Standard Operating Procedure for Water Quality Grab Sampling

07/02/02
Version 2.1

Prior to leaving the office

- ✍ Gather sampling equipment - see Equipment & Supplies List on page 11
- ✍ Inspect all sampling equipment for damage, dirt, etc.
- ✍ Pack a cell phone and telephone number directory
- ✍ Check equipment batteries, replace if expired and carry extras
- ✍ Verify that the multi-probe unit and turbidimeter have been recently calibrated by checking the calibration log.
- ✍ Pack field notebook, extra paper, SOP, QAPP, Chain Of Custody (COC) sheets, and shipping addresses (should be in QAPP or SOP)
- ✍ Check bottles needed for sampling - see Grab Sample List on page 2
- ✍ Affix labels to appropriate bottles or pack appropriate labels
- ✍ Prepare Blank samples and reference solution bottles (If applicable)
- ✍ Get Ice (Blue Ice or crushed ice)

At the sampling site

- ✍ Fill in the labels on the bottles
- ✍ Collect all necessary samples - see the appropriate Quality Assurance Project Plan for a constituent/bottle list for the project
- ✍ Filter and preserve samples as needed - see Grab Sample List on page 2
- ✍ Store samples in a cooler on ice and cover with ice
- ✍ Fill out field notebook and field log (field log and field notebook are the same for Reclamation.) and COC sheet(s)

After sampling

- ✍ Package coolers for shipping (fill out shipping label, affix cooler seal). Place COC in plastic bag in cooler before sealing.
- ✍ Ship the samples at the end of each day of sampling
- ✍ Post-calibration of equipment
- ✍ Clean and store field equipment
- ✍ Copy pages from field notebook and store in a secure location in the office after sampling session.
- ✍ Copy field notebook, field log and COC and send to appropriate parties.

1. Grab Sampling

The sample bottle or churn splitter is used to collect a water grab sample. Care is exercised not to disturb sediment while sampling. Avoid surface debris when collecting samples. The sample bottle and/or churn splitter is rinsed with environmental water three times. If bottles are pre-preserved, rinsing with environmental water is not appropriate.

prior to collecting the sample and water is run through the pour spout of the churn splitter during each rinse. Do not disturb the location where sample is to be taken with discarded rinse water. The preferred method of collecting whole (unfiltered) samples is to dip the sample bottle with the mouth pointed up-stream in the current. Filtered and Quality Assurance (QA) samples must be collected in a churn splitter. If used, the churn splitter is cleaned at each site after sample collection by 1) carefully inspecting and removing any foreign material, 2) rinsing the exterior, and 3) rinsing the interior three times with De-Ionized (DI) water. Allow DI water to run through the pour spout during each rinse.

See Table 1 for a list of constituents, appropriate bottles, filtration, and sample preservation information.

Table 1. Grab Sample List

Constituents	Bottle	Filtered	Preservation
Nutrients: NH4, (NO_2+NO_3) as N, TKN, Total P	1,000 ml HDPE	No	4?C 2 ml H_2SO_4
Ortho PO_4	500 ml HDPE	No	4?C
Trace Metals: B, Mo, Se	500 ml HDPE **(level one)**	No	4?C 2 ml $HN0_3$
Trace Metals: Ag, Al, As, Cd, Cr, Cu, Fe, Ni, Pb, Sb, Tl, Zn, Ca+Mg	500 ml HDPE **(level one)**	Yes	4?C 2 ml $HN0_3$
Mercury	250 ml HDPE **(level one)**	Yes	4?C 1 ml $HN0_3$
Hydrogen Sulfide (Sulfide)	250 ml HDPE	No	4?C NaOH
Biological Oxygen Demand (BOD)	1,000 ml HDPE	No	4?C
Chlorophyll a (USBR)	1000 ml Dark HDPE	No	4?C Then Freeze
Chlorophyll a (PacifiCorp)	250 ml Dark HDPE	No	4?C Then Freeze
Total Dissolved Solids (TDS)	250 ml HDPE	Yes	4?C
Algae Speciation	250 ml HDPE	N	4^oC, 5ml Lugol

2. Van Dorn Sampler

The Van Dorn sampler is used to collect samples from a site where it is not possible to directly fill the sample bottles or churn splitter, such as reservoir sampling from a bridge. Rinse the Van Dorn sampler with environmental water three times prior to the collection of sample water. The Van Dorn sampler is lowered, the trigger

mechanism activated, and then raised to the surface. The water is then poured from the Van Dorn sampler into the churn splitter. The Van Dorn sampler is cleaned at each site after sample collection by 1) carefully inspecting and removing any foreign material, 2) rinsing the exterior, and 3) rinsing the interior three times with DI water.

