

Appendix E. General Sampling Procedures for Surface Waters

Sampling team members must determine whether the weather conditions will be adequate for sampling, such that low-flow (ambient) samples are collected during dry conditions and storm-flow samples are collected after a predetermined amount of rain has fallen. The critical times to sample for point sources and nonpoint sources vary. For point sources, the critical evaluation period is when potential dilution is at a minimum (i.e., during low-flow conditions). For nonpoint sources, however, critical conditions occur during high-rainfall periods, and especially right after the start of heavy rains which tend to "flush" bacteria from surface soils into surface water.

The following procedures should be used when collecting grab or composite samples during ambient (low-flow) conditions and during storm events.

Preparatory Procedures for Sampling

1. Monitor weather in order to predict when sampling should occur and to make preparations.
2. When a sampling trip is planned, contact all staff who will participate and the laboratory that will analyze the samples.
3. Check with the laboratory to determine bottle type and volume, sampling methods, and all other requirements for your sampling event. Have bottles pre-labeled, coolers and ice available, at least two sampling personnel ready, and chain of custody forms and shipping labels on hand before each sampling event.
4. Bring all necessary sampling equipment and paperwork to the site.
5. For safety, wear appropriate clothing, such as close-toed shoes, rubber boots or waders, nitrile gloves, and long pants.
6. Before samples are collected, sampling equipment and sample containers (if bottles are being reused) must need to be cleaned in a laboratory or cleaning facility using detergent, mineral acids, and reagent water, as appropriate, and dried. Sampling equipment and containers must be kept clean during transport to the site.
7. Keep accurate field notes in field log book of the entire sampling event. Record weather information, date and times, personnel, and a list of each activity you perform.
8. A minimum of two people is required on the sampling team. One member of the sampling team is designated "dirty hands" and the second member is designated "clean hands." All operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle are handled by the individual designated as "clean hands." "Dirty hands" is responsible for preparation of the sampling equipment, recording information in the log book, serving as the quality control (QC) officer of that sampling event to ensure that all forms and labels

are properly completed, and performing all other activities that do not involve direct contact with the sample.

Collecting Grab Samples During Ambient Conditions

In general, sample away from the streambank in the main current. Never sample stagnant water. The outside curve of the stream is often a good place to sample, since the main current tends to hug this bank. In shallow stretches, carefully wade into the center current to collect the sample.

A boat will be required for deep sites, or samples may be collected from a bridge using special equipment. Sampling personnel will need to maneuver the boat into the center of the main current to collect the water sample.

When collecting a water sample for analysis in the field or at the lab, follow the steps below. Label the bottles ahead of time, if possible. The sample label should include the sample location, sample ID number, date, time, analyte or pollutant, and preservation method (if used).

Collecting Samples in Whirl-Pak Bags (can be used for microbiological samples)

Whirl-Pak bags are appropriate to use for microbiological samples that will be driven (not shipped) to a lab for analysis. To collect water samples using Whirl-Pak Bags, use the following procedures:

1. Label the bag with the site number, date, and time.
2. Just before collecting a sample, tear off the top of the bag along the perforation above the wire tab. Avoid touching the inside of the bag. If you accidentally touch the inside of the bag, use another one.
3. If wading into the stream, try to disturb as little bottom sediment as possible. In any case, be careful not to collect water that contains bottom sediment. Stand facing upstream. Collect the water sample in front of you.
4. Hold the two white pull tabs in each hand and lower the bag into the water on your upstream side with the opening facing upstream. Open the bag midway between the surface and the bottom by pulling the white pull tabs. The bag should begin to fill with water. You may need to "scoop" water into the bag by drawing it through the water upstream and away from you. Fill the bag no more than three-quarters full.
5. Lift the bag out of the water. If necessary, pour out excess water to allow airspace. Pull on the wire tabs to close the bag. Fold the ends of the wire tabs together at the top of the bag, being careful not to puncture the bag. Fold the top of the bag over at least four or five times quickly to seal the bag. Don't try to squeeze the air out of the top of the bag.
6. Fill in the sample information on the appropriate field data form. Place the samples in a cooler with ice or cold packs. Complete the chain of custody form and make a

copy of it for the project records. Deliver the samples and chain of custody form to the lab.

Collecting Samples in Screw-Cap Bottles

Screw-cap bottles are appropriate for the collection of most water samples. Refer to the monitoring plan or Quality Assurance Project Plan for the appropriate bottle type (glass or plastic) and size for specific pollutants being sampled. To collect water samples using screw-cap sample bottles, use the following procedures:

1. Label the bottle with the site number, sample number, date, time, and analyte.
2. Remove the cap from the bottle just before sampling. Avoid touching the inside of the bottle or the cap. If you accidentally touch the inside of the bottle, use another one.
3. If wading into the stream, disturb as little bottom sediment as possible. In any case, be careful not to collect water that contains bottom sediment. Stand facing upstream. Collect the water sample on your upstream side, in front of you. You may also tape your bottle to an extension pole to sample from deeper water. If collecting samples from a boat, carefully reach over the side and collect the water sample on the upstream side of the boat.
4. Hold the bottle near its base and plunge it (opening downward) below the water surface. If you are using an extension pole, remove the cap, turn the bottle upside down, and plunge it into the water, facing upstream. Collect a water sample 8 to 12 inches beneath the surface or midway between the surface and the bottom if the stream reach is shallow.
5. Turn the bottle underwater into the current and away from you. In slow-moving stream reaches, push the bottle underneath the surface and away from you in an upstream direction.
6. Leave a 1-inch air space (except for DO, BOD, and microbiological samples where you should fill the bottle to the top). Do not fill the bottle completely (so that the sample can be shaken just before analysis). Recap the bottle carefully, remembering not to touch the inside.
7. Fill in the sample information on the appropriate field form and on the chain of custody sheet.
8. If the samples are to be analyzed in the lab, place them in the cooler for transport to the lab. Complete the chain of custody form and deliver or ship to the lab with the samples. Retain a copy of the chain of custody form for the project records.

Collecting Stream Samples During a Storm Event

Grab samples, composite samples, or a combination of the two can be collected during storm events, depending on the monitoring needs.

A composite sample consists of individual samples collected over the course of the storm and combined to form one sample. The sample should either be flow proportional or time composites. For flow proportional samples, the individual aliquots are collected for specific amounts of stream discharge over the course of the storm (i.e., collect 1 liter of water for every 10,000 cubic feet of flow). For time composite samples, the individual aliquots are collected at specific intervals throughout the storm (i.e., collect 1 liter of sample every 15 minutes after the start of the rainfall event). This composite sample may be kept in one container or thoroughly mixed and then divided into individual sample bottles, depending on the laboratory requirements. Composite samples are appropriate when you are trying to characterize the average conditions of a water body over a certain time period.

Grab samples are samples that are collected at one time and are not combined with any other samples. Only grab samples and not composite samples should be taken for water quality measurements and microbiologicals, as composite samples are not appropriate for these parameters. Grab samples may be collected at various intervals during the storm event or only during a specific part of the storm event, such as the rise, peak, or fall of the stream level.

Sample Collection Procedures for Grab Samples

Follow the instructions for collecting grab samples during ambient conditions. Samples may be collected during the rise, peak, and fall of the storm's hydrograph, or they may be collected at one specific time during the rainfall event. This should be determined ahead of time by the project manager.

Sample Collection Procedures for Composite Samples

1. Refer to appendices B through E for the specific procedures to follow depending on the analyses that will be performed. Go to the sampling location and note the exact time you collect the first sample.
2. When collecting composite samples over the course of a storm event, collect individual portions in a wide-mouth bottle or other sampling container at predetermined intervals according to sampling design (either time or flow proportional sampling may be performed) and mix at the end of the sampling period or combine in a single bottle as collected (for composite sampling only). If preservatives are used, add them to the sample bottle just after collecting the sample, when possible, so that all portions of the composite are preserved as soon as collected.
3. Whenever possible, collect samples facing upstream and upwind to minimize any contamination. Collect composite samples from surface water by using the grab sampling technique and then pouring the samples into one sample bottle for each analyte at the end of the composite sampling period.
4. When using an automatic sampler, flush the intake/discharge teflon tubing and the silastic tubing of the peristaltic pump with 1 liter of organic-free water prior to collecting the first sample with new tubing.

