STANDARD OPERATING PROCEDURES MANUAL

Virginia Department of Environmental Quality

Water Quality Monitoring

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Commonwealth of Virginia
Department of Environmental Quality
Water Quality Monitoring and Assessment
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WQM SOP Revision #	History/Changes	Effective Date
22	1. Updated calibration schedule. See section 3.3.3 and Tables 3-1 and 3-2. Mid-week calibrations for pH and specific conductance dependent on previous day post-check. Previously calibrated daily. 2. Added collection methods from filamentous algae monitoring program (section 4.10). 3. Numerous minor edits. Superseded methods from previous SOP versions moved to Appendix G	4/22/2024
22.1	Updated table 3-2 and section 3.3.9 to maintain consistency with CBP SOPs. Threshold for maintenance after end-of-day check changed from 0.30 to 0.20 mg/L. Threshold for data entry of field parameters now inclusive of threshold value. Formerly was limited to values exceeding the threshold.	5/13/2024

TABLES

FIGURES

Introduction to Water Quality Monitoring and Assessments Operating Procedures Manual

This document describes the routine operations and quality control activities performed by the Department of Environmental Quality (DEQ) in most of its ongoing data generating programs. Outlining procedures for sampling and field monitoring activities helps ensure that these procedures are standardized geographically across the state and between monitoring programs. Many of the DEQ water quality monitoring programs have similar sample collection, field testing activities, and quality assurance requirements. Data generated from these programs must meet the needs of the data users. Comparability of data between DEQ's sampling programs and regional offices is an important quality objective.

The procedures described in this manual help ensure that sampling precision, accuracy, representativeness, comparability, and completeness of the data are obtained and documented. The sample collection procedures described in this document must be followed for all Water Quality Monitoring Programs unless the program is specifically covered under an SOP and/or Quality Assurance Project Plan that has been approved by WQMA QA Coordinator.

The terms **General** and **Routine** are used throughout this document to refer to programs, instructions, and processes that are regularly performed by DEQ monitors. These are set apart from programs that explicitly identify processes for special studies, less common monitoring activities, and monitoring for responses to emerging water quality concerns in the state. Documented differences in such programs are either:

1. Explicitly described in a subsection of this document.

   OR

2. Have their own independent SOP and/or Quality Assurance Project Plan (QAPP).

   OR

3. Are responses to emerging water quality issues that have an SOP and/or QAPP in development.

Adding New Collectors in CEDS

When a new collector needs to be added to CEDS, managers must confirm that the new monitor has:

1. Has received the necessary training to collect samples and record data in the field or will be sampling with an experienced monitor until such training is complete.
2. Successfully passed the SOP test.

1 PREPARATION

Prior to departure for a sampling run, make a checklist of all routine material and equipment needed. Make separate checklists for specialized sampling such as clean metals, sediment, and boat sampling.

At a minimum, the checklist should include the following items:

1. Field data sheets for the scheduled run including sites where Quality Assurance (QA) samples are collected.
2. List of sampling containers needed, preservatives, and labels, including QC samples, extra containers, and labels.
3. Equipment for field measurements, sampling devices, coolers, and ice.
4. Topographic or similar map of the monitoring run and GPS unit to confirm site locations.
5. Safety gear relevant to the monitoring activity being conducted. Refer to **Section 7** of this document for suggested equipment.
6. Cell phone, STARS radio, or other form of emergency communication.
7. Verify all sampling equipment is clean, in good working condition and any equipment batteries are charged.

Before leaving on a sample run, inform the designated contact or supervisor the location of the run, expected return time and contact method if you are overdue.

Calibrate all field probe instruments according to manufacturer guidelines outlined in **Section 3** of this document and enter the calibration information into the calibration log sheet. A template for the calibration log sheet is available in **Appendix A**.

Note: Several sections of this document include steps that require **lab grade water** for a variety of purposes. For the purposes of this document, lab grade water is typically deionized (DI) water, which can be obtained from DI water systems at each regional office. Some programs may specify a particular type of lab grade water (or “reagent water”), which may be supplied by a laboratory. Always follow program-specific SOPs and QAPPs where applicable.

2 CLEANING AND PREPARATION OF SAMPLING EQUIPMENT

2.1 SAMPLING EQUIPMENT

A variety of handling and cleaning methods are used to maintain sampling equipment depending on use and application requirements. For example, if collecting metals or similar samples, the use of non-metallic materials like plastic or Teflon is required. Organic samples collection requires non-organic or inert materials, such as stainless steel or Teflon.

