Total and Dissolved Water Sampling

Introduction

Water samples will be collected to measure total selenium, total mercury, dissolved methyl-mercury, total trace metals (arsenic, cadmium, copper, silver, zinc), nutrients (total nitrogen, total phosphorus, ammonia), and Chlorophyll-a.

This SOP was adapted and updated from the original SOP (Naftz, 2006) prepared as part of the Utah Division of Water Quality's project, Development of a Selenium Standard for the Open Waters of Great Salt Lake (CH2M HILL, 2008).

Pre-sampling Checklist

The pre-sampling checklist of materials needed during water sampling includes the following:

- A GPS unit
- Multi-parameter probe for field water quality measurements
- A map showing sampling sites with coordinates
- Bound field log book
- Cleaning supplies – deionized water, hydrochloric acid (HCl), Liquinox solution
- Waders or wading boots, as required
- Up to 1-L/min delivery rate portable peristaltic pump (Refer to EPA method 1630/1631 for pump specification)
- Teflon® or Masterflex® tubing suitable for the pump
- 0.45µm mesh capsule filters
- 500-mL to 1-L glass bottles (fluoropolymer glass) with fluoropolymer or fluoropolymer-lined cap with labels
- Discrete depth sampler, e.g. Kemmerer bottles
- Ziploc® Bags
- Digital camera
- Disposable powderless nitrile gloves/elbow gloves
- Labels
- Marker pens and pencils
- Cell phones in case of emergency
- Cooler filled with ice
- Disposable paper towels
- First-aid kit
- Distilled water

Cleaning Procedures

Verify that tubing, processing chamber, and sampling bottles and equipment are clean. If equipments and sample bottles are supplied by the laboratory that will perform analysis, it should be the laboratory's responsibility to generate acceptable blanks to demonstrate that the equipments and containers are free of contamination before they are shipped to the field sampling team. If not clean or for field cleaning, the follow procedures will be used:

Sample Tubing Cleaning Procedure

Laboratory Cleaning

1. Soak in 0.2% Liquinox solution for 30 minutes. Scrub with brush.
2. Change gloves.
3. Rinse 3 times with tap water*.
4. Change gloves.
5. Soak in 5% HCl solution for 2-3 hours. (skip this step if your equipment has ANY non-removable metal)
6. Change gloves.
7. Rinse 3 times thoroughly with deionized water (DIW)*.
8. Double bag equipment.

**To facilitate flow of solutions thru the tubing, use a peristaltic pump or large syringe*.

Field Cleaning

1. Pump 1-L of DIW through tubing and rinse tubing ends just before sampling.
2. Inspect tubing
    - If tubing is visibly dirty or sampling site is contaminated continue to step 3.
    - If dirt is not visible continue to step 5.
3. Pump 1 L of 0.1% Liquinox solution through tubing and on ends.
4. Pump 1 L of tap water or DIW
5. Carefully pump 1 L of 5% HCl solution through tubing and on ends. Capture and dispose of HCl.
6. Pump 2 L of DIW through tubing and on ends.
7. Double bag equipment.
8. Discard neutralized solutions appropriately.
9. Clean stainless steel connections or metal tubing using detergent wash and tap water/DIW rinse procedures.

Sampling Equipment Cleaning Procedure

1. Clean equipment using NFM protocols (See TWRI book 9, Chapter A3.2.1)
2. Soak in 0.2% Liquinox solution for 30 minutes. Scrub with brush.
3. Change gloves.
4. Rinse 3 times with tap water.
5. Change gloves.

6. Soak in 5% HCl solution for 2-3 hours. (skip this step if your equipment has ANY non-removable metal)
7. Change gloves.
8. Rinse 3 times with DIW.
9. Double bag equipment.