5. Collect the entire volume of water at once, which is immediately added to a large “composite” bottle to be divided into individual analyte bottles at the end of the sampling period for shipment to the lab. To do this, use the following steps:
 - a. Grasp the side or arm of the container that will be used to grab the samples and remove the cap (if one exists) without touching the rim or inside of the bottle or cap. It might be necessary to use more than one type of container (e.g., glass containers and bottles with TFE-lined lids for collecting samples for pesticides and oil and grease analyses and high density polyethylene bottles for samples for metal analyses.)
 - b. To collect the sample for wadeable streams and shallow surface waters, invert the sterile sampling container and rapidly submerge it several inches below the surface of the water body, turning to an upward 45 degree angle (lightly pump the bottle up and down if necessary) until filled with water. Bring container straight up out of the water. For deeper streams or water bodies that are not wadeable, you can collect samples from a boat, bridge (use a sampling pole or a weighted rope), or from a streambank using a sampling pole
 - c. If compositing into a separate container, remove the cap from the container labeled for the composite sample and pour all the water into this container. Recap the container. Make sure not to contaminate the bottle or its cap each time the cap is removed or replaced as additional sample water is added.
 - d. Rinse the container with deionized water between samples.
 - e. Repeat steps a and b at the same location for each additional grab sample. Note time of collection and other observations as required.
 - f. If the composite sampling period is long, keep the composite container in a cooler or bucket filled with ice, making sure no water leaks into the sample container.
 - g. If compositing samples, at the end of the composite sampling time period, the composite sample may need to be divided into the separate bottles for each analyte, depending on the laboratory requirements. When doing this, make sure not to contaminate the sample, bottle, or lid. The sample may be poured through a clean funnel into each bottle in order to minimize spillage if necessary. Mix the water thoroughly before pouring each time either by stirring or shaking the water in the sample container.
 - h. Add remaining preservatives to the bottles of any analytes with preservation requirements.
 - i. Tightly seal all bottles and make sure all sample bottles are labeled appropriately. Place them in the cooler for transport to the lab. Complete the chain of custody form. Retain a copy of the chain of custody form for the project records. Deliver or ship the samples and chain of custody form to the lab.

Cleaning and Preparation of Sampling Containers

Reused sample containers and glassware must be cleaned and rinsed before the first sampling run and after each run by following either Method A or Method B described below. The most suitable method depends on the parameter being measured.

Method A: General Preparation of Sampling Containers

The following method should be used when preparing all sample containers and glassware for monitoring conductivity, total solids, turbidity, pH, and total alkalinity. Wear latex gloves.

- Wash each sample bottle or piece of glassware with a brush and phosphate-free detergent.
- Rinse three times with cold tap water.
- Rinse three times with distilled or deionized water.

Method B: Acid Wash Procedure for Preparing Sampling Containers

This method should be used when preparing all sample containers and glassware for monitoring nitrates and phosphorus. Wear powder-free latex or nitrile gloves.

- Wash each sample bottle or piece of glassware with a brush and phosphate-free detergent. Rinse three times with cold tap water.
- Rinse with 10 percent hydrochloric acid.
- Rinse three times with deionized water.

Documentation and Records

Thorough documentation of all field sample collection and handling activities is necessary for proper processing in the laboratory and, ultimately, for the interpretation of study results. Field sample collection and handling will be documented in writing for each site sampled using the following forms and labels:

- A field log notebook for general observations and notes.
- A field data form that contains information about observations and water quality measurements made at the site.
- Checklists for each sampling episode, sampling point, and sampling time.
- A sample identification label that accompanies and identifies each sample.
- A chain of custody form that provides constant tracking information for all samples .

A detailed description of each sample collected by each sampling team should be recorded on a chain of custody form provided by either CBP or the laboratory. The form should

document the sampling date and time, sampler's name, sample description, and sampling site location and description. A copy of the form should be made for the sampling team to keep.

A sample identification label (to be placed on the sample bottle or container) should be completed to accompany each sample throughout the chain of custody. The label should document the sampling location, sample number, analyte for analysis, preservation method used, sample type, and date of sample. All entries should be made in indelible ink and should coincide with sample information on the field data form. If samples are to be shipped to the laboratory, labels should be covered with clear packing tape to prevent damage from water leakage.

Proper chain of custody procedures are necessary for tracking sample possession from field to laboratory. Field sampling teams must notify the laboratory of an incoming shipment so that the laboratory is properly prepared.

References

APHA. 1998. Standard methods for the examination of water and wastewater. 20th ed. American Public Health Association, Washington, DC. River Watch Network. 1998.

Appendix F. Water Quality Measurements

Water quality measurements include measurements of dissolved oxygen (DO), pH, temperature, and specific conductance (conductivity). These measurements can be taken in the field without the use of a laboratory. The easiest way to take accurate measurements of water quality is to use a calibrated water quality probe or multimeter. The following brands of equipment include: Hydrolab, Horiba, and YSI. Other brands of equipment with the same specifications may also be used, based on approval from the data quality officer of the project.

Alternatively, DO, pH, temperature, and conductivity may be measured separately, using the procedures in the following pages. Procedures must be approved by the data quality officer before sampling begins.

Continuous water quality data (such as in 30-minute increments) can be collected using a water quality meter or probe that is permanently attached in the stream. Continuous data can be used for trend analyses and to determine compliance with current and proposed water quality standards.

Continuous data are especially useful when monitoring 303(d) listed waters. For collection of continuous data, a reliable water quality meter should be installed at various locations. One piece of equipment that is currently being used by the Department of Ecology for the collection of continuous temperature data is an Onset Stow Away Tidbit® temperature logger, one deployed in water and one in air. The loggers are shaded with a PVC pipe and installed in a location representative of the surrounding environment. The loggers are installed about 6 inches off the stream bottom to minimize the potential influence from groundwater inflow. The loggers are placed in a free flowing location at a depth to avoid exposure to air resulting from low flows (see the section on temperature in Appendix B for more details).

The sampling methodology will vary between sampling locations, depending on what parameters are being monitored. All sampling team members must use the same or comparable procedures for all sampling activities. Some of the organizations that are currently monitoring water quality are using the methods shown in Table F-1.

Table F-1. Methods and Equipment Used for Water Quality Measurements

Agency/Organization	Temperature	DO	pH	Conductivity	Flow
Chehalis River Council	YSI® meter				Swoffer meter
Confederated Tribe of Chehalis	Hydrolab				NA
Ecology	Thermistor	Titration	Glass electrode	Electrode	Swoffer or Price AA meter
Thurston County	Hydrolab multimeter				Swoffer or Price AA meter

1. Dissolved Oxygen (DO)

In contrast to lakes, where DO levels are most likely to vary vertically in the water column, the DO in rivers and streams changes more horizontally along the course of the waterway. This is especially true in smaller, shallower streams. In larger, deeper rivers, some vertical stratification of dissolved oxygen might occur. The DO levels in and below riffle areas, waterfalls, or dam spillways are typically higher than those in pools and slower-moving stretches. If you wanted to measure the effect of a dam, it would be important to sample for DO behind the dam, immediately below the spillway, and upstream of the dam. Since DO levels are critical to fish, a good place to sample is in the pools that fish tend to favor or in the spawning areas they use.

An hourly time profile of DO levels at a sampling site is a valuable set of data because it shows the change in DO levels from the low point just before sunrise to the high point sometime in the midday. However, this might not be practical for some monitoring programs. It is important to note the time of your DO sampling to help judge when in the daily cycle the data were collected.

DO is measured either in milligrams per liter (mg/L) or "percent saturation." Milligrams per liter is the amount of oxygen in a liter of water. Percent saturation is the amount of oxygen in a liter of water relative to the total amount of oxygen that the water can hold at that temperature.