2.1.1 Grab Sampling Equipment Storage and Transport

Most sites are sampled using buckets or similar types of grab sampling equipment. Sample equipment must be clean and well maintained to ensure accurate sample results. Follow the following general guidelines when using grab sampling equipment:

1. Never store or carry equipment such as the sampling spool in the sample bucket. Doing so can contaminate the equipment and cause nicks and scratches to the bucket.
2. Examine equipment for dirt, rust, or scratches. Clean or replace as necessary. Dirty or scratched equipment can allow residue and bacteria to remain after cleaning. Label damaged equipment as such and notify managers or team leads.
3. Dispose and replace sample bottles or containers if cracks or contamination are present.
4. Bulk shipments of plastic sample containers often have lids shipped separately. When storing containers, keep opened boxes covered or closed to reduce dust and other contaminants from entering exposed container openings or lids.
5. When assembling plastic sample containers, wash hands or wear powder free gloves to reduce potential contamination from entering the bottle.

2.1.2 General Water Grab Sampling Equipment

1. Sampling rope on spool.
2. Stainless steel bucket with a fitting for mounting bacteria sample bottle on the outside, or other suitable sampling device (Van Dorn, Kemmerer, pump and hose, etc.).
3. Clean sample bottles and/or cubitainers suitable for the samples being collected.
4. Syringe or vacuum pump, filter paper, filter holder etc. for samples requiring filtering.

2.1.3 Sediment Grab Sampling Equipment

1. Sampling rope on spool.
2. Certified pre-cleaned glass jar(s) with Teflon-lined lid.
3. Teflon coated or plastic spoon and stainless-steel spoon.
4. Sample dredge (such as Petite Ponar) depending on sediment type and depth of water.
5. Appropriately sized stainless-steel pans.

2.2 Sampling Equipment Preparation and Cleaning

The guidelines below cover the procedures to ensure proper equipment function and minimize sample contamination for routine sampling runs frequently encountered by field teams.

Preparation procedures may be modified to fit specific project goals. If sampling within a sample matrix or for parameters not covered in this section, or to review project-specific procedures that deviate from these, refer to project-specific SOPs or QAPPs or contact the QA Coordinator.

2.2.1 Water Sampling Equipment Cleaning and Maintenance

At the end of each sampling day:

1. Rinse grab sample equipment with lab grade water and air dry. If buildup remains, clean as outlined in the weekly or monthly schedule.
2. For pump and hose apparatus, refer to the Equipment Maintenance section of the Chesapeake Bay Program Tidal SOP manual at https://www.deq.virginia.gov/our-programs/water/water-quality/monitoring/chesapeake-bay-monitoring.
3. If using another depth sampling device like a Kemmerer or Alpha Bottle, follow the manufacturer's recommendations for cleaning.

Weekly maintenance:

1. Wash stainless steel water sampling equipment (buckets, bacteria samplers, etc.) with lab grade soap (e.g., Liquinox or Alconox) using a brush to remove all surface deposits. Soak plastic sampling equipment (e.g., chlorophyll syringe) in a lab grade soap solution.
2. Rinse thoroughly with tap, then lab grade water, and allow to air dry at room temperature.
3. If rust or other deposits remain on stainless steel equipment, scour clean using a soft brush or clean cloth and baking soda and water paste. Scour along the steel grain. After cleaning, repeat steps 1 and 2.

Monthly Maintenance:

1. For the pump and hose apparatus, refer to the Equipment Maintenance section of the Chesapeake Bay Program Tidal SOP manual listed above.

Annual maintenance:

1. Inspect rope used to lower sampling equipment for fraying and replace as needed.
2. Inspect rubber tubing to hold bacteria sample bottles for wear and replace as needed.
3. For the pump and hose apparatus, refer to the Equipment Maintenance section of the Chesapeake Bay Program Tidal SOP manual listed above.

2.2.2 Trace Equipment Cleaning and Maintenance

Follow these procedures to clean sampling equipment used for trace sampling such as clean metals and PCB. At the end of each sampling day or prior to sampling:

1. Wash equipment using clean scrub brushes and lab grade detergent (e.g., Alconox or Liquinox) and rinse with lab grade water until all residues are removed. For PCB equipment, skip to step 3.
2. For equipment used in trace metals sampling, repeat washing and rinsing procedure using lab grade acid cleaner/detergent (e.g., Citranox) and lab grade water.
3. Rinse with pesticide grade ethanol or methanol to remove organic compounds.
4. Rinse thoroughly with lab grade water until all ethanol or methanol is removed.
5. Dry equipment at room temperature away from potential sources of contamination.
6. Visually inspect equipment for any contamination prior to storage. Such contamination would include water spots, dust or sediment, rust, and similar substances. If contamination is observed, repeat steps 1-6.
7. Cover cleaned equipment with clean aluminum foil until next use. Ensure that all surfaces that may contact any sample are covered in foil and are not susceptible to contamination during storage or transport.

2.2.3 Trace Equipment Field Cleaning Instructions

If trace sampling equipment needs to be cleaned in the field, the following procedure should be followed.