Samples may also be collected using a battery operated 12v DC submersible pump (Ben Meadows Model DC60, ABS body, stainless steel propellers and chemically inert seals). The pump fitted with 30 m of 3/8" ID Tygon tubing is lowered to the desired sampling depth and run until 5 tube volumes have been pumped. The sample bottles are then filled sequentially as the pump continues to operate. For QA samples (regular, duplicate, and spikes) the pump is used to fill the churn splitter. Sample bottles are filled from the churn splitter as described below. The pump is rinsed with distilled water between sample locations. At the end of the sampling period the pump and tubing are rinsed with distilled water followed by a dilute chlorine bleach solution.

3. Churn Splitter

The churn splitter allows different sub-sample volumes to be obtained from the composite sample while still maintaining the same basic chemical and physical properties of the original sample. The volume of the churn splitter limits the volume of sample that can be divided. Suspended inorganic sediments coarser than 62 micrometers (um) cannot be split. Samples may be taken from a plastic (Nalgene^{TM}) churn splitter for analysis of all other dissolved and suspended inorganic constituents.

Sub-samples totaling 10 liters may be withdrawn from the 14-liter churn. The 4 liters remaining in the 14-liter churn should not be used for unfiltered sub-samples because they will not be representative. However, the sample water remaining in the churn splitter may be used for filtered sub-samples for the determination of dissolved constituents.

The procedure for cleaning and use of the churn splitter is as follows:

A. The Klamath Basin Area Office (KBAO) will clean the churn splitter between sampling events. They will use gloves while doing this. After removing any foreign material from the churn splitter with a nylon brush, soap & water, the churn splitter is rinsed three times with DI water.

B. Pour about 200 ml of dilute (i.e. 6%) nitric acid into the churn splitter (if sampling for low level metals constituents). Wet all inside surfaces of churn splitter with the acid. Acid is run through the pour spout. Dispose of dilute acid down a drain with a good flow of tap water.

C. Rinse the churn splitter with DI water three times. Drain DI water from the spout during each rinse. The churn splitter is now ready for field use.

D. The churn splitter is rinsed with environmental water three times in the field at each sample site prior to sample water collection. Drain environmental water through pour spout during each rinse.

E. Fill out the labels on all sub-sample containers. Set aside the filtered sample bottles (at the QA site there are multiple bottles to be filtered) that will contain filtered environmental water. These samples will be filtered from the remaining environmental water in the churn splitter after the other unfiltered samples have been collected. The remaining bottles (unfiltered sample bottles) are rinsed three times with environmental water after the churn splitter has been rinsed and filled. Only rinse the bottles that will contain water collected at the current site. The churn splitter is rinsed three times with DI water after each site.

F. If QA samples are not collected at a site, then approximately 6 liters of environmental water is required at each site. Fill the churn splitter so as to have enough water for all samples. The last 4 liters of sample in churn cannot be used for non-filtered samples. It is important to sufficiently fill the churn splitter to have adequate water supply for all samples.

G. For QA samples, the churn splitter may have to be filled more than once to collect all the required samples. Duplicate and triplicate (spike or reference) samples are collected at the QA site. Three sample bottles (regular, duplicate, and spike) are filled from the same churn splitter volume for most of the constituents. All three bottles for these constituents must be collected from the same churn splitter volume. Triplicate (spike) samples are collected for mercury, trace metals, Mg & Ca, orthophosphate, and nutrients. The field sampler adds a spike solution to a known volume of environmental water for these constituents. For some of the constituents, only two sample bottles (regular and duplicate samples) of environmental water are filled from the same churn splitter of water and the third is filled with a reference solution. A third bottle of environmental water is not collected for total alkalinity, BOD, or TDS triplicate (spike/reference) samples. A reference solution of known concentration is poured into the spike/reference bottle by the sampler for this constituent. Specific preparation of QA samples is discussed in the “Sample Quality Control and Quality Assurance” section of this SOP.

H. It is sometimes necessary to composite water into the churn splitter from a sampling devise. A Van Dorn sampler can be used for this. Where a Van Dorn sampler cannot be used, a sample bottle is used over and over to fill the churn splitter. Swirl the water in sample bottle prior to pouring into the churn splitter in order to minimize the amount of suspended material lost in transferring from the bottle to the churn splitter. As stated in the Grab Sampling section above, it is preferred to collect unfiltered environmental water directly into a sample bottle. QA samples (regular, duplicate, and triplicate) must be dispensed from a single churn splitter volume.