Capsule Filter Cleaning Procedure

1. Attach pump tubing to inlet connecter of capsule filter. **Make sure direction of flow through capsule filter matches the direction-of-flow arrow on the side of capsule.**
2. Select a short length of clean tubing onto capsule filter outlet extending into a drain.
3. Pump 1 L (large-capacity >600cm^2 filter) or 100 mL (small-capacity 19.6 cm^2 filter) through capsule filter.
4. Remove tubing from DIW reservoir and continue operating pump in forward at mid-range speed to drain remainder of DIW in capsule filter.
5. Detach capsule filter from tubing.
6. Put in clean, Ziploc® bag until ready for use.

Sample and Collection Bottles Cleaning Procedure

1. Heat bottles to 65^{O}C in 4N HCl for 2-3 hours.
2. When bottles cool down, rinse them 3-4 times thoroughly with deionized water.
3. Fill bottles with deionized water containing 0.4% (v/v) HCl and cap tight.
4. Place the bottles overnight in a clean oven at 60^{O}C.
5. When bottles cool down, rinse 3-4 times thoroughly with deionized water.
6. Refill bottles with deionized water containing 0.4% (v/v) HCl and cap tight.
7. Store bottles in a clean bench until the outside of the bottles are dry.
8. Tighten bottle caps and double-bag the bottles in new Ziploc® bags.
9. Store in wooden or plastic boxes until used.

Pre-Rinse Sample Bottles

(*For glass, and acid-rinsed bottles - this step can be done in the laboratory prior to going into the field*)

1. Put on powderless nitrile gloves.
2. Fill each bottle about ¼ full of DIW and cap.
3. Shake vigorously and decant DIW.
4. Repeat steps 2 and 3 two more times.
5. Following final rinse, fill each bottle half full with DIW and cap.
6. Rinse exterior of bottle with DIW and dry with lint-free laboratory tissue.
7. Store bottles in doubled Ziploc® bags when transported to field.

Label bottles with site id, date, time, and sample designation code (FA for filtered samples and RA for unfiltered samples).

Clean Hands/Dirty Hands Technique

Clean Hands/Dirty Hands technique will be used for all sample collection and sample processing. Before field work begins, the clean hands (CH) person and dirty hands (DH) person should be designated. Table 1 designates the duties of CH/DH. In summary of Table 1, the CH person has the only contact with the sample bottle; transfers sample from sampler to splitter; filters, extracts, and preserves sample. The DH person operates sampling equipment and manages any contact with sources of contamination (for example, the pumps). CH works inside processing chamber while DH works outside the processing chamber.

Table 1 – Clean Hands/Dirty Hands Techniques for Water Quality Sampling

- Clean Hands/Dirty Hands techniques require two or more people working together.
- At the field site, one person is designated as Clean Hands (*CH*) and a second person as Dirty Hands (*DH*). Although specific tasks are assigned at the start to *CH* or *DH*, some tasks overlap and can be handled by either, as long as the prescribed care is taken to prevent contaminating the sample.
- *CH* and *DH* wear appropriate disposable, powderless gloves during the entire sampling operation and change gloves frequently, usually with each change in task. (Wearing multiple layers of gloves allows rapid glove changes.) **Gloves must be appropriate to withstand any acid, solvent, or other chemical substance that will be used or contacted.**
- *CH* takes care of all operations involving equipment that contacts the sample; for example, *CH*
  - Handles the surface-water sampler bottle
  - Handles the discharge end of the surface-water or ground-water sample tubing
  - Handles the inner protective bag on the churn splitter
  - Transfers sample to churn or cone splitter
  - Prepares a clean work space (inside vehicle)
  - Sets up processing and preservation chambers
  - Places equipment inside chambers (for example, sample bottles, filtration and preservation equipment)
  - Works exclusively inside chambers during collection/processing and preservation
  - Changes chamber covers, as needed
  - Sets up field-cleaning equipment and cleans equipment
- *DH* takes care of all operations involving contact with potential sources of contamination; for example, *DH*
  - Works exclusively exterior to processing and preservation chambers
  - Prepares and operates sampling equipment, including pumps and discrete samplers, peristaltic pump switch, pump controller, manifold system
  - Operates cranes, tripods, drill rigs, vehicles, or other support equipment
  - Handles the compressor or other power supply for samplers
  - Handles tools such as hammers, wrenches, keys, locks, and sample-flow manifolds
  - Handles single or multiparameter instruments for field measurements
  - Handles the churn carrier, including outer protective bags
  - Handles stream-gaging or water-level equipment
  - Sets up and calibrates field-measurement instruments
  - Measures and records water levels and field measurements