A. Meter and Probe

There are several ways to measure DO. One way is to use a DO meter or multiparameter meter with a DO probe. A DO meter is an electronic device that converts signals from a probe that is placed in the water into units of DO in milligrams per liter. Most meters and probes also measure temperature. The probe is filled with a salt solution and has a selectively permeable membrane that allows DO to pass from the stream water into the salt solution. The DO that has diffused into the salt solution changes the electric potential of the salt solution and this change is sent by electric cable to the meter, which converts the signal to milligrams per liter on a scale that the volunteer can read.

The advantage of a meter/probe is that you can measure DO and temperature quickly at any point in the stream that you can reach with the probe. You can also measure the DO levels at a certain point on a continuous basis. The results are read directly as milligrams per liter, unlike the titration methods, in which the final titration result might have to be converted by an equation to milligrams per liter. If using a DO meter, follow the manufacturers instructions for calibration and maintenance needs.

To measure DO using a meter/probe, follow the manufacturers instructions. The barometric pressure must be known or measured to accurately calibrate a DO meter. To do this, use an aneroid barometer or a mercury barometer, and follow the manufacturers instructions.

B. Winkler Method for Measuring DO

DO can also be measured by using some variation of the Winkler method. For this method, samples are collected in a special BOD bottle: a glass bottle with a "turtleneck" and a ground glass stopper. You can fill the bottle directly in the stream if the stream is wadable or boatable, or you can use a sampler that is dropped from a bridge or boat into water deep enough to submerge the sampler.

Method - *Standard Methods for the Examination of Water and Wastewater*. 20th Edition, No. 4500-O C. Winkler Method, Azide Modification⁴.

Holding time - up to 4 days

Detection Limit - 0.1 mg/L

Precision - 0.1 mg/L

Limitations - ferrous iron/L should be < 1 mg/L in water sample.

Equipment

- Stainless steel sampling bucket (similar to design presented in Figure 4500-0:1 of the 20th Edition of Standard Methods)
- Rope
- DO box
- BOD bottles, 300 mL
- Plastic BOD bottle water seal caps
- Manganous sulfate solution
- Alkali-iodate-azide reagent
- 2 mL pipettes
- Deionized water squirt bottle
- Deionized water
- 10% HCl

Cleaning

The DO sample bucket and BOD bottles are rinsed with deionized water after each run. BOD bottles are stored upside down in the DO box to keep dust out and promote drying. The sample bucket is stored with at least 3 centimeters (cm) of deionized water standing in the bottom of the bucket.

This is a slight modification of azide modification method presented in the 20th edition of *Standard Methods*, which calls for the addition of 1 mL of manganous sulfate and azide instead of 2 mL. The excess reagents are accounted for by using 203-mL volumetric flasks rather than 201-mL flasks.

Field Preparation

Record the BOD bottle number(s) on the field data report form. Rinse the sampling bucket, top, and filler tubes with deionized water. Place the BOD bottle into the sampling bucket. Orient the top of the sampling bucket to ensure that a filler tube is inserted into the BOD bottle and fitted into place.

Sample Collection

The water sample should be taken from the main part of the channel or thalweg where possible. Lower the sample bucket to the water surface. Then lower the bucket rapidly into the water until it has completely submerged to minimize sampling of surface film. Retrieve the bucket when the bubbles from the vent tube stop (bucket is full). A swift current may take the bucket downstream before it completely fills. If so, pull the bucket from the water, allow it to swing upstream, and then drop it back into the water. This step may need to be repeated a few times until the bucket fills. Retrieve the filled bucket, taking care to not dislodge bridge debris into it.

Field Processing

At the site (or at a nearby location), carefully remove the top from the sampling bucket by standing on the bucket feet and pulling on the top. Remove the BOD bottle. Try to avoid contamination of the water remaining in the sampler. If necessary, tap the side of the BOD bottle to dislodge any air bubbles clinging inside. Insert a glass stopper in the bottle and carefully discard the displaced water. Remove the stopper and fix the sample by adding approximately two milliliters of manganous sulfate solution followed by two milliliters of alkaline-azide solution using the disposable pipettes reserved for each solution. Add these reagents by immersing the tip of the pipette in the water before injecting them into the solution (avoids splashing and entraining air bubbles in the reagent stream). Replace the stopper and mix the contents by inverting the bottle a few times. Add a few milliliters of deionized water around the stopper to form a water seal and cover the bottle top with a plastic cap. Place the fixed DO sample in the sample box.

Laboratory Analysis

Equipment

- Graduated burette, 25 mL with 3-way stopcock
- Volumetric burette, 10 mL with 3-way stopcock
- Erlenmeyer flasks, 1000 mL
- Magnetic stirrer
- Stirring bars
- 203-mL Volumetric flask
- Concentrated sulfuric acid
- Aqueous starch solution
- Sodium thiosulfate, 0.025 M
- Potassium bi-iodate, 0.025 M
- Liquinox soap

Cleaning

Thoroughly wash and rinse glassware using Liquinox soap and water before every analysis.

Titration Procedure

Note: It is important to dilute the chemicals going into the sink during the following process with a continuous stream of tap water to prevent damage to the building plumbing.

1. Put on the plastic apron and Nitrile gloves.
2. Remove the plastic caps from the BOD bottles.
3. Pour off the water seal and invert the bottle several times to mix the floc.
4. Allow the floc to settle into the lower half of the bottle while rinsing needed flasks, flasks, and stirrers.
5. Put on the face shield.
6. Remove the glass stoppers.
7. Remove the bottle-top dispenser containing sulfuric acid from the acid storage cabinet and make sure its volume adjustment is set to 2 ml.
8. Add 2 mL of sulfuric acid to each sample and put the acid bottle back into the cabinet.
9. Re-stopper the bottles and invert them several times over the sink until the precipitate has completely dissolved.
10. Fill a 203 mL volumetric flask with a portion of a DO sample and transfer the sample to an Erlenmeyer flask.
11. Empty any the sodium thiosulfate from the volumetric burette.
12. Agitate the sodium thiosulfate storage bottle and loosen the plastic lid.
13. Open the volumetric burette stopcock. Then lower and raise the sodium thiosulfate storage bottle above and below the stopcock a few times to help flush the buret.
14. Fill the burette until sodium thiosulfate escapes from the top nipple.
15. Slide a stir bar into the flask containing a sample and place the flask on the magnetic stirrer.
16. Turn the stirrer on and titrate the sample, using the automatic burette with 0.025 N sodium thiosulfate until it turns to a pale yellow color.
17. Add 1 to 2 mL of the starch solution and continue titrating the sample until the purple color just disappears to establish the titration end point¹. Record the measurement on the Field Data Report Form. Note: The titration end point should be sharp and distinct; if it is not, see the trouble shooting section below.

Check the titration end points of questionable samples by adding a drop or two of bi-iodate into the flask. If the end point is correct, the purple color should reappear. If more than 1 or two drops of bi-iodate are required then the end point was overrun. Back-titrate the sample with the bi-iodate standard (1 drop = 0.05 mg/L) and correct the final value. Record the titration volume in the proper column on the Field Data Report Form. If the value is in between 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). After all titrations are completed, refill the burette, clean up all spills, and put away all equipment in clean working order.

Sodium Thiosulfate Normality Check

After the first sample has been titrated to its end point, add 10 mL of the bi-iodate standard² to the sample and re-titrate. Repeat this procedure on the first sample of the third day of the run or when an additional amount of sodium thiosulfate has been added to the burette fill bottle. Record the volume of the sodium thiosulfate needed for each normality check on the Field Data Report Form and on sheet of paper located on the clipboard next to the titration station. The average of the two normality checks is entered into the correction factor field when entering the field data into the ambient database. These checks should be very close, within 0.2 mL. If they are not, then run several more until you have three very close readings.

Trouble Shooting

Problem: Floc remains in BOD bottle after the addition of sulfuric acid.

Solution: Agitate again and allow 5-6 minutes for the precipitate to dissolve. If the floc still has not dissolved then add small amounts of sulfuric acid until floc is completely dissolved.