I. Churn the sample at a uniform rate of about 9 inches per second (in/s). The churning disc should touch the bottom of the tank on every stroke and the stroke length should be as long as possible without breaking the water surface. If the churning rate is significantly greater than 9 in/s or if the churning disc breaks the water surface, excessive air is introduced into the sample and may change the dissolved gases, bicarbonate, pH, and other characteristics of the sample. On the other hand, inadequate stirring may result in non-representative sub-samples.

J. After churning the sample in the splitter for at least 10 strokes to assure uniform dispersion of the suspended material, begin the withdrawal of sub-samples. As sub-samples are withdrawn and the volume of sample in the churn decreases, maintain the churning rate of about 9 in/s. If a break in churning is necessary, the stirring rate must be reestablished (i.e., 10 strokes) before withdrawals are continued.

K. While operating the churn, withdraw an adequate volume of sample water to field rinse bottles for unfiltered sub samples. Rinse each bottle three times with sample water.

L. Withdraw sub-samples for unfiltered samples first. The first sub-sample withdrawn should be the largest sub-sample required (usually 1 liter of sample).

M. After all the required unfiltered sub-samples have been withdrawn, the environmental water remaining in the churn may be filtered for sub-samples required for dissolved constituents. Remember to field rinse bottles three times with **filtered** sample water prior to filling. Procedures for filtering and preserving samples are described later.

N. After all filtered sub-samples have been withdrawn, empty the churn splitter and clean the mixing tank, lid, and churning disc three times with DI water. Allow the DI water to run through the pour spout during each rinse.

4. Filtering Water Samples

Water samples are filtered using a peristaltic pump and 0.45um inline filter. The inlet tube to the pump is rinsed with environmental water then placed in the churn splitter. An inline filter is attached to the exit tube of the pump. About 500-ml of environmental water is pumped through filter before any sample water is collected. This water should not be used to rinse sample bottles. Rinse all filtered sample bottles three times with the filtered environmental water. Continue filtering until all filtered samples have been collected. After using the pump at a sample site, discard the inline filter and pump about a 500-ml of DI water through the tubing. Rinse the outside of the inlet and outlet tubing with DI water.

If the peristaltic pump fails or is unusable for any reason, samples can be filtered with a filter syringe. The filter syringe is used as follows: Disassemble a clean 100-ml filter syringe. Rinse the inside of syringe with environmental water three times. Place a new 0.45um disc style filter on the end of the syringe. Fill the filter syringe with environmental water. Push 10-15 ml of environmental water through the filter before any sample water is collected. Filter approximately half of the water in the syringe into the sample bottle and rinse. Shake sample bottle and discard water. Rinse the sample bottle three times with the filtered environmental water. Fill the sample bottle with filtered water using the syringe-filter procedure. Refill the syringe if more sample water is needed and the filter has not clogged. If filter is clogged, attach a new filter, rinse as stated above and continue.

5. Water Sample Preservation

Physical preservation techniques are used for all samples and include cooling and keeping the samples out of the sunlight. Some of the water samples are also preserved with acid to prevent degradation of constituents before they are analyzed. Specific requirements for the field preservation of the samples are listed in the Grab Sample List (Table 1) on page two of this SOP. All samples will be preserved immediately at the collection site.

Metals
Preserve metals in water for a 6 month hold time with nitric acid. Mercury has a hold time of only 28 days. 1 ml of 70% nitric acid is used for each 250 ml of sample water. The sample is also chilled to 4^{o}C in the field.

Nutrients
The 1,000 ml nutrient suite bottle requires 2 ml of H_2SO_4 and has a hold time of 28 days. The sample is also chilled to 4^{o}C in the field.

Other Samples
No acid preservation is used for orthophosphate, BOD, total alkalinity, and TDS. Total alkalinity and TDS samples have a 14-day hold time. Orthophosphate samples have a 48-hour hold time. BOD samples have a 48-hour hold time. Hydrogen Sulfide (Sulfide) samples are preserved with NaOH and have a 7-day hold time. The samples are also chilled to 4^{o}C in the field.

If in doubt about any sample, it is best to keep it chilled and out of the sunlight.

6. Dispensing Acid from Ampule for preserving samples

Rubber, latex or vinyl gloves and safety glasses are worn to prevent acid from contacting hands or eyes while preserving samples. If acid is present in the neck of the ampule, gently tap until all of the acid is in the body of the ampule. Place the provided ampule

"breaker" over the ampule, point away from face, and apply steady pressure until the ampule snaps at the prescored line. Hold the ampule upside down over the sample bottle between the thumb and index finger of one hand. With the other index finger, lightly tap the bottom of the ampule until all of the acid is dispensed. Properly discard the empty acid ampules.

