. "QAN-1"), swing the back page (pink) page away from the top two pages of the form, and enter the name of the station where the QA samples are to be collected (this helps keep the station "blind" to the lab).

- 6.3 Pre-Run Procedure (Morning of First Day).
- 6.3.1 Turn on the cell phone.
- 6.3.2 Put several scoops of ice into each sample cooler needed for the Run day and set the coolers into the van. If on a multiple day Run that includes an overnight stay, then consolidate the ice needed into a cooler for each day and top the cooler(s) off with several frozen Gel-Ice.
- 6.3.3 Soak the pH and conductivity probes in tap water for at least 30 minutes (overnight is better) before calibrating.
- 6.3.4 Rinse the pH probe filling solution chamber with deionized water (DI water). Then rinse and refill the probe chamber with fresh probe filling solution. *Note: This helps probe performance and probe life.*
- 6.3.5 Empty and refill the dedicated 6.97 and 9.15 pH buffer calibration bottles with fresh buffer solution that are the same temperature and at least 8 °C.
- 6.3.6 Calibrate pH meter following the meter instruction manual for a two point calibration and store the probe in tap water.
- 6.3.7 Calibrate the van barometer using the digital barometer located in the OC wet lab (or by another means such as a local weather station).
- 6.3.8 Check the calibration of the long-line thermistor with an alcohol thermometer and note the result on the Meter Calibration Log Form.
- 6.3.9 Clean the inside of the filter apparatus by pumping 10 % HCL through it (if necessary use a brush) followed by flushing it with DI water for about 10 seconds with DI water from the 2 L storage bottle located in the sink.
- 6.3.10 Insert a new filter and wet the new filter with DI water to help keep it in place.
- 6.3.11 Reassemble the filter apparatus and turn the filter pump on for 10 seconds to further flush the apparatus.
- 6.3.12 Select an empty BOD bottle from the DO box, record its number on the Field Data Report Form, set it in the DO sampler bucket, and secure the bucket lid.
- 6.3.13 Consolidate the 10% HCl solution from the two dedicated 1 L nutrient grab sample bottles (marked up with black permanent ink) into one of the bottles, triple rinse the empty bottle with DI water, and secure it in a DO sampler bottle holder location.

- 6.3.14 Rinse a dedicated 1 L pH and conductivity grab sample bottle (marked with red permanent ink) with DI water and secure it in another DO sampler bottle holder location.
- 6.3.15 Secure clean 1 L and 0.5 L sample bottles in the remaining DO sampler bottle holder locations.
- 6.3.16 Secure a bacteria sample bottle in the bacteria sampler.
- 6.3.17 Clean the conductivity probe cells with a Q-Tip and rinse the probe with DI water.
- 6.3.18 Calibrate the conductivity meter noting the meter I.D. number, standard, the initial and final cell constants, and any other required information on the Meter Calibration Log Form (see Attachment C for form). *Note: the conductivity standard is easily contaminated. Keep it tightly capped and avoid splashing other solutions or water into it. Also, freshly opened standard may be used for up to 5 days before discarding.*
- 6.3.19 Store the conductivity probe in tap water. (Avoid storing it with the pH electrode).
- 6.3.20 Re-calibrate the pH meter after arriving at the first sample station also noting buffer temperature, slope³, and the other calibration information on the Meter Calibration Log Form. The second calibration helps ensure that the pH meter has warmed up and was calibrated properly. Calibrate pH meter following the meter instruction manual for a two point calibration and store the probe in tap water.
- 6.4 Sampling Procedure. There are three basic methods used to collect samples: DO sampler (mostly used to collect samples from bridges), hand dip, and extension pole. **Note: Always survey the sample location for hazards (such as boating traffic or floating woody debris) that must be avoided when using the sampling gear.**
- 6.4.1 If necessary, put on a high-visibility safety vest, turn on the amber strobe beacon light or vehicle emergency flashers, and put out the traffic cones and warning signs.
- 6.4.2 DO Sampler Method. Carry the sampling gear needed to sample at the station (e.g., DO sampler, sample bottles, bacteria sampler, sample ropes, and long-line thermistor) onto the bridge to a well mixed location such as the main part of the channel where representative stream samples may be collected. If called for, collect metals samples⁴ first by following the Metals Sampling Method (see procedure 6.5).
- 6.4.2.1 Lower the thermistor probe into the water and let it equilibrate for at least two minutes while completing some of the other sampling tasks.

³ A slope of 102 or higher indicates a bad standard.

⁴ Metal samples are collected at a few stations every other month.

- 6.4.2.2 If called for, measure the stream stage height⁵ and record the result in the Yellow Field Logbook (Flow Book). Also, record the weighted measuring tape correction factor or check bar measurements. Note: The keys to the gage houses and wire weight gage boxes are located on the key ring stored in the van above the sampling ropes.
- 6.4.2.3 Attach the sampling rope to the DO sampler⁶, remove all the bottle caps, and set the caps aside where they can remain clean.
- 6.4.2.4 Carefully lower the DO sampler to the water surface, taking care to not dislodge any 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. Then rapidly lower the sampler about 0.5 meters to submerge it. *Note: This minimizes the sampling of surface film and any debris from the bottom of the sampler.*
- 6.4.2.5 When the bubbles from the bucket vent tube stop (bucket is full), retrieve the sampler taking care not to dislodge bridge debris into it. If a swift current carries the sampler downstream (before it can completely fill), then pull the sampler above the water, allow it to swing upstream, and then drop it back into the water. This action may need to be repeated a few times until the bucket is full.
- 6.4.2.6 Set the DO sampler aside and replace the bottle caps.
- 6.4.2.7 Memorize or record the water temperature, retrieve the thermistor probe, and set the thermistor aside.
- 6.4.2.8 Attach the sampler rope to the bacteria sampler, remove the aluminum foil-covered stopper or cap from the bacteria bottle, and place the aluminum foil-covered stopper or cap where contamination can be avoided.
- 6.4.2.9 Move a few feet over from where the DO Sampler was retrieved and carefully lower the bacteria sampler to the water surface, taking care to not dislodge bridge debris or the DO Sampler retrieval water 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.*
- 6.4.2.10 Lower the sampler part way into the water but do not submerge the lip of the sample bottle. 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. *Note: This minimizes the sampling of surface film and prevents contamination from the bacteria sampler.*

⁵ Stream stage height measurements are obtained at some stations from a reference point (RP) by using a weighted measuring tape, a USGS weighted wire gage, or a staff gage.