Sample Collection

Unfiltered Samples

1. *CH/DH*: Put on gloves.
2. *CH*: Prepare a clean processing area and surface. The processing area will be a plastic surface that is protected from wind.
3. *DH*: Assemble processing chamber.
4. *CH*: Insert processing chamber bag.
5. *CH/DH*: Change gloves.
6. *DH:* Remove capped sample bottle from transport bag and insert in processing chamber.
7. *CH:* Field rinse sampler bottles with small amount well mixed raw sample *(raw sample must be well mixed by slowly inverting the capped sample bottle 3-5 times. Do not aerate the sample by shaking vigorously).* This is applicable only to samples that are not preserved.
    a. If bottles were previously rinsed and half-filled with DIW, discard DIW and rinse once with well mixed sample.
    b. If bottles were not pre-rinsed with DIW, rinse twice with DIW, followed by one rinse with well mixed sample.
8. *CH:* Transfer well mixed sample from sampler bottle into appropriate sample bottle and cap.
9. *CH*: If sample bottles do not contain preservatives, preserve sample using preservative if needed,
10. Remove sticker from preservative vial and stick it on the field sheet for lot tracking.
11. Dispose of empty preservative vial in waste container.

Filtered Samples

1. *CH/DH*: Put on one or several layers of powder-free gloves.
2. *CH*: Assemble clean processing chamber, attach chamber cover, and change gloves.
3. *CH*: Place capsule filter, sample bottles, and discharge end of peristaltic pump into chamber.
4. *CH*: Open DIW container and cover with plastic bag.
5. *CH*: Insert intake end of peristaltic pump tubing through the plastic covering and into a 1-L container of DIW.
6. *DH*: Attach tubing to peristaltic pump head and pump DIW to fill tubing.
7. Discharge waste rinse water through a sink funnel or a toss bottle.
8. Discard DIW stored in DIW-pre-rinsed sample bottles. If not pre-rinsed, rinse twice with DIW.

Filtering a sample

1. Field rinse peristaltic pump tubing with the water to be sampled
    a. *CH*: Rinse the outside of each end of the pump tubing.
    b. *CH*: Transfer intake end of pump tubing into composite sample.
    c. *DH*: Start pump to slowly pump sufficient sample to completely fill tubing.
    d. *CH*: Discard rinse water through appropriate receptacle. Prevent water from ponding in processing chamber.
    e. *DH*: Stop pump after tubing is field rinsed.
2. Field rinse capsule filter:

a. *CH*: Remove cleaned capsule filter from plastic bag and attach discharge end of pump tubing to filter inlet connector.
b. *DH*: At low speed, pump sample through the tubing to capsule filter.
c. *CH*: Turn capsule filter so outlet is point up and flow of the sample forces trapped air out of capsule filter. **Do not let sample spray onto chamber cover. Chamber cover must be changed if sample has sprayed on to it.**
d. *DH*: Stop pump as soon as filter is full of sample.

3. Collect Sample Filtrate**.**
   a. *CH*: Check that there is a tight connection between the pump tubing and the capsule filter.
   b. *DH*: Check the intake tube is properly inserted in the sample and start pump.
   c. *CH*: Collect a maximum of 25 mL of the water to be sampled. **Do not exceed 25 mL.**
   d. *CH*: Field rinse a pre-cleaned FA sample bottle.
   e. *DH*: Stop pump in time to prevent losing filtrate.
   f. *CH*: Cap bottle, shake, and discard rinse water.
   g. *DH*: Start pump and resume flow.
   h. *DH*: Stop pump after bottle is filled.
   i. *CH*: Field rinse any remaining sample bottles. **Use no more that a total of 100 mL of filtrate per capsule filter to field rinse any remaining bottles for filtered samples.**

Sample Preservation if Required

All *CH* person.