Problem: Slight blue or purple flakes or specks that resist titration, or the end point is not clear (mushy).

Solution: Replace starch solution.

Problem: End point is over run by a large volume (> 5 drops of bi-iodate must be added for bluecolor to reappear).

Solution: Titrate a 50-mL sample remaining in the BOD bottle. Use the following formula to calculate PPM DO. $\text{PPM DO} = \text{volume sodium thiosulfate} \times 203\text{mL}/50\text{mL}$

¹The volume of sodium thiosulfate used to titrate 203 mL of each sample equals the PPM of dissolved oxygen in the water.

²The automatic volumetric buret measures out the 10mL bi-iodate standard above the 3-way stopcock (no standard needs to be between the stopcock and buret tip). Air should be trapped in and below the stopcock and a drop of sample in the tip when dispensing the 10ml of standard.

2. pH

Overview

The pH of a water sample is defined as the negative logarithm of hydrogen ion activity. pH values range from 0 to 14, 0 being highly acidic, 14 being highly alkaline and 7 neutral. Each pH unit represents a tenfold change in the hydrogen ion activity. Natural waters usually fall within the pH range of 4 to 9, with Washington waters typically being from 6.5 to 8.5. The pH measurements made by the Freshwater Monitoring Unit are used in the calculation of ammonia toxicity and to determine if waters are in compliance with state pH standards.

Equipment

- pH meter or multimeter with pH probe
- pH probes (2)
- 1 M electrode filling solution (probe specific)
- Deionized water
- low ionic strength pH 4 buffer
- low ionic strength pH 6.97 buffer
- low ionic strength pH 9.27 buffer
- Plastic pipette
- Deionized water squirt bottle
- Sample container
- 10 percent HCl
- Meter Calibration Log Form (Appendix B)

Calibration

Remove the storage cap on the pH probe. Rinse off all salt deposits with deionized water. Replace the pH electrode filler solution in the probe using the plastic pipette. Refill the probe with the correct (1 M KCl) reference solution. Soak the pH probe in tap water for at least thirty minutes before calibration. Replace the buffers. Follow instrument manual for a two-buffer calibration.

Re-calibrate the pH probe a second time after arriving at the first sample station to insure that it has warmed up.

If the meter fails to calibrate properly soak the probe for one minute in 10 percent HCl solution, then in deionized water. Recalibrate the meter. If calibration fails again, refer to the troubleshooting section.

Sample Collection

The pH levels can be measured on a subsample of the water from the DO sample container.

Sample Measurement

Rinse the pH sample cup with deionized water or sample water. Then agitate the water in the

DO sample bucket and over fill the sample cup. Place the pH probe in the sample, taking care not to submerge the probe fill hole. Turn the meter on and let it notify and hold on a stable reading (denoted by the word “ready” on the meter display and also signaled by an audible beep). Press the measure button and allow the meter to notify and hold on a stable reading a second time.

Note: A small amount of drift is normal. If the drift is greater than 0.1, the first reading was probably premature. Record the measurement on the Field Data Report Form to the nearest 0.01 pH units.

Quality Control

The calibration of the pH meter should be checked against the buffer periodically (several times a day if sampling multiple locations in one day). To check the calibration, rinse the probe with deionized water, place it in the buffer, and proceed as if the buffer were a typical water sample. The results are recorded on a data sheet or in the field notebook. If the pH is not within 0.1 of the true pH, then recalibrate the meter. If the meter will not calibrate properly then refer to the Troubleshooting section below. Also, be sure to note meter problems on the forms and report them to your supervisor when you return.

pH Meter\Probe Storage

At the end of the day, fill the probe protective cap about half full of electrode reference solution and secure the cap to the electrode. Cover the fill hole with the protective sleeve or the rubber plug (depends upon electrode). During freezing weather, store the meter, probe, and buffer in a heated room.

Troubleshooting

If you suspect an inaccurate measurement, the reading drifts, or the meter takes longer than 90 seconds to notify and hold on a stable reading then check the meter calibration after doing one or more of the following:

1. Change the pH buffer and pH probe solutions.
2. If there is a slow response or the reading drifts, then alternately soak the probe in 10 percent HCl and deionized water several times for one to two minute intervals.
3. If the reading drifts, then alternately soak the probe in household ammonia and pH 4 buffer several times for up to 5-minute intervals. Since the ammonia can be a problem for the conductivity probe and other equipment, you should do this process outside the van.
4. Refer to meter instrument manual and perform self-test.
5. Refer to probe manual and review the troubleshooting section. Replace the probe if this does not fix the problem.
6. If you can not fix the problem, the equipment must be sent in for repair or replaced.

References

APHA. 1998. *Standard methods for the examination of water and wastewater*. 20th ed. American Public Health Association, Washington, DC.

River Watch Network. 1998. *Total alkalinity and pH field and laboratory procedures* (based on University of Massachusetts Acid Rain Monitoring Project). July 1.

3. Temperature

Overview

Temperature is a major factor that influences the metabolism and structure of the biological communities in rivers and streams. Stream temperature can be influenced by many factors including: discharge (flow), stream gradient, depth, stream cover, water color, time of day, season, stream segment, intensity of solar radiation, and human activities. Temperature is inversely related to dissolved oxygen levels. As temperature levels increase the solubility of oxygen decreases. This relationship become more important as temperatures rises.

Metabolism of most species within an aquatic community increases with temperature resulting in a higher oxygen demand for respiration. Increased demand for oxygen combined with reduced availability can lead to displacement of all but the least sensitive species. Possibly just as important as the relationship between temperature and dissolved oxygen is the effect temperature can have on the toxicity of various pollutants.

Temperature in a stream will vary with width and depth. It can be significantly different in the shaded portion of the water on a sunny day. In a small stream, the temperature will be relatively constant as long as the stream is uniformly in sun or shade. In a large stream, temperature can vary considerably with width and depth regardless of shade. If it is safe to do so, temperature measurements should be collected at varying depths and across the surface of the stream to obtain vertical and horizontal temperature profiles. This can be done at each site at least once to determine the necessity of collecting a profile during each sampling visit. Temperature should be measured at the same place every time.

Temperature is measured in the stream with a thermometer or a meter. Alcohol-filled thermometers are preferred over mercury-filled because they are less hazardous if broken. Armored thermometers for field use can withstand more abuse than unprotected glass thermometers and are worth the additional expense. Meters for other tests, such as pH (acidity) or dissolved oxygen, also measure temperature and can be used instead of a thermometer. Temperature can be measured continuously in 30-minute intervals, when possible, to collect the most reliable and defensible data.

Continuous Temperature Measurements

Continuous data is especially useful when monitoring 303(d) listed waters or when checking for violations of water quality standards. For these, a reliable temperature probe should be installed at various locations. One piece of equipment that is currently being used by the Department of Ecology is an Onset Stow Away Tidbit® temperature logger, one deployed in water and one in air. The loggers are shaded with a PVC pipe and install in a location representative of the surrounding environment. The loggers are installed about six inches off the stream bottom to minimize potential influence from groundwater inflow. The loggers are placed in a free flowing location at a depth to avoid exposure to air resulting from low flows.

Equipment

- Onset Stow Away Tidbit temperature logger, or other permanently installed temperature probe
- Alcohol thermometer 1 – 50 °C

Calibration

Check the calibration of the logger or water quality meter as required by the manufacturer. To do this, place the probe and an alcohol thermometer in a bottle of tap or deionized water. Allow at least two minutes for them to equilibrate. Record the logger/meter and thermometer readings on a calibration log form. Also note the correction factor for the logger/meter on the form.

Measurement

Install the logger in a shaded PVC pipe in a location representative of the surrounding environment. It should be installed approximately six inches off the stream bottom to minimize potential influence from ground water inflow. Place the logger in a free flowing location at a depth to avoid exposure to air resulting from low flows.

Follow the manufacturers instructions for operation and data downloads.