⁶ The DO sampler with sample bottle holders can simultaneously collect DO, turbidity, total suspended solids, pH, conductivity, and nutrient samples.

- 6.4.2.11 Retrieve the bacteria sampler taking care to not dislodge bridge debris onto it.
- 6.4.2.12 Carefully replace the aluminum foil-covered stopper or cap in a way that avoids contamination to the inside of the bottle.
- 6.4.2.13 Return to the van with all the sampling gear.
- 6.4.3 Stream Side (1-L Funnel and hand dip) Method. This method is typically used to collect samples within reach of the water surface when standing in or near the stream.
 - 6.4.3.1 Carry the funnel, thermistor, and needed sample bottles using vest pockets and an empty bucket to a well mixed location such as the deepest part of the active channel or another location where a representative sample may be collected. Do not contaminate the sample location by wading upstream of it and do not collect a sample from an eddy.
 - 6.4.3.2 Put the thermistor probe in the water and let it equilibrate for at least two minutes while completing some of the other sampling tasks.
 - 6.4.3.3 If called for, measure the stream stage height⁷ and record the measurement in the Yellow Field Logbook (Flow Book). Also, record the weighted measuring tape correction factor or check bar measurements. *Note: The keys to the gage houses and wire weight gage boxes are located on the key ring stored in the van above the sampling ropes.*
 - 6.4.3.4 Rinse the funnel in the stream.
 - 6.4.3.5 Invert the funnel or orient the open end of the funnel upstream and slowly submerge it until it and the funnel tubing completely fills avoiding any entrainment of air bubbles.
 - 6.4.3.6 Pinch the end of the funnel tubing and remove the funnel (top end first) from the water.
 - 6.4.3.7 Insert the end of the funnel tubing into the bottom of a BOD bottle, allow the funnel to overflow the bottle until it is nearly empty, and then quickly withdraw the tubing (do not use any samples that were aerated by the final discharge from the funnel). Insert the glass stopper in the BOD bottle and cap it.
 - 6.4.3.8 Hold the base of one of the sample bottles with one hand and remove the bottle cap. Then invert the bottle, 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. Allow the bottle to fill, take it out of the water, replace the cap, and repeat the bottle filling process to fill the remaining sample bottles.
 - 6.4.3.9 Memorize or record the water temperature, retrieve the thermistor probe.

⁷ Stream stage height measurements are obtained at some stations from a reference point (RP) by using a weighted measuring tape, a USGS weighted wire gage, or a staff gage.

- 6.4.3.10 Return to the van with all the sampling gear.
- 6.4.4 Extension Pole Method. This method is typically used to reach a more representative or undisturbed sample location from the stream bank or to sample shallow stream.
- 6.4.4.1 Carry the extension pole, funnel, thermistor, and needed sample bottles using vest pockets and an empty bucket to a well mixed location such as the deepest part of the active channel or another location where a representative sample may be collected. Do not contaminate the sample location by wading upstream of it.
- 6.4.4.2 Put the thermistor probe in the water and let it equilibrate for at least two minutes while completing some of the other sampling tasks.
- 6.4.4.3 If called for, measure the stream stage height⁸ and record the measurement in the Yellow Field Logbook (Flow Book). Also, record the weighted measuring tape correction factor or check bar measurements. *Note: The keys to the gage houses and wire weight gage boxes are located on the key ring stored in the van above the sampling ropes.*
- 6.4.4.4 Secure one of the sample bottles in the extension pole clamp (Collect the FC sample last⁹), remove the cap from the bottle, and place the cap where contamination can be avoided.
- 6.4.4.5 Use the extension pole to position the bottle just over the desired sample location.
- 6.4.4.6 Invert the bottle and in one quick motion plunge the mouth of the bottle into the water about 15 cm (6 inches) and then tip the bottle mouth toward the water surface. Wait until the bottle has filled, then take it out of the water, replace the cap, and remove the bottle from the clamp.
- 6.4.4.7 Repeat this bottle filling process to fill the remaining grab samples.
- 6.4.4.8 The DO sample must be collected following 1L funnel procedure noted in 6.4.2 above or in combination with the extension pole.
- 6.4.4.9 Memorize or record the water temperature, retrieve the thermistor probe.
- 6.4.4.10 Return to the van with all the sampling gear.

⁸ Stream stage height measurements are obtained at some stations from a reference point (RP) by using a weighted measuring tape, a USGS weighted wire gage, or a staff gage.

⁹ Collect the FC sample first in really slow moving streams. This avoids the potential of having the other sampling gear contaminate the sample location for the bacteria sample.

- 6.5 Metals Sampling Procedure. This sampling procedure generally follows 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.
- 6.5.1 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.
- 6.5.1.1 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.
- 6.5.1.2 After the bottle empties, set the sampler down and replace the bottle cap.
- 6.5.1.3 Then fit the sample bottle into the base of the stainless steel metals sampler.
- 6.5.1.4 Remove the bottle cap and place it in the clean plastic bag it shipped in.
- 6.5.1.5 Lower the sampler bottle cap lifting arm until the sampler cap covers the bottle opening (make sure the lifting arm can move up freely).
- 6.5.1.6 Attach the sampling rope.
- 6.5.1.7 Move to a well-mixed location such as the deepest part of the active channel where a representative sample may be collected.
- 6.5.1.8 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.*
- 6.5.1.9 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.*
- 6.5.1.10 Retrieve the filled bottle taking care to not dislodge bridge debris onto it or the sampler.
- 6.5.1.11 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.