Note: For cleaning equipment in the laboratory, refer to the previous section.

1. Wash contact surface with Liquinox detergent.
2. Rinse contact surface with lab grade water.
3. Rinse contact surface with pesticide grade acetone or ethanol (save rinsate for disposal back at the lab).
4. Rinse contact surface with lab grade water.
5. Drain off as much water as possible and wrap in aluminum foil until ready for use.

2.3 Routine Sample Container Handling and Preservation

Proper sample containers and sample preservation are essential to sample integrity. Refer to the DCLS laboratory catalog in CEDS for the appropriate preservation procedures. Samples not preserved properly may be rejected by DCLS.

Containers used by DEQ are parameter and program specific to meet agency and DCLS sample size, purity, construction, and material requirements. Do not substitute sample containers listed in CEDS without first consulting the WQM QA Coordinator or DCLS.

Storage:

- Mark boxed or packaged sample containers with the date of receipt and stock on shelves. Mark sample container boxes with the date the box was initially opened. Use the oldest dated box/packages first. Keep sample container boxes closed while in storage to prevent dust or foreign material from entering.
- Discard sample containers that are damaged or have foreign material inside the container.

Sampling:

- After collecting the sample, tightly secure lids to prevent water leakage.
- Sample containers and coolers should be stored with the tops securely fastened. Replace caps or tape loose cooler fasteners to prevent loss of sample contents.
- Include a temperature bottle in each cooler so DCLS can determine sample temperature.
- Unless specified, pack sample coolers with collected samples as follows:
    - Place all samples in an ice filled cooler immediately after collection.
    - Always place sample containers upright.
    - If possible, cover containers with ice so container openings are just above the ice.
    - Store filtered pad samples (e.g., chlorophyll *a*) in a zip-top bag resting on top of the ice in the cooler. To prevent water from entering the bag, keep the sealed bag zipper opening outside of the cooler by placing the zipper opening between the cooler body and lid on the hinge side of the cooler or seal the top of the bag with clear packing tape.
    - Place bacteria sample bottles in mesh bags in coolers and surround with wet ice.
- To minimize breakage, wrap glass sample containers in bubble wrap or similar materials.
- Prior to shipping, drain melted ice from the cooler and top off the cooler with fresh ice to the level of necks of sample bottles.

2.4 SAMPLE IDENTIFICATION

At a minimum, each sample container must be identified with the following information:

1. Station ID
2. Sample date and time (military time)
3. Sample depth
4. Collector initials
5. Parameter group code
6. Lab processes code (if applicable)
7. Container number (see below)
8. Preservative used (if any)
9. Volume filtered (if any, record in preservatives section)

Figure 2-1. Example of a sample container label

For most sample containers, use a laser printer to print sample tag information on an adhesive Avery-style label and apply directly to the container exterior. For cubitainers and bottles that do not adhere well with labels, attach the label to a wire tag. Secure the wire tag by tying the wire to the container below the bottom lid lip next to the bottle shoulder.

Record any hand-written information such as time collected on the sample tag using indelible ink. Sharpie permanent markers with a fine or ultrafine tip work well for writing on labels.

Information on the sample tag must match exactly what is scheduled in CEDS field data screen. DCLS will reject samples where information on the tag does not match exactly what is entered into CEDS, including the sample time. If more than one container is needed for a group code, each container collected for that group code must have a label with identical information in addition to an indication of 1 of 3, 2 of 3, etc., as required.

The sample time must exactly match what is entered into CEDS. For routine and other non-compliance samples, it is acceptable to record sample time to the nearest 15 minutes. Record the exact time of sampling for compliance or chain of custody samples.

Only print labels from CEDS using a laser printer to avoid the labels from smudging when wet. If a label is needed where a station is not yet established in CEDS or if CEDS is down, label blank sample tags and attached to the bottle.

Always check the label information against scheduled station/sampling documentation to ensure label accuracy.

Some sample types may require specific labeling. Such requirements are typically detailed with the sampling guidelines provided upon receipt of the sample bottles. Improperly labelled samples may be rejected by the laboratory.

2.4.1 Labeling QC Samples

Label QC samples as above and follow the steps in this section to properly identify them as QC samples. Two fields are used to ensure proper identification of QC samples and differ from "Regular" samples:

Blank/Dups field - Be sure to enter this sample designation in CEDS upon return to the office.

Replicate Samples: Label with **S1**, **S2** (triplicates or additional split samples use S3 and subsequent designations).

Equipment Blanks: Label with **EB**

Note: DO NOT use code "R" if collecting a QC sample

Container # field – Do not use the same number more than once per sampling event. The number on the sample tag or label and the number in this block must match with what is entered in CEDS and/or COCR form.

Replicate Samples: Use 11-19.

Equipment Blanks: Use