One-time Temperature Measurements

Equipment

- Thermistor with attached probe (50 meter), or other multiparameter meter with a temperature probe attached
- Alcohol thermometer 1 – 50 °C

Calibration

Check the calibration of the thermistor before departing on a run by placing the probe and the thermometer in a bottle of tap or deionized water. Allow at least two minutes for them to equilibrate. Record the meter and thermometer readings on the Meter Calibration Log Form. Also note the correction factor for the thermistor on the form.

Measurement

The thermistor probe is lowered at the thalweg (mid channel) of the sampling location to about 0.03 meters below the water surface. Turn the meter on and allow the probe to equilibrate. Record the temperature. Note: Do not apply the correction factor prior to entering a result on the Field Data Report Form. The correction factor is applied when entering the result into the database.

In general, sample away from the streambank in the main current. The outside curve of the stream is often a good place to sample since the main current tends to hug this bank. In

shallow stretches, wade into the center current carefully to measure temperature. If wading is not possible, tape your thermometer to an extension pole or use a boat. Reach out from the shore or boat as far as safely possible. If you use an extension pole, read the temperature quickly before it changes to the air temperature.

If you are doing a horizontal or vertical temperature profile, make sure you can safely reach all the points where a measurement is required before trying.

References

SM 1998. *Standard Methods for the Examination of Water and Wastewater*. 20th Ed., American Public Health Association, Washington DC.

Mason, C.F. 1981. *Biology of freshwater pollution*. Longman Inc. New York, NY. 250 pp.

Reed, G.K., and R.D. Wood. 1976. *Ecology of inland waters and estuaries*, 2nd Ed., D. Van Nostrand, New York, NY. 485 pp.

Brungs, W.S., and B.R. Jones. 1977. *Temperature criteria for freshwater fish: protocols and procedures*. EPA-600/3-77-061. Environ. Research Lab, Ecological Resources Service, U.S. Environmental Protection Agency, Office of Research and Development, Duluth, MN.

4. Conductivity

Overview:

Conductivity is the ability of the water to conduct an electrical current, and is an indirect measure of the ion concentration. The more ions present, the more electricity can be conducted by the water. This measurement is expressed in microsiemens per centimeter (uS/cm) at 25 degrees Celsius.

Equipment:

- Conductivity meter or multi-parameter water quality meter
- distilled water
- data sheet.

Calibration:

Calibrate the conductivity meter according to the manufacturer's instructions and record the reading.

Measurement:

Turn the conductivity meter on and place the probe into the water column and stir with the probe. Wait until the meter stabilizes to obtain the reading for conductivity. The meter should be in the "Conductivity Mode". Record the conductivity reading on the data sheet. Place the conductivity meter in the "TDS Mode" and obtain the "Total Dissolved Solids" reading while stirring with the probe. Record the TDS reading on the data sheet.

A second sample should be taken in the field each sampling day and the results recorded for conductivity on the data sheets. Do this before rinsing the probe. Rinse the probe with distilled water. Recheck the standard of the instrument after each sampling, and record the reading. Also recheck the standard at the end of the day and record the reading.

Turn off the conductivity meter and be careful when handling the meter and probe so as not to damage it while in the field.

Reference:

Bordin, Carol. Chehalis River Council, 1996. *Water quality monitoring* .

Appendix G. Collecting Samples for Laboratory Analyses

Analytical Methods

The following table gives a list of EPA-approved analytical methods for each parameter that might be analyzed under this monitoring plan. The same method should be used by each lab so that results are comparable.

Table G-1. Approved Analytical Methods

Chemical Parameters			
Parameter	Acceptable EPA or SM Method	Acceptable Method Type	Units
Ammonia	EPA 350.1/ SM 4500-NH ₃ H	Automated phenate	0.01 mg/L
Enterococci	EPA 1600	Membrane filter	1 colony/100 mL
E. coli	SM 9221F	Membrane filter	1 colony/100 mL
Fecal coliform	SM 16-909C or SM9222D	Membrane filter	1 colony/100 mL
Nitrate + Nitrite	EPA 353.2/SM 4500-NO ₃ -I	Colormetric	0.01 mg/L
Total Phosphorus (TP)	EPA 365.3 or 365.1/SM 4500-P I	Colormetric	0.01 mg/L
Total Suspended Solids	EPA 160.2/SM 2540D	Solids Weighed Filter	1 mg/L
Orthophosphate	EPA 365.3/SM 4500-P G	Dissolved Colormetric	0.01 mg/L
Total Persulfate Nitrogen (TPN)	SM 4500-N-B	Colormetric	0.01 mg/L
Turbidity	SM 2130	Nephelometric	1 NTU
Field Data/Water Quality Measurements.			
Parameter	Acceptable Method	Acceptable method type	Unit
Temperature	APHA 4500-H+	Thermistor, multi-meter	0.1°C
PH	APHA 4500-H+	Glass electrode	0.1 unit
Dissolved oxygen	APHA 4500-O G	Winkler titration, DO meter, multi-meter	0.1 mg/L
Specific conductivity	APHA 2510 B	Electrode, multi-meter	1 μmhos/cm (μS/cm)
Barometric pressure		Aneroid barometer 0.02 inches Hg	

EPA = *Environmental Protection Agency Method*

SM = *Standard Methods for the Examination of Water and Wastewater*, 20th edition.

4.3 Bottles and other Equipment

Once sampling locations and frequencies have been decided, a table should be completed that lists the required sample bottles and sample volumes for each parameter that will be measured, such as shown in Table G-2. If this information is not known, the laboratory that will be conducting the analyses will be able to provide this information.

In addition, the preservation requirements and holding times must be followed for each parameter sampled. Table G-3 provides a list of preservation requirements and holding times for some of the pollutants that might be sampled.

Table G-2. Recommended Sample Bottles and Sample Volumes

Parameter	Recommended Sample Volumes	Sample Bottle	Additional Volume for Quality Control	Sample Bottle
BOD	2,000 mL	2 - 1L HDPE	1,000 mL	1L HDPE
TSS	500 mL	1 - 1L HDPE	250 mL	
Ammonia as nitrogen	800 mL	1L HDPE	800 mL	1L HDPE
Nitrate/nitrite	200 mL		200 mL	
COD	100 mL	250 mL HDPE	100 mL	250 mL HDPE
TOC	50 mL	250 mL HDPE	50 mL	
TKN	1,500 mL	1L HDPE	1,000 mL	2- 1L HDPE
Total phosphorus	250 mL	1L HDPE	100 mL	
Dissolved phosphorus	250 mL	1L HDPE	100 mL	
Oil and grease as hexane extractable material (HEM)	2,000 mL (in two, 1,000-mL containers)	1L glass 1L glass 125 mL glass	2,000 mL (in two 1,000 mL containers)	1L glass 1L glass 125 mL glass
Metals	1,000 mL	1L HDPE	1,000 mL	1-L HDPE
Pesticides/herbicides	1,000 mL	1L amber glass with PTFE-lined top	1,000 mL	1L amber glass with PTFE-lined top
Total coliform	125 mL	125 mL sterile Whirl-Pak bags or Bacti bottles	None required	None
Fecal coliform	125 mL	125 mL sterile Whirl-Pak bags or Bacti bottles	None required	None
<i>Escherichia coli</i>	125 mL	125 mL sterile Whirl-Pak bags or Bacti bottles	None required	None
<i>Enterococci</i>	125 mL	125 mL sterile Whirl-Pak bags or Bacti bottles	None required	None

Table G-3. Sample Handling Requirements

Parameter	Maximum Holding Time	Preservation Required
BOD	48 hours	Cool, 4 °C
TSS	7 days	Cool, 4 °C