- 6.5.1.12 Repeat the procedure to obtain a second metals sample.
- 6.5.1.13 Return to the van with the samples and sampling gear.
- 6.5.2 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.
 - 6.5.2.1 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.*
 - 6.5.2.2 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.
 - 6.5.2.3 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.
 - 6.5.2.4 Allow the bottle to fill and then take it out of the water.
 - 6.5.2.5 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.
 - 6.5.2.6 Repeat the procedure to obtain a second metals sample.
 - 6.5.2.7 Return to the van with the samples and sampling gear.
- 6.5.3 Extension Pole Method. This method is typically used to reach a more representative or undisturbed sample location from the stream bank or slow moving stream.
 - 6.5.3.1 Secure the metals sample bottle in the extension pole clamp.
 - 6.5.3.2 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 and do not collect a sample from an eddy.*
 - 6.5.3.3 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
 - 6.5.3.4 Position the bottle over the desired sample location.
 - 6.5.3.5 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.

- 6.5.3.6 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.
- 6.6 Field Processing Procedure. Field processing fulfills three essential purposes: to preserve (fix) the DO sample, to prepare the individual samples for shipment to the lab, and to obtain field measurements for conductivity, pH, and barometric pressure. The typical field processing consists of the following procedure:
- 6.6.1 Put all the sampling gear into the van.
- 6.6.2 Tag the fecal coliform sample with the appropriate tag and place it in a cooler of ice.
- 6.6.3 Reload the bacteria sampler with an empty fecal coliform sample bottle and set it aside for the next station¹⁰.
- 6.6.4 Remove the BOD bottle from the DO sampler bucket.
- 6.6.5 If necessary, tap the side of the BOD bottle to dislodge any air bubbles clinging to the inside of the bottle. Then insert a glass stopper in the BOD bottle and tip it to discard the displaced water.
- 6.6.6 Remove the stopper and fix the sample by adding two milliliters of manganous sulfate reagent followed by two milliliters of alkaline-azide reagent using the disposable pipettes reserved for each reagent. Add these reagents by dispensing them onto the inside neck of the bottle near the top of the sample (do not immerse the tip of the pipette). This should avoid splashing and entraining air bubbles into the sample and prevent any contamination of the reagents.
- 6.6.7 Replace the stopper and invert the bottle a few times to mix the reagents into the sample.
- 6.6.8 Add a few milliliters of DI water around the stopper to form a water seal and cover the bottle top with a plastic BOD bottle cap.
- 6.6.9 Place the fixed sample into the DO box. Note: samples must be analyzed within four days.
- 6.6.10 Get into the van and record the stream temperature and the approximate sample time on the Field Data Report Form.
- 6.6.11 Rinse the pH and specific conductivity measurement cups and probes with DI or sample water.

¹⁰ Note: collect a 500 mL bacteria sample during the afternoon of each Run day (MEL uses the additional volume for a QC analysis).

- 6.6.12 Remove the pH and conductivity grab sample bottle (marked with red permanent ink) and gently over fill the pH and conductivity measurement cups with the sample water
Note: excessive agitation of the sample water will affect pH.
- 6.6.13 Turn on the pH11 and conductivity meters and allow them a few minutes to stabilize while completing some of the other field processing tasks.
- 6.6.14 *Note: special study samples such as alkalinity, dissolved organic carbon (DOC), total organic carbon (TOC), filtered total phosphorus, filtered total nitrogen, and suspended sediment total (SST) samples should be sub-sampled and processed at this time. If alkalinity is needed, then collect an additional 500mL grab or use the 500mL sample typically collected for the turbidity sample for alkalinity and collect the general chemistry (turbidity) sample from the DO Sample over fill water (water remaining in the sample bucket).*
- 6.6.15 Open a 125mL preserved nutrient bottle (contains 0.25 mL of sulfuric acid) and a 60 mL preserved nutrient bottle (contains 0.25 mL of hydrochloric acid) set them in the sink bottle holders¹². Avoid contact with the acid. Shake the 1 L nutrient sample and fill each of the preserved nutrient bottles to the bottle shoulder. Cap the bottles and tip them to mix the acid into the samples and set them aside. Also collect a Hardness sample if Metals samples were collected at the station.
- 6.6.16 Turn on the filter pump and put the intake hose in the remaining 1 L nutrient sample. Allow the filtered sample water to run through the filter apparatus for 10-15 seconds to ensure that the DI water has been purged from it. Then fill a 125-mL amber bottle (no preservative) to the shoulder with filtered sample water, cap it, and set it aside.
- 6.6.17 Remove the intake hose from the 1 L nutrient sample bottle and the rinse hose exterior with DI water. Then put the hose in DI water and let the pump run for 10-15 seconds to flush the interior of the filter apparatus.
- 6.6.18 If the pH meter has a stable reading, then verify it by moving the pH probe about an inch in the sample and by pushing the meter re-measure button. If the next stable reading is relatively unchanged from the initial stable reading (within 0.02 pH units), then record the result and the temperature of the sample on the Field Data Report Form.
Note: Always record the pH as soon as the meter has a verified stable result (sample pH changes with time).

¹¹ The pH meter should be set up to notify and hold (beep and display freezes) when it has a stable measurement (see the instrument manual for the meter).

¹² Make sure there are a few drops of acid in each bottle.