PacifiCorp site samples will be preserved using acid from re-closable plastic vials. Gloves and safety glasses are also worn during the use of the re-closable vials to protect hands and eyes from acid. Vials should also be properly discarded once empty.

7. Sample Handling and Transportation

Sample handling and transportation vary depending upon the analysis requested, sample preservation requirements, and the distance to the laboratory. However, once preserved, some samples will remain stable for long periods of time. All samples for KBAO projects will be shipped overnight delivery on the day they are collected.

All water samples will be shipped in a cooler or ice chest. This provides protection, insulation, and containment in case of breakage or spillage. When shipping samples that require chilling, pack adequate quantities of frozen blue ice or crushed ice with the samples. Seal the ice chests securely with duct or packing tape to ensure they do not accidentally open.

8. Sample Quality Control and Quality Assurance

A. Objective

Quality control of samples during collection, transportation and processing is an integral part of a sampling program. Quality control procedures are implemented to assess potential sampling and analytical bias.

B. Techniques

Production Samples
A production sample is a sample taken at a site where no QA samples are collected. A production sample has the abbreviation of "P".

Regular Samples
A regular sample is the production sample at the QA site and has associated QA samples. A regular sample has the abbreviation of "R".

Duplicate Samples

A split sample is a portion or sub-sample of a total sample. The duplicate sample has an identical water matrix as the regular sample. This sample is used to determine analytical precision within a laboratory. A duplicate sample has the abbreviation of "D".

Triplicate Samples (Field Spikes and Reference Solutions)
These are reference solutions used to fill the sample bottles or chemical solutions (spikes) that are added to specified volumes of environmental water. A graduated cylinder is used to measure the volume of environmental water used for the "spiked" samples. All of the triplicate sulfide nutrient and trace metal samples are "spiked". Rinse the graduated cylinder three times with sample water. Using the graduated cylinder, measure out the appropriate volume of sample water (total triplicate sample volume – volume of spike = volume of environmental water). Pour approximately half of the sample water from the graduated cylinder into the sample bottle. Add the "spike" solution to the sample bottle. DO NOT add the spike to the graduated cylinder. Rinse the inside of the "spike" container with sample water from the graduated cylinder and add to the sample bottle. Pour the remaining half of the sample water from the graduated cylinder into the sample bottle. A reference solution is used for the total alkalinity BOD and TDS triplicate sample. In this case the triplicate (reference solution) is not mixed with environmental water, instead the reference solution is used to fill the entire sample bottle. A triplicate sample has the abbreviation of "S".

Blanks
A blank sample is used to test laboratory analysis and ensure the bottles are not contaminated. Blank sample bottles are rinsed three times with DI water. The sample bottles are then filled with DI water and corresponding preservatives are added. The blank should be prepared in the lab/office to avoid field contamination and carried in the field while sampling. A blank sample has the abbreviation of "B".

Rinsate Blanks
A rinseate blank tests the field crew techniques and sampling equipment for contamination. After the sampling equipment has been cleaned with DI water at the last sampling site , the rinseate blank is collected. Rinseate blanks are prepared by pouring DI water into the sample collection equipment (Van Dorn, etc). Wet all internal surfaces. The rinseate water is then collected into the churn splitter. The sample bottles are rinsed three times with the rinsate water before sample collection. Fill the sample bottles with rinsate water. Filter rinsate water for filtered constituents using a peristaltic pump and filter. Preservation is added to samples requiring it. A rinseate blank has the abbreviation of "RB".

Standards
Standards or reference materials are used for equipment that requires calibration. Use of reference standards is an integral component of quality control. Both field and laboratory equipment must be periodically calibrated to assure the instruments accuracy. Laboratories should calibrate equipment as required by the analysis method. The field equipment, such as the Hydrolab H20 unit and the Hach 2100P turbidity meter require regular calibration. The Hydrolab H20 unit will be calibrated as described in the KBAO

Hydrolab calibration SOP. PacifiCorp will calibrate the YSI 600 in the office and/or field as per manufacturer specifications. The manufacturer's instructions for calibrating the turbidimeter will be followed.

C. Sample Identification

A unique sample identification (ID) number is used for samples collected at different sites. The same number is used for all sample bottles collected at a given site on a given day. A letter prefix associated to the specific sampling project precedes the sample ID number. For example, a letter prefix of KRWQ identifies the sample as part of the Klamath River Water Quality Monitoring Program. These sample identification numbers are pre-selected by the KBAO and/or other sampling agency.