Parameter	Maximum Holding Time	Preservation Required
Ammonia as nitrogen	28 days	Cool, 4 °C; H ₂ SO ₄ to pH < 2
Nitrate/nitrite	28 days	Cool, 4 °C; H ₂ SO ₄ to pH < 2
COD	28 days	Cool, 4 °C; H ₂ SO ₄ to pH < 2
TOC	28 days	Cool, 4 °C; H ₂ SO ₄ to pH < 2
TKN	28 days	Cool, 4 °C; H ₂ SO ₄ to pH < 2
Total phosphorus	28 days	Cool, 4 °C; H ₂ SO ₄ to pH < 2
Dissolved phosphorus	28 days	Cool, 4 °C; H ₂ SO ₄ to pH < 2; Filter on-site or have lab filter immediately upon receipt
Oil and grease as hexane extractable material (HEM)	28 days	Cool, 4 °C; H ₂ SO ₄ to pH < 2 when held > 4 hours
Metals	28 days for mercury, 6 months for others	Cool, 4 °C; HNO ₃ to pH < 2
Pesticides/herbicides	7 days before extraction	Cool, 4 °C (preservation varies with the pesticide/herbicide)
Total coliform	8 hours	Cool, 4 °C
Fecal coliform	8 hours	Cool, 4 °C
<i>Escherichia coli</i>	8 hours	Cool, 4 °C
<i>Enterococci</i>	8 hours	Cool, 4 °C

The following pages describe the specific procedures that should be used when collecting samples for biological oxygen demand, total suspended solids, nutrients, metals, microbiologicals, and pesticides. Refer to Section 5 of the Chehalis Watershed Monitoring Plan for quality assurance/quality control (QA/QC) requirements for field duplicates, laboratory duplicates, and field blanks.

1. Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand, or BOD, measures the amount of oxygen consumed by microorganisms in decomposing organic matter in stream water. BOD also measures the chemical oxidation of inorganic matter (i.e., the extraction of oxygen from water via chemical reaction). A test is used to measure the amount of oxygen consumed by these organisms during a specified period of time (usually 5 days at 20 C). The rate of oxygen consumption in a stream is affected by a number of variables: temperature, pH, the presence of certain kinds of microorganisms, and the type of organic and inorganic material in the water.

BOD directly affects the amount of dissolved oxygen in rivers and streams. The greater the BOD, the more rapidly oxygen is depleted in the stream. This means less oxygen is available to higher forms of aquatic life. The consequences of high BOD are the same as those for low dissolved oxygen: aquatic organisms become stressed, suffocate, and die.

Sources of BOD include leaves and woody debris; dead plants and animals; animal manure; effluents from pulp and paper mills, wastewater treatment plants, feedlots, and food-processing plants; failing septic systems; and urban storm water runoff.

Sampling Considerations

BOD is affected by the same factors that affect dissolved oxygen (see above). Aeration of stream water by rapids and waterfalls, for example will accelerate the decomposition of organic and inorganic material. Therefore, BOD levels at a sampling site with slower, deeper waters might be higher for a given volume of organic and inorganic material than the levels for a similar site in highly aerated waters.

Chlorine can also affect BOD measurement by inhibiting or killing the microorganisms that decompose the organic and inorganic matter in a sample. If you are sampling in chlorinated waters, such as those below the effluent from a sewage treatment plant, it is necessary to neutralize the chlorine with sodium thiosulfate. (See APHA, 1992.)

BOD samples should be analyzed by a laboratory for the most accurate results. The procedures for collecting samples for BOD testing consist of the same steps described for sampling for dissolved oxygen, with one important difference. At each site a second BOD sample may be necessary for DO testing at the lab after the 5-day incubation period. Contact the lab for their volume requirements.

References

APHA. 1992. *Standard methods for the examination of water and wastewater*. 18th ed. American Public Health Association, Washington, DC.

2. Suspended Solids

Method - *Standard Methods for the Examination of Water and Wastewater*. 20th Ed.,
No: 2540 D. Total Suspended Solids dried at 103-105 °C.

Holding Time - 7 days

Detection Limit - 1 mg/L

Precision - 1 mg/L

Overview

Total suspended solids (TSS) refers to the material retained on a standard glass filter after filtration and heating to 103-105 °C. TSS is a direct measurement of the concentration of suspended material present in a water sample.

Equipment

1-L poly bottle

Sample Collection

The water sample for TSS determination is collected in a 1-L poly bottle.

Field Processing

The water sample for TSS determination does not require any field processing. The sample bottle is tagged and placed in a cooler of ice before sending to the lab for analysis.

3. Nutrients

Methods:

Ammonia - *Standard Methods for the Examination of Water and Wastewater*. 20th Ed., No. SM4500-NH3 H Ammonia (phenate) Method by Colormetric Flow Injection Analysis.

Total Persulfate Nitrogen - *Standard Methods for the Examination of Water and Wastewater*. 20th Ed., No. 4500-N B Method by Colormetric Flow Injection Analysis.

Nitrate + Nitrite - *Standard Methods for the Examination of Water and Wastewater*. 20th Ed., No. 4500 -NO3 I Method by Colormetric Flow Injection Analysis.

Total Phosphorus - *Standard Methods for the Examination of Water and Wastewater*. 20th Ed., No. 4500- P I Method by Colormetric Flow Injection Analysis.

Ortho Phosphate - *Standard Methods for the Examination of Water and Wastewater*. 20th Ed., No. 4500- P G Method by Colormetric Flow Injection Analysis.

Holding Times:

Ammonia ----- 28 Days
Total Persulfate Nitrogen 28 Days
Nitrate + Nitrite ----- 28 Days
Total Phosphorus ----- 28 Days
Ortho Phosphate ----- 48 Hours

Reporting Limits:

Ammonia ----- 0.01 mg/L
Total Persulfate Nitrogen ----- 0.01 mg/L
Nitrate + Nitrite ----- 0.01 mg/L
Total Phosphorus ----- 0.01 mg/L
Ortho Phosphate ----- 0.003 mg/L

Precision: See current Water Year Report for summary of latest QA data.

Overview

Nitrogen and phosphorus are the nutrients that most often limit aquatic algae growth in freshwater. When phosphorus is limiting, an increase in concentration can result in increased algal production, which can have aesthetic and ecological impacts. The typical phosphorus concentration of many of Washington's rivers and streams is very low, often less than 0.01 mg/L, which makes them especially susceptible to increases in phosphorus input.

Equipment

- Stainless steel DO sample bucket

- One 1-L HDPE (poly) bottle
- Rope
- Peristaltic pump
- Tubing (silicon)
- Filter apparatus (stand, polyethylene mesh support screen, under- and over-drain support,
- O-ring, wing nuts)
- Filters, cellulose acetate 0.45 μm pore size
- Deionized water squirt bottle
- Bottles, 125mL, brown poly (without preservative)
- Bottles, 125mL, clear poly (with sulfuric acid preservative)
- Deionized water
- 10 percent HCl
- Cleaning brush (toothbrush)

Cleaning

Contamination of the sampling equipment or sample bottles can result in an overestimate of phosphorus concentration. Cleanliness and standardized procedures are essential when collecting nutrient samples, particularly from oligotrophic streams. If soap is needed to clean the equipment, use "Liquinox." Other soaps usually contain trace amounts of phosphorus.

Acid-Washing of Nutrient Sample Collection Bottles

About 500 mL of 10 percent HCl is transferred from one 1-L poly nutrient sample bottle to the other. The acid-rinsed bottle is triple rinsed with deionized water and placed in the bottle holder attached to the DO sample bucket. The nutrient sample bottle containing the 10 percent HCl is shaken and set aside to soak. This process is repeated between each sampling event.

Filter Apparatus

The filter apparatus should be acid-washed before each run. Loosen the wing nuts and remove upper filter holder. Scrub the inside of both the upper and lower filter supports and the polyethylene screen with a brush. Then rinse the apparatus with deionized water, reassemble, and cycle 10 percent HCl solution through it. (Start by placing the tubing from the pump in the 1-L bottle containing the 500ml of HCl and set the bottle under the filter outlet. Turn the pump on. After about 30 seconds, remove the hose from the acid and let the tubing purge itself of the remaining acid). Then rinse the apparatus for 30 seconds with deionized water.