- 6.6.19 If the pH result equals 6.5 or less or 8.5 or higher, then check the calibration of the pH meter using the closest low ionic strength buffer (6.97 or 9.15). Record the calibration check result on the Field Data Report Form and if necessary, recalibrate meter, and re-measure the sample¹³.
- 6.6.20 Check the calibration of the pH meter after the first, middle, and last station of the day using the 6.97 low ionic strength buffer. Record the result on the Field Data Report Form and if necessary, recalibrate meter, and re-measure the sample.
- 6.6.21 Record the conductivity result in the on the Field Data Report Form or Field Logbook. The meter displays results to the nearest tenth, so round the result to the nearest whole number. If the tenths digit > 0.5, then round up; if it is < .5, then round down; and if it is = to 0.5 round to the nearest even number. For example, a conductivity result of 103.5 would be rounded to 104 and a result of 62.5 would be rounded to 62.
- 6.6.22 Record the barometric pressure, stream stage height, and any other measurements on the Field Data Report Form. Also note any weather or unusual site specific observations
Note: spend some time on this as the narrative observations can help explain any anomalous data. Also note missing data or equipment issues.
- 6.6.23 Label the all sample bottles with the appropriate sample tags, double check the station ID on the tag, and place them in ice in a cooler.
- 6.6.24 Remove and discard the used filter from the filter apparatus, rinse the inside of the apparatus with DI water, and insert a new filter.
- 6.6.25 Wet the new filter with DI water to keep it in place, reassemble the filter apparatus, and then turn the filter pump on for 10-15 seconds to flush the apparatus with DI water.
- 6.6.26 Select an empty BOD bottle from the DO sample box, record its number on the Field Data Report Form, place it in the stainless DO sampler bucket, and secure the bucket lid.
- 6.6.27 Rinse the used nutrient sample bottle with DI water and pour the 10% acid solution from the spare bottle into the newly rinsed bottle. Cap it, shake it, and set it aside in the sink to soak until the next station.
- 6.6.28 Triple rinse the newly emptied nutrient sample bottle with DI water, and secure it in a DO sampler bottle holder location.
- 6.6.29 Rinse the dedicated 1 L pH and conductivity grab sample bottle with DI water and secure it in another DO sampler bottle holder location.

¹³ If the difference between the pH meter result and the standard is greater than or equal to 0.05 pH units then recalibrate the meter, if the difference between the pH meter result and the standard is greater than or equal to 0.10 pH units, then recalibrate the meter, re-read the sample, and "J" data since last calibration check.

- 6.6.30 Secure clean 1 L and 0.5 L sample bottles in the remaining DO sampler bottle holder locations.
- 6.6.31 Repeat the Sample Collection and Processing Procedures (see procedures 6.4 and 6.5 above) at the rest of the sampling stations. *Note: the calibration of the pH meter must be checked after the first, middle, and last stations of the day. The conductivity meter needs to be checked after the first and last stations of the day. Record the results on the Field Data Report Form and on the Meter Calibration Log Form.*
- 6.7 Metals Field Processing Procedure.
 - 6.7.1 Total Recoverable Metals and Total Mercury.
 - 6.7.1.1 Put on vinyl gloves.
 - 6.7.1.2 Remove the disposable filter unit from the large Ziploc bag and set the bag and filter unit aside.
 - 6.7.1.3 Remove the cap from the first sample bottle (do not set the cap down)
 - 6.7.1.4 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.
 - 6.7.1.5 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.
 - 6.7.1.6 Attach the Total Metals and Total Recoverable Mercury sample tag to the sample bottle.
 - 6.7.1.7 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.
 - 6.7.2 Dissolved Metals.
 - 6.7.2.1 Attach the hand pump hose to the filter unit.
 - 6.7.2.2 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.*
 - 6.7.2.3 Cap the empty sample bottle and put it into the large Ziploc bag that also contains the tagged total metals sample.
 - 6.7.2.4 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.

- 6.7.2.5 Filter as much of the sample as possible (at least half).
- 6.7.2.6 Empty deionized water from an unused Teflon bottle and put the cap on the bottle opening.
- 6.7.2.7 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.
- 6.7.2.8 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.
- 6.7.2.9 Attach the Dissolved Metals sample tag to the sample bottle.
- 6.7.2.10 Place the tagged sample in its original Ziploc bag along with the empty (capped) Teflon vial.
- 6.7.2.11 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.
- 6.7.2.12 Eliminate air from the large Ziploc bag and place the bagged samples on ice in a cooler.
- 6.8 Quality Assurance / Quality Control Sampling Procedures. Stations for Quality Assurance / Quality Control (QA/QC) samples are assigned at random prior to the water year. A typical Run has two field blank stations and ten field replicate/field split stations per year. As a result, one QA sample station is assigned per Run per month. This sampling follows the regular sampling process for the station.
- 6.8.1 Field Replicate/Field Split Samples¹⁴.
- 6.8.1.1 Repeat the normal sample collection and processing procedures (See section 6.6) to collect a second set of field grab samples at the station. Then collect two sets of split samples out of the of the 1 L nutrient grab sample (instead of one set). *Note: the split samples for the station are usually just nutrient samples but they may also include non-nutrient samples such as hardness, TOC, and DOC.*
- 6.8.1.2 Label a complete set of collected samples with the QA_-1 (field replicate) tags and label the additional split samples with the QA_-2 (field split) tags. *Note: There is no need to split any sample that is collected directly in the bottle and sent to the lab.*

¹⁴ Split samples are collected after the normal set of samples have been collected, processed, and the sampling equipment has been set up to sample another station. These samples are intended to assess contamination from field processing.