1. Change gloves.
2. Move samples requiring chemical treatment to preservation chamber.
3. Place first preservative and its waste container insider chamber.
4. Change gloves.
5. Add preservative to FA bottles.
6. Change gloves.
7. Disassemble and clean chamber frame.

For filtered samples that do not require preservation.

1. *CH*: Set samples outside processing chamber
2. *DH*: Check that information on bottle is correct and complete.
3. *DH*: Pack samples for shipping or in ice if cooling is required.
4. *CH*: Rinse all reusable equipment with DIW immediately-before equipment dries.
5. Discard the capsule filter after filtering each sample-do not reuse.

Field Measurements

All field water quality parameters (temperature, pH, dissolved oxygen, conductivity) will be simultaneously measured with water sample collection using Multi-parameter probe.

Multi-probe Calibration

1. Check the display logger to determine the battery level to see if recharging or new batteries are necessary.
2. Prior to calibration, all instrument probes on the multi-probe must be cleaned according to the manufacturer's instructions. Failure to perform this step can lead to erratic measurements. The probes must also be cleaned by rinsing with deionized water before and after immersing the probe in a calibration solution.
3. For each of the calibration, solutions used should provide just enough volume so that the probe and the temperature sensor are sufficiently covered. When done with the calibration solutions, do not return it to the original bottle. Save solution in separate container or dispose properly.
4. All calibration should be done using manufacturer's instruction and using manufacturer recommended calibration solution before every sampling event.

All calibration should be done in the following order: temperature, conductivity, pH, dissolved oxygen.

Field Measurement Procedure

Field measurements commonly are monitored within a cross section of the surface-water body to (a) help determine how well mixed the stream is, and consequently the sampling method to be used (NFM 4.1), and (b) determine the field-property values of the water body at the selected site. In situ use of a multi-parameter instrument is the most efficient means of obtaining such data

1. Wait a minimum of 60 seconds for the sensors to reach thermal equilibrium with the water temperature at each new location. Some instruments require a longer equilibration time; check the manufacturer's recommendations.
2. At each measuring point, allow the field-measurement values on the instrument display to stabilize within an established criterion as specified in the QAPP before recording final field measurements. Field-measurement values will be considered stable if the variability among three or more consecutive readings, spaced some number of minutes apart, conforms to the designated criteria specified in QAPP.

Field Logbook

Field activities will be documented through journal entries in a bound field logbook, which is dedicated to this project. The field logbook will be water-resistant, the pages will be sequentially numbered, and all entries will be made in indelible ink. Each page of the field logbook will be dated and signed by the person making the entry. The field logbook will contain all pertinent information about sampling activities, site conditions, field methods used, general observations, and other pertinent technical information. Examples of typical field logbook entries include the following:

- Date and time of sample collection
- Name of personnel present
- Referenced sampling location description (in relation to a stationary landmark), GPS coordinates, and maps
- Daily temperature and other climatic conditions

- Field measurements, activities, and observations (e.g., depth of water, condition of water, other relevant conditions)
- Media sampled
- Sample collection methods and equipment
- Types of sample containers used
- Sample identification and cross-referencing
- Types of analyses to be performed
- Site sketches
- Visitors to the site
- Color photographs taken during sampling activities will be numbered to correspond to photo log entries. The name of the photographer, date, time, site location, and photograph description will be entered sequentially in the photo log as photographs are taken.

Additional information will be recorded in the field notebook as required by DWQ.

Reference

Naftz, D. Total and Dissolved Water Sample. Program Manual for Development of Selenium Standard for Open Waters of Great Salt Lake. Utah Department of Environmental Quality, Division of Water Quality. May 1, 2006.

CH2M HILL. 2008. Development of Selenium Standard for Open Waters of Great Salt Lake. Utah Department of Environmental Quality, Division of Water Quality, Salt Lake City, Utah.