Set up the apparatus for filtering. (Loosen the wing nuts and remove the top of the apparatus. Insert a 0.45 μm cellulose nitrate filter on the filter holder. Prevent leaking by making sure the O-ring is in place. Wet the new filter with deionized water and reassemble the filter apparatus). Then turn on the filter pump and flush the apparatus with deionized water for 10-15 seconds).

Sample Collection and Processing

The nutrient samples are collected in a 1-L new or acid-washed bottle. This bottle can be attached to the DO sample bucket if the sample bucket is already being used. Open a 125-mL preserved nutrient bottle (contains two milliliters of sulfuric acid) and set it in the sink bottle holder. Avoid contact with the acid. Agitate the 1-L nutrient sample and pour approximately 100 mL of the sample into the 125-mL bottle. Cap and agitate the 125-mL bottle to insure that the acid gets mixed into the sample.

Turn on the filter pump and put the intake hose in the 1-L nutrient sample. Be sure the filtration apparatus has been rinsed with deionized water and has a new filter (See cleaning above). Allow the filtered sample water to run through the filter for 10-15 seconds to ensure that the deionized water has been purged from the apparatus. Then fill the bottle to the shoulder, and cap it. Remove the inlet hose from the 1-L nutrient sample bottle and the rinse hose exterior with deionized water. Next put the hose in the deionized water and allow the pump to flush the filter apparatus for 10-15 seconds.

Label the sample bottles with the appropriate sample tags and place them in the ice in a cooler.

References

- APHA. 1998. *Standard methods for the examination of water and wastewater*. 20th ed. American Public Health Association, Washington, DC.
- Black, J.A. 1977. *Water pollution technology*. Reston Publishing Co., Reston, VA.
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- Dates, Geoff. 1994. Monitoring for phosphorus or how come they don't tell you this stuff in the manual? *Volunteer Monitor*, Vol. 6(1), spring 1994.
- Hach Company. 1992. *Hach water analysis handbook*. 2nd ed. Loveland, CO.
- River Watch Network. 1991. *Total phosphorus test* (adapted from Standard Methods). July 17.
- River Watch Network. 1992. *Total phosphorus* (persulfate digestion followed by ascorbic acid procedure, Hach adaptation of Standard Methods). July 1.
- USEPA. 1983. *Methods for chemical analysis of water and wastes*. 2nd ed. Method 365.2. U.S. Environmental Protection Agency, Washington, DC.

4. Metals

Methods:

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

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

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

Holding Time – Mercury 28 days, all the rest 6 months

Detection Limit – Refer to Table 6., Page 119, *Manchester Lab Users Manual*, 5th Ed. (Oct. 2000)

Overview

The long-term river and stream monitoring of ambient metals by the program was most extensive in the early and mid 1990s.

Equipment

- Stainless steel metals sampler
- Rope
- 500-mL Teflon bottles
- Small Teflon vials containing 5 ml Concentrated Nitric Acid
- 125-mL narrow mouth poly bottle containing sulfuric acid preservative (hardness sample bottle)
- Disposable 0.45 micron cellulose nitrate filter unit (precleaned Nalgene #450-0045, type S)
- Hand pump for filter unit

Sample Collection

Water samples are collected as single grabs using the stainless steel metals sampler and a 500-ml Teflon bottle. Care must be used at all times to avoid contaminating the inside of the sample bottle with debris or ambient air. Also, samples need to be placed in ice in a cooler as soon as possible after collection.

The sample collection procedures are as follows:

1. Invert the Teflon bottle sample bottle, remove the cap, and let the deionized water empty out of the bottle.
2. Replace the cap, as soon as the bottle has emptied, to minimize ambient air contamination.

3. Fit the sample bottle into the stainless steel metals sampler.
4. Completely loosen the lid and attach the sampler lid clamp while keeping the lid on the bottle.
5. Remove the lid from the attached hardness sample collection container.
6. Lower the sampler in the thalweg (mid-channel) of the river or stream to the water surface, taking care to not dislodge bridge debris into the bottle or the attached hardness sample container.
7. Allow the sampler to orient itself in the current with the metals sample bottle upstream. Then lower the sampler rapidly into the water until it has completely submerged to minimize sampling of surface film. Note: At about 25 cm under the water surface, the sampler should automatically raise the bottle lid and allow the bottle to fill.
8. Retrieve the filled bottle taking care to not dislodge bridge debris.
9. Loosen the sampler lid clamp while keeping the lid on the bottle and tighten the bottle cap.
10. Cap and remove the filled sample bottle from the sampler, place it in the ziploc bag it shipped in, empty the hardness sample collection container, and repeat steps 1-8 to obtain a second metals sample.
11. Cap the second metals sample. Pour approximately 100 mL of the sample collected in the attached hardness sample collection container into a 125 mL hardness sample bottle. Cap and agitate the hardness sample bottle to insure that the acid gets mixed into the sample. Note: Avoid contact with the acid.
12. Label the hardness sample and place the sample in ice in a cooler.
13. Rinse the hardness sample collection container attached to the metals sampler with deionized water and recap it.

Field Processing

Dissolved Metals

1. Remove the disposable filter unit from its resealable bag.
2. Attach the hand pump hose to the filter unit.
3. Loosen the tape on one side of the top of the filter unit.
4. Remove the cap from one of the filled sample bottles and empty the contents into the filter unit. Note: Avoid touching or contaminating the inside of the filter unit.

5. Cap the used sample bottle and set it aside.
6. Draw a vacuum on the filter unit by squeezing the hand pump.
7. Filter as much of the sample as possible (at least half).
8. Empty the deionized water from an unused Teflon bottle and place the cap over the opening.
9. Remove the bottom of the filter apparatus containing the filtered sample, remove the cap from the top of the unused sample bottle (do not set the cap down) and fill the bottle with the filtered sample.
10. Carefully add the nitric acid from a Teflon vial to the sample and screw the cap on tight.
11. Label the sample with the appropriate dissolved metals sample tag and place it into its original resealable bag along with the empty (capped) Teflon vial. Then put the bagged filtered sample along with the empty Teflon bottle into the larger Ziploc bag that contained the filter unit.

Total Recoverable and Total Mercury

1. Remove the cap from the second sample bottle (do not set the cap down)
2. If necessary, gently squeeze the side of the sample to liberate about 5 mL of sample to make room for the Nitric acid.
3. Carefully add the Nitric acid from a Teflon vial to the sample and screw the cap on tight.
4. Label the sample with the appropriate total metals sample tag(s).
5. Place the sample in its original resealable bag along with the empty (capped) Teflon vial and put them in the larger filter unit resealable bag already containing the dissolved metals sample.
6. Eliminate air from the ziploc bags, fold the larger bag in half, put tape around the outside of the bag, and place the bagged samples on ice in a cooler.

References:

Ward, William J., Ed. *Stream sampling protocols for the environmental monitoring and trends section*. October 2001. Publication No. 01-03-036.

5. Fecal Coliform and Enterococci Bacteria

Fecal Coliform Method - *Standard Methods for the Examination of Water and Wastewater*. 20th Ed. No: 9222D 24 hour Membrane Filter (MF) method.

Enterococci Method - EPA 1600 24 hour MF method.

Holding Time - 24 hours

Detection Limit - 1 colony per 100 mL

Precision - 1 colony per 100 mL

Limitations - highly turbid waters

Overview

There are many potential disease-causing microorganisms that remain viable in fresh water. It is impractical, both with respect to time and money to test ambient water samples individually for the presence of all potential vectors. The practical approach is to test the water samples for the presence of indicator organisms. Fecal coliform bacteria concentration is currently used as the preferred indicator organism in Washington State. However, enterococci are being proposed as a replacement indicator. Fecal coliform and enterococci bacteria are present within the intestinal tract of warm-blooded animals and remain viable in freshwater for a variable period of time.

Equipment

- Rope
- 250-mL autoclaved or new sterile bacteria sample bottles or Whirl-Pak bags
- Fecal coliform sampler

Sample Collection

Care should be used at all times to avoid contamination of the inside of the sample bottle, or the foil covered silicon stopper or bottle cap. Also, the sample needs to be placed in ice in a cooler as soon as possible after collection.