- 6.8.2 Field Blank Samples
- 6.8.2.1 Remain in the van. Fill the 1 L nutrient grab sample bottle and 1 L pH and conductivity grab sample bottle with DI water.
- 6.8.2.2 Fill the conductivity measurement cup with water from the pH and conductivity grab sample bottle, allow the probe to stabilize, and record the measurement.
- 6.8.2.3 Go through the normal process of obtaining the preserved nutrient bottle samples and filtered nutrient samples from the nutrient grab sample bottle.
- 6.8.2.4 Do not collect fecal coliform, total suspended solids, turbidity, or DO samples or take pH or temperature measurements. Label the bottles with the appropriate QA_-1 tags, place them in ice in a cooler, and note the time and conductivity measurement on the Field Data Report Form.
- 6.8.3 Metals Field Blank Samples¹⁵. Follow the Dissolved Metals processing procedure (see procedure 6.7.2) and filter de-ionized water from one of the 500mL Teflon FEP bottles that was pre-filled by the lab. *Note: The empty 500mL Teflon FEP bottle the sample came from may be reused for the filtered bank sample.*
- 6.9 End of Day QC Procedures.
- 6.9.1 Check the calibration of the pH meter using the 6.97 low ionic strength buffer. Record the result on the Field Data Report Form and if necessary, recalibrate meter, and re-measure the last sample.
- 6.9.2 Check the calibration of the conductivity meter. Record the result on the Field Data Report Form. If the conductivity measurement is not within 5 μ mhos/cm of the standard then troubleshoot the meter¹⁶ and if necessary re-measure all of the samples using the general chemistry sample.
- 6.9.3 Review the information recorded on the Field Data Report Form for completeness, sign the form, and remove the back (pink) sheet.
- 6.10 OC Walk-in Cooler Shipping Procedures.
- 6.10.1 Put the Field Data Report Form pink sheet in the courier's inbox tray located near the cooler.
- 6.10.2 Drain the ice water from the sample cooler(s), top the samples off with a couple scoops of ice, and set the cooler(s) in the walk-in cooler.

¹⁵ One Metals blank is collected per Run per year.

¹⁶ If the meter is in the non-linear function (nLF) and the temperature coefficient is 25, then use an unopened conductivity standard to verify the meter calibration (the standard is easily contaminated). If the meter needed to be changed to the non-linear function, temperature reference 25, or be recalibrated, then re-measure all of the samples.

- 6.11 Greyhound or motor freight (truck) Shipping Procedures
Note: If possible, avoid shipping on Greyhound because this method can delay the receipt of the samples by the lab.
- 6.11.1 Fold the Field Data Report Form pink sheet, put it in a plastic sandwich bag, and tape the bag under a sample cooler lid.
- 6.11.2 Drain the coolers of ice water, and top them off with several frozen Gel-Ice (Blue-Ice). The amount of Gel-Ice may need to be increased during hot weather to ensure that the samples remain at or below 4° C during shipment. Do not overload the cooler with Gel-Ice because this can freeze the samples. *Note: all sample coolers used to ship samples must be in good condition and not leak.*
- 6.11.3
- 6.11.4 Tape the cooler drain plug and lid using ¾ or 1 inch reinforced tape. It works best to tape over the drain plug first and then wrap tape twice around the narrow end of one end of the cooler and cooler lid.
- 6.11.5 Check the sample cooler(s) in at the package service counter of the shipper and provide Ecology's account number along with any other necessary information.
- 6.11.6 If the shipper indicates any problems with the shipment schedule, then notify the courier.
- 6.12 Airfreight Shipping Procedures. GoldStreak – Alaska Airlines/Horizon Air Cargo is the current provider of this service for the sample cooler shipments. Note: The airline may require a 24 hour advance notification procedure.
- 6.12.1 Fold the Field Data Report Form pink sheet, put it in a plastic sandwich bag, and tape the bag under a sample cooler lid.
- 6.12.2 Transfer the iced samples into an empty (dry) sample cooler that is in good condition and will not leak. Be sure that the all the sample container lids are tight.
- 6.12.3 Top off the samples with several frozen Gel-Ice. The amount of Gel-Ice may need to be increased during hot weather to ensure that the samples remain at or below 4° C during shipment. If the Gel-Ice were kept frozen with dry ice, then use fewer Gel-Ice to top off the samples¹⁷.
- 6.12.4 Hold off taping the coolers but take the tape with you so it can be done after the coolers have been checked in and inspected.

¹⁷ Dry ice freezes Gel-Ice colder and some samples could be frozen if several of them are used.

- 6.12.5 Check the sample cooler(s) in at the airline airfreight office or ticket counter. They will need Ecology's Customer ID number, your personal and Ecology ID, and possibly other necessary information. They will weigh the coolers and give them to an officer from the Transportation Security Administration (U.S. Department of Homeland Security).
- 6.12.6 The officer will do an inspection and pass the coolers back to the airline staff.
- 6.12.7 At this point, ask them if you can secure the cooler lid to the cooler with our $\frac{3}{4}$ or 1 inch reinforced tape. **Note: Tape the drain plug and then secure the cooler lid by taping completely around the narrow end of one end of the cooler and lid twice.**
- 6.12.8 The process allowed to get the cooler lids secured with tape varies at each airport. Some airport staff will let us tape the coolers using our tape, others will tape them using our or their tape (ask if you can watch for chain-of-custody reasons), and sometimes they will tape the lids but not allow you to watch.
- 6.12.9 Contact the lab courier with the **air waybill number** after the coolers have been shipped and indicate any shipment schedule problems.
- 6.13 End of Day Procedures
- 6.13.1 Call the contact person noted on the Field Work Plan & Contact Person Form.
- 6.13.2 Lift the tube out of the DI water for the filter apparatus, lay the tube across the top of the apparatus, turn on the pump, and pump the filter apparatus dry.
- 6.13.3 If the overnight air temperatures will be below 45 °F, then move the meters, probes stored in stream sample or tap water, and standards into a heated room (hotel room, regional lab, or operation center).
- 6.13.4 If the overnight air temperatures will be at or below freezing, then also move the DI water, and DO box containing DO samples into a heated room to prevent freezing or loss to breakage.
- 6.14 DO Analysis - Note: Always dilute chemicals going into the sink with a continuous stream of tap water to prevent damage to the plumbing.
- 6.14.1 Initial Cleaning Procedure:
- 6.14.1.1 Put on a plastic apron and Nitrile gloves.
- 6.14.1.2 Thoroughly rinse the flask and stir bar with deionized water.
- 6.14.1.3 Check and if necessary fill the Potassium bi-iodate dispenser and starch squirt bottle.
- 6.14.1.4 Fill the Sodium thiosulfate reservoir and loosen the reservoir cap.