9. Field Notebooks

A bound field notebook is used to document collection of a sample, sample ID number, field observations, and other pertinent information necessary to reconstruct the sample collection processes. All entries are made in permanent waterproof ink. Any corrections made to the field notebooks are lined out, initialed, and dated. The person who collected the sample signs the field notebook. Field personnel will carry the field notebook during sampling. Past physical measurements and observations can be compared to current conditions. The field crew will make copies of the field notebook once they have returned to the office. Making copies will minimize the amount of data lost in the event the field notebook gets lost or damaged.
Field notebooks include:

- Sample Identification Information (including Field ID)
- Field Measurements (Water temp., pH, DO, etc)
- Equipment Information (serial number, model number, manufacturer, etc.)
- Sample Types (P, R, D, S, B, RB)
- Sample Collection (what analysis/constituents requested, etc.)
- Sample Preservation Information
- Date and Time of Collection
- Weather Conditions
- Comments

Field notebooks provide a convenient system for tracking the monitoring and analysis requests for each site in a particular project. Further, the field ID provides the cross-reference to laboratory results and sampling locations. The field crew keeps the field notebooks on file when the program is complete.

10. Chain of Custody

A COC accompanies all samples to record possession and transportation of samples. Field identification number, sample type, requested analysis, date of collection, and time

of collection as well as other information is recorded on the COC. COC's are completed with permanent ink. Any corrections made to the COC's are lined out, initialed, and dated. All samples are kept in a secured area accessible only to authorized personnel during sample collection and transport. Upon completion of the field collection of the samples, the COC sheet accompanies the samples to the lab. COC sheets are also legally binding and act as a work order for the laboratory. It is critical that the field identification numbers are properly recorded on the field notebook and COC forms. Sample collectors, individuals transferring samples, and those receiving samples, all sign the COC. The COC forms are in triplicate and field personnel should remove only the field copy (pink sheet).

11. Calibration Log

A bound calibration logbook is used to store calibration information for equipment requiring calibration. Calibration information for the Hydrolab H20 unit and Hach 2100P turbidimeter will be recorded in a bound calibration logbook. When instruments are calibrated in the field, all appropriate calibration information is recorded in the field notebook.

12. Ringed Field Binder

A ringed binder is used to store information pertinent to a sampling project. The binder can be used to store a copy of the SOP, Quality Assurance Project Plan, level one clean-bottle certificates, acid purity certificates, certificates for in-line filters, COC sheets, copy of field notebook, and other pertinent information.

13. Security Shipping Seals

When shipping samples a security seal is attached across the lid and side of the ice chests. The seal is signed and dated by the sampling personnel. The seal is attached so that it must be broken when the container is opened.

Equipment & Supplies List

Equipment and Supplies

- Field notebook
- Field datasheets
- Clipboard
- Chain Of Custody form
- Zip-lock bag for COC form
- "Sharpie" felt tip pens
- Ball point pens
- Van Dorn sampler with rope
- Churn splitter
- Peristaltic pump and in-line filters
- Prepared bottles and labels
- Extra sample bottles
- Extra bottle labels
- Sulfuric acid ampules
- Nitric acid ampules
- Waste container for broken acid ampules
- Rubber, latex, or vinyl gloves
- Safety glasses
- Spikes
- Graduated cylinder
- 10 gallons DI water
- Squeeze bottle for DI water
- Hydrolab? H20 unit, spare battery and cables
- Bucket for Hydrolab?
- Turbidity meter
- Ice chests
- Ice packs (Blue ice)
- Packing tape
- UPS overnight shipping forms
- Rope
- Waders (Waders may be knee, hip, or chest)
- Cell phone and telephone numbers
- Knife/scissors
- Maps
- Paper towels
- Camera and film
- GPS unit
- Extra batteries
- Tools
- Syringe filters (back-up filters)

Personal Supplies

-Drinking water / food
-Leather gloves
-Sunglasses
-Hat
-Extra socks
-Sun block
-Anti-bacterial hand gel

Contact Information

Laboratory Addresses (Jason, Richard update as appropriate)

Basic Laboratory
2218 Railroad Ave
Redding, California 96001
530-243-7234
Parameters: BOD, Alk, PO_4, TP, NO_3-NO_2, NH_4, TKN

SEM

Aquatic Analysts
7975 SW Tennis Ct
Wilsonville, OR 97070Parameters: Algae speciation and chlorophyll a
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Agency Addresses

USBR Addresses

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