Samples may be collected by hand, if conditions are appropriate. If using a fecal coliform sampler, fit the bacteria sample bottle into the sampler. Multiple sample bottles may be necessary if both fecal coliform and enterococci tests are conducted. Remove the aluminum foil cover stopper and place it where contamination can be avoided. Lower the sampler in the thalweg (mid-channel) of the river or stream to water surface, taking care to not dislodge bridge debris into the bottle. When the sampler touches the water allow the fin to orient it in the current with the bottle upstream. Then lower the bottle rapidly into the water until it has completely submerged to minimize sampling of surface film. Retrieve the filled bottle taking care not to dislodge bridge debris into it. Before the foil-covered cap is replaced, pour out a little of the sample to establish the water level at the bottle shoulder. There must be adequate air space in the sample bottle.

Field Processing

No field processing is required. Label the sample bottle with the appropriate tag and place it on ice in a cooler to be delivered within the maximum holding time to the laboratory. Determine the maximum holding time by reviewing the QAPP or speaking to the lab.

References:

Ward, William J., ed. *Stream sampling protocols for the environmental monitoring and trends section*. October 2001. Publication No. 01-03-036.

Appendix H. Water Flow Measurement Procedures

This procedure is to be used to measure stream discharge or flow. Flow meters allow the calculation of the mean velocity of a surface flow at a given point. The number of wheel revolutions over a specific number of seconds is related to the water velocity of the flow measured by using an individual rating curve for each meter.

Precautions:

1. **USE EXTREME CAUTION WHEN COLLECTING DISCHARGE MEASUREMENTS IN WADEABLE STREAMS.** Streams that are deeper than 2.5–3 feet may become unsafe to wade due to excessive velocity. This is particularly true during storm events in urban and suburban watersheds, as conditions can change from safe to unsafe in a matter of minutes because of rainfall in the upper parts of the watershed.
2. To obtain consistent and correct results, care should be taken to avoid damage to the meter that may alter its operating characteristics. Never allow the rotor cups to come in contact with rock or gravel in the streambed.
3. When taking measurements, always stand downstream and to the side of the instrument.
4. Examine the meter cups, pivot and bearing, and shaft for damage, wear, or faulty alignment before and after each use. Replace a fractured, rough, or worn pivot. Keep the travel pivot in place when the meter is not in use to protect the pivot and bearing.
5. Before using the meter, check the alignment of the rotor axis with the wading rod and adjust the conductor wire to prevent interference with the rotor cup's spin.
6. Clean and oil meters daily when in use.

Be sure to obtain at least one level measurement from the staff plate or flow meter if the intent of the discharge measurement is to develop a relationship between stream stage and discharge. Ideally, determine stage at the beginning and at the end of the measurement to confirm that no significant increase in discharge occurred during the measurement, a common occurrence during storm events. Take an average of the two readings if a change has occurred so that the measured discharge is associated with a single level value.

Equipment

Price Type "AA" Current Meter
Price Type "Mini" Current Meter
Weatherproof field notebook or field data sheet
Pencil or waterproof pen
Hip waders or hip boots
Headphones and/or revolution counter
Stopwatch
Measuring tape

Wading rod
Chaining pins or ¼" rebar

Procedure

1. Test the flow meters to ensure they are working properly prior to use (they are calibrated at the factory). Perform a spin test to check the condition of meter bearings. A spin test consists of spinning the bucket wheel, the moving part of each meter, and recording the time measured for the wheel to come to rest. Maintain the bucket wheel shaft in a vertical position and protect the cups from air currents during the test.

The Price Type "AA" meter should spin freely for at least 3-1/2 minutes.

The Price Type "mini" meter should spin freely for at least 1 minute.

If the wheel comes to rest in less than the required time, do not use the meter. Place a hold tag on the unit. The meter may be used only after it is repaired and the hold tag is removed. If the meter passes the spin test, connect all accessories and verify proper functioning.

2. Choose the meter best suited for expected flow conditions at each monitoring station. For streams that are 2.5 feet deep or less, use the mini meter. For streams of a depth greater than 2.5 feet, the AA meter. Another brand of flow meter may be used with prior approval from the data quality officer of the project.
3. Observe physical characteristics of the stream and measure stream dimensions (width of the wetted surface). Record the characteristics and measurements in the field notebook or on a field data sheet, including station identification, location/coordinates (site drawing optional), date, time of arrival at the station, stream gauge level reading, weather conditions, and flow condition.
4. Select a section of stream for the measurement. Ideally, this section will be a straight section with a well armored, stable bottom, away from large rocks, aquatic vegetation, logs, beaver dams or other debris, or factors that cause unusual flow currents or eddies. If the section is ideal in all other ways, small blockages can be removed. Wait 15 to 30 minutes to allow flow patterns to stabilize. The section can be upstream or downstream of the point where you measure level in the stream. However, avoid going up or downstream of tributaries and keep the section within 300 feet of the staff plate or flow meter sensor to avoid excessive inputs of groundwater into the discharge measurement. Try to keep the measurement section as near as possible to the place where level is measured. However, if a choice is to be made between an ideal section that is away from the staff plate or flow meter versus a fair or poor section near the level measurement point, choose the ideal section.
5. Stretch a tape across the stream channel and anchor the zero point near the edge of water on the left bank looking downstream using the chaining pin or rebar. Secure the other end by wrapping the tape around the other pin and placing it into the right bank. Make the tape tight and perpendicular to the stream flow.

6. Begin collecting velocity measurements along the cross section. The zero point is recorded as zero velocity. Move to the next section and set the meter at the desired depth. If the stream is more than 2.5 feet deep, measurements should be taken at 20 percent and 80 percent of the depth of the stream. The average of the two measurements is nearly equal to the mean velocity in a vertical section. A single measurement at 60 percent of the depth is taken for depths of less than 2.5 feet.
7. Decide on the number of partial sections required across the stream to obtain stream flow measurements and the location for placement of the meter in each partial section. For small flows, less than 2 cubic feet per second (cfs), a minimum of three subsections should be used. Each subsection should contain approximately the same flow. This means that each subsection might vary in width. For flows greater than 2 cfs, subsections should be made based on experience and judgment. In general, each section measured should contain no more than 10 percent of the total flow. Record the section reference, section configuration (width, number of velocity measurements), equipment to be used (type, meter reference, testing), and water depth in a table in the field notebook or on a field data sheet. The water depth for each subsection should represent the average depth.
8. In each subsection, place the flow meter at the appropriate depth and location and start a stop watch on an initial signal (click of the rotor). The next click is counted as one. Count the number of clicks for at least 40 seconds. Record this value (number of clicks) and the period of time (start, end) in a field notebook or on a field data sheet. Use the rating table supplied with your meter to convert the number of clicks to a velocity.
9. Once you have completed the measurement, read the stream gage or staff plate to determine level in the stream. Compare this reading to the reading obtained at the beginning of the measurement. Take an average of the two readings if level has changed during the measurement.
10. To obtain the discharge volume, multiply the cross-sectional area times the measured velocity to determine the flow in each partial section. Calculate the total discharge of the stream by summing the discharges of all the partial sections. (This can be done in the field notebook, on the field data sheet, or by using a spreadsheet).

Troubleshooting

1. Headphones should receive a discernable single click for each revolution of the bucket wheel. The top-setting wading rod should adjust freely and hold in set positions. The meter should fit securely to the rod, and all wire connections should be well-insulated. A revolution counter should be used in place of the headphones if necessary.
2. Perform duplicate measurements at 5 to 10 percent of the total number of subsections. For small streams, perform at least one duplicate measurement. The re-measurement should be no greater than 15 percent different than the first measurement. If an unacceptable difference is observed, continue re-measuring the velocity at the point until two subsequent measurements are obtained that do not differ by more than 15 percent. Record the last measurement as the velocity for the section.

3. The QC Officer should review the field notebook or field data form as soon as possible after data collection to ensure that all necessary data have been recorded.
4. Data transfers and flow calculations should be double-checked by a second person.