- 6.14.1.5 Open the volumetric burette stopcock to a fill position.
- 6.14.1.6 Raise and lower the sodium thiosulfate storage bottle reservoir above and below the volumetric burette a few times to flush the burette and to mix the sodium thiosulfate in the reservoir.
- 6.14.1.7 Clamp the reservoir onto the workstation lab-frame above the volumetric burette.
- 6.14.1.8 Move the volumetric burette stopcock to fill the burette and also get rid of any air around the stopcock and burette tip.
- 6.14.2 Titration Procedure:
 - 6.14.2.1 Remove the plastic cap from the BOD bottle.
 - 6.14.2.2 Pour off the water seal and invert the bottle several times to mix the floc.
 - 6.14.2.3 Allow the floc to settle to the lower half of the bottle.
 - 6.14.2.4 Put on the face shield.
 - 6.14.2.5 Remove the bottle-top sulfuric acid dispenser from the acid storage cabinet. The dispenser should already be pre-set to dispense 2 mL of acid.
 - 6.14.2.6 Remove the glass stopper of the BOD bottle. Dispense 2 mL of the acid into the DO sample and put the acid bottle back into the cabinet. **Note: Concentrated sulfuric acid is a very dangerous chemical and should be handled very carefully. Never add water to it and always immediately rinse and dispose of gloves that get any acid on them.**
 - 6.14.2.7 Re-stopper the BOD bottle and invert it several times over the sink until the precipitate has completely dissolved. The sample should have a clear yellowish color. If some floc remains in BOD bottle, then invert the bottle several times to mix the floc and allow 5-6 minutes for the precipitate to dissolve. If the floc still has not dissolved then add a few drops of sulfuric acid from the sulfuric acid dispenser until floc completely dissolves.
 - 6.14.2.8 Slide a magnetic stir bar into an empty 500 mL Erlenmeyer flask.
 - 6.14.2.9 Fill a 203 mL volumetric flask with the DO sample, transfer the sample to the Erlenmeyer flask, and set the flask in the sink.
 - 6.14.2.10 Refill the volumetric burette with sodium thiosulfate (make sure the sodium thiosulfate escapes from the top nipple).

- 6.14.2.11 Place the Erlenmeyer flask containing the sample on the magnetic stirrer and turn on the stirrer to the lowest setting.
- 6.14.2.12 Titrate the sample with the Sodium thiosulfate from the volumetric burette until it turns to a pale yellow color.
- 6.14.2.13 Squirt 1 to 2 mL of the starch solution into the sample. Note: the addition of the starch solution earlier than this can cause a less distinct titration endpoint.
- 6.14.2.14 Continue the titration process by adding the sodium thiosulfate by quickly twisting the burette stopcock past the discharge point or by slowly adding individual drops until the purple color of the sample just disappears. This is the titration end point and it should be sharp and distinct. Care should be taken to avoid an end point overrun.
- 6.14.2.15 Check the titration end point of any sample that was possibly overrun by adding a drop of bi-iodate from a 3 mL graduated disposable transfer pipette to the titrated sample. If the end point is correct, a faint purple color should reappear. If more than one drop of bi-iodate is required to get a faint purple color, then the end point was overrun. Do a Back-Titration (see 6.4.3 – Back-Titration) to correct the titration volume of the sample.
- 6.14.2.16 Record the titration result or corrected titration result in the proper column on the Field Data Report Form or in the field notes as mg/L of DO. If the value is between the 0.1 mL marks on the burette, round the even numbers down and the odd numbers up (e.g., 10.25 to 10.2 and 10.35 to 10.4).
- 6.14.3 Back-Titration Procedure
- 6.14.3.1 Back-titrate an overrun end point sample using bi-iodate drops from a 3 mL graduated disposable transfer pipette (1 drop = 0.05 mg/L). Correct the final value if the back-titration requires fewer than or equal to 8 drops and record the result without qualification. If the back-titration requires more than 8 drops but less than or equal to 20, correct the final value and record the result with a "J" qualification (twenty drops are equivalent to 1 mg/L). If the back-titration requires more than 20 drops, do not record a result, but make a comment on the Field Data Report Form indicating the titration error.
- 6.14.3.2 If a graduated burette or pipette is available, then carefully back-titrate to the overrun end point sample using a measured quantity of bi-iodate and subtract the amount used to correct the final result.
- 6.14.4 Sodium Thiosulfate Normality Check. The test is done to verify the strength of the Sodium Thiosulfate solution and get a data correction factor. The normality check result should almost always be 10.0 mL if the Sodium Thiosulfate has been stored properly (a 9.95 or 10.05 result is considered a 10.0 result). The result should also be very similar to those that others have recently recorded in the Titration Log.

- 6.14.4.1 After the first sample has been titrated to its end point, add exactly 10 mL of the biiodate standard using a 10 mL volumetric burette, w/3-way stopcock, or glass volumetric pipette, rinse the inside wall of flask with starch solution, and re-titrate.
- 6.14.4.2 Repeat this procedure mid-way through the batch of samples to be titrated.
- 6.14.4.3 Record the volume of the sodium thiosulfate needed for each normality check on the field note book or worksheet and on the titration log located next to the titration station (The average of the two normality checks is used as a correction factor for the field data). Note: These normality checks should be very close, within 0.1 mL. If they are not, then do at least two more until you have three consecutive results (within 0.1 mL of each other) to use to calculate a correction factor.
- 6.14.4.4 If you get less than a 9.95 mL result, then repeat the normality check but do the following first:
- 6.14.4.4.1 Eliminate air from the tip of the Potassium Biiodate bottle-top dispenser to ensure it gives you 10.0 mL,
- 6.14.4.4.2 Gently dispense the Potassium Biiodate into the titrated solution in the bottom of the Erlenmeyer flask and avoid getting any on the inside flask wall,
- 6.14.4.4.3 Rinse the inside flask wall with starch solution to ensure that all of the Potassium Biiodate is in the titrated solution, and
- 6.14.4.4.4 Eliminate Sodium Thiosulfate drops/residue from the outside of the refillable burette tip and tube connection.
- 6.14.5 Correcting Titration End Point Results with Normality Check (NC) Results
- 6.14.5.1 Divide the average of the two or more normality check results into 10 to get the correction factor ($10/NC_{avg.}$) and then multiply the final result by the correction factor (CF) to get the corrected final result ($DO_{final} \times CF$).
- 6.14.5.2 For example, if the average of the normality checks was 9.9 mL and the sample titration result was 11.5 mL, then:
- 6.14.5.3 Correction Factor Multiplier = $(10/NC_{avg.}) = (10/9.9 \text{ mL}) = 1.01CF$
- 6.14.5.4 Corrected Final Result = $(DO_{final} \times CF) = (11.5 \text{ mL} \times 1.01CF) = 11.6 \text{ mL}$
- 6.14.5.5 Note: The corrected final result is the volume, in mL, of sodium thiosulfate used to titrate a 200mL sample. This volume is equivalent to the concentration of DO in mg/L.

- 6.14.6 Clean Up Procedure
 - 6.14.6.1 Move the sodium thiosulfate reservoir back to its storage area on the counter.
 - 6.14.6.2 Open the volumetric burette stopcock to a fill position (this allows the thiosulfate in the volumetric burette to return to the reservoir).
 - 6.14.6.3 Tighten the reservoir cap and turn the volumetric burette stopcock to a closed position.
 - 6.14.6.4 Thoroughly rinse the used flasks and stir bar(s), and final rinse them with DI water.
- 6.15 End of Run Procedures.
 - 6.15.1 Rinse the pH and conductivity sample cups with DI water and store them upside down.
 - 6.15.2 Rinse the filter apparatus with DI water and pump the lines dry.
 - 6.15.3 Plug the pH probe fill hole with the rubber plug, fill the probe storage cap with probe storage (or filling) solution, and attach the cap to the probe.
 - 6.15.4 Rinse the conductivity probe with DI water.
 - 6.15.5 Store the meters and probes in a warm and dry area in the regional lab or operation center.
 - 6.15.6 Refill the manganous sulfate monohydrate and alkali-iodine-azide reagent containers in the DO box.
 - 6.15.7 Refill the DI water containers (2 L bottles and 5 gallon carboy)
 - 6.15.8 Empty the van of trash and vacuum it out.
 - 6.15.9 Top off the gas tank (tank must be at least $\frac{3}{4}$ full).
 - 6.15.10 If warranted, get the van oil changed.
 - 6.15.11 Turn any malfunctioning equipment into the Operation Center Technician along with a completed Equipment Problem Report Form for repair at the end of each Run. Malfunctioning equipment may result in unsafe sampling conditions and lost sampling opportunities.
 - 6.15.12 Enter the field data results and comments into our Access-based database, review the entries for accuracy, and turn in the printout of the Run Field Data sheet along with the other documentation to the database manager.

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 The data are entered into our Access-based database, reviewed and verified following the Quality Control and Quality Assurance procedures, uploaded into EIM, and posted on our web page http://www.ecy.wa.gov/programs/eap/fw_riv/rv_main.html.

8.0 Quality Control and Quality Assurance Section

- 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 a field quality control (QC) sample during each sampling run. Our QA program is described in detail in Hallock and Ehinger (2003).
- 8.2 The field QC samples are collected as a duplicate (sequential) field sample. This consists of the collection of an additional sample approximately 15-20 minutes after the initial collection at a station. This sample represents the total variability due to short-term, in-stream dynamics, sample collection and processing, and laboratory analysis.
- 8.3 The annual field QC metals sample is a filtered field blank sample. This sample captures potential contamination from sample processing and laboratory analysis.
- 8.4 A two-tiered system is used to evaluate data quality of individual results based on field QC. The first tier consists of an automated evaluation of the data. Results exceeding pre-set limits are flagged. The second tier QC evaluation is a manual review of the data flagged in the first tier. Data are then coded from 1 through 9 (1 = data meets all QA requirements, 9 = data are unusable). Criteria for assigning codes are discussed in more detail in Hallock and Ehinger (2003). We do not routinely use or distribute data with quality codes greater than 4.
- 8.5 The overall quality of data collected during the sampling year are evaluated in our annual reports (e.g., Hallock, 2006)

9. 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. 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 EPA, 1996. Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. Washington, D.C.
- 10.4 Hallock, D. and W. Ehinger, 2003. Quality Assurance Monitoring Plan: Stream Ambient Water Quality Monitoring. Washington State Department of Ecology, Olympia, WA. 27pp. Publication No. 03-03-200.
www.ecy.wa.gov/biblio/0303200.html
- 10.5 Hallock, D., 2006. River and Stream Water Quality Monitoring Report for Water Year 2005. Washington State Department of Ecology, Olympia, WA. 18pp. + appendicies. Publication No. 06-03-032. <http://www.ecy.wa.gov/biblio/0603032.html>

Attachment A – Run Checklist

Pre-Run Preparation

- ___ Hotel Reservations
- ___ Field Work Plan Form
- ___ Sample Tags
- ___ Field Data Report Forms
- ___ Meter Calibration Log Form
- ___ Yellow Flow Book
- ___ Run Directions Binder
- ___ Van Binder
- ___ Cell Phone
- ___ Gas Van
- ___ Soak Probes
- ___ Sample Bottles

Van/Safety Equipment

- ___ Yellow Hazard Beacon
- ___ Flashlight
- ___ Tool Chest
- ___ Tire Chains
- ___ Jumper Cables
- ___ Flares or Reflectors
- ___ First Aid Kit
- ___ Foil Blanket
- ___ Orange Vests
- ___ 2 Gallons Drinking Water
- ___ Hand Towels

Standards & Sampling Supplies

- ___ pH 7 & 10 Buffers
- ___ pH Probe Filling Solution
- ___ Conductivity Standards
- ___ Filters
- ___ Pipettes
- ___ Deionized Water
- ___ D.O. Reagents
- ___ 250 mL 10% HCl
- ___ Disposable Powder Free Vinyl Gloves
- ___ Extra 9-Volt Batteries

Personal Gear

- ___ Sun Glasses
- ___ Watch
- ___ Extra Clothing
- ___ Hat

Meters/Instruments

- ___ pH Meter
- ___ Conductivity Meter
- ___ Long-line Thermistor
- ___ Alcohol Thermometer
- ___ Barometer

Sampling Equipment

- ___ USGS Keys
- ___ Stainless D.O. Bucket Sampler
- ___ Fecal Coliform Sampler
- ___ Metals Sampler
- ___ Weighted Measuring Tape
- ___ Ropes 1 @ 35 ft. & 2 @ 55 ft.
- ___ D.O. Sample Box
- ___ Filter Apparatus
- ___ Map/Gazetteer
- ___ Gloves
- ___ Knee Boots
- ___ Rain Gear

Pre-Departure Preparation

- ___ Check Road Conditions
- ___ Acid Wash Filter Apparatus
- ___ Calibrate Barometer
- ___ Change pH Probe Solution
- ___ Change pH & Conductivity standards
- ___ Check Thermistor Calibration¹
- ___ Calibrate pH meter¹
- ___ Calibrate Conductivity Meter¹
- ___ Ice Chests and Ice

¹Enter Observations on Meter Calibration Log Form

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Attachment C

Meter Calibration Log Form

Run: _____ Date: _____ Sampler: _____

Meter ID Numbers		Pre-Run Calibration			
Cond.		(a) Thermometer (°C)		Van pressure (Pre-cal.)	
pH		(b) Thermister (°C)		Lab pressure	
pH probe		Correction (a minus b)		Adjusted?	Y/N
Temp.		Was that corr. expected?	Y/N		

DAY 1								
Cond Meter	Standard:		Initial Meter Reading:		Initial Cell Const:		Final Cell Const:	

pH Meter	Slope ^a :		Time:	
	mv @ pH 4/10:		Buffer Temp:	
	mv @ pH 7:		Response Time ^b :	
	True pH	Meter pH	Time	Recal?
QA Check #1		c		Y / N
QA Check #2		c		Y / N
QA Check #3		c		Y / N

pH of buffers at various temperatures					
Temp	pH7	pH9	Temp	pH7	pH9
10	7.01	9.27	20	6.98	9.19
11	7.01	9.26	21	6.98	9.19
12	7.00	9.25	22	6.97	9.18
13	7.00	9.25	23	6.97	9.17
14	7.00	9.24	24	6.97	9.16
15	7.00	9.23	25	6.97	9.16
16	6.99	9.22	26	6.96	9.15
17	6.99	9.22	27	6.96	9.14
18	6.99	9.21	28	6.96	9.13
19	6.98	9.20	29	6.95	9.13

Cond Meter	Standard:		Meter Reading:	d	Cell Const:		Time:	
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DAY 2								
Cond Meter	Standard:		Initial Meter Reading:		Initial Cell Const:		Final Cell Const:	

pH Meter	Slope ^a :		Time:	
	mv @ pH 4/10:		Buffer Temp:	
	mv @ pH 7:		Response Time ^b :	
	True pH	Meter pH	Time	Recal?
QA Check #1		c		Y / N
QA Check #2		c		Y / N
QA Check #3		c		Y / N

Footnotes:
^a If <90%, buffers, probe, or cable may be bad.
^b If > 45 seconds try 1) cleaning probe, 2) changing cable, 3) new probe
^c If meter pH is >± 0.05 units, recalibrate; if > ± 0.10 units, recalibrate, re-read sample, & "J" data since last calibration.
^d If meter conductivity is >± 5µs/cm, recalibrate, re-read sample, & "J" data since last calibration.

Cond Meter	Standard:		Meter Reading:	d	Cell Const:		Time:	
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DAY 3								
Cond Meter	Standard:		Initial Meter Reading:		Initial Cell Const:		Final Cell Const:	

pH Meter	Slope ^a :		Time:	
	mv @ pH 4/10:		Buffer Temp:	
	mv @ pH 7:		Response Time ^b :	
	True pH	Meter pH	Time	Recal?
QA Check #1		c		Y / N
QA Check #2		c		Y / N
QA Check #3		c		Y / N

Comments:

Cond Meter	Standard:		Meter Reading:	d	Cell Const:		Time:	
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Attachment C

DAY 4

Cond Meter	Standard:		Initial Meter Reading:		Initial Cell Const:		Final Cell Const:		
pH Meter					<u>Comments:</u>				
Slope ^a :			Time:						
mv @ pH 4/10:			Buffer Temp:						
mv @ pH 7:			Response Time ^b :						
	True pH	Meter pH	Time	Recal?					
QA Check #1		c		Y / N					
QA Check #2		c		Y / N					
QA Check #3		c		Y / N					
Cond Meter	Standard:		Meter Reading:	d	Cell Const:		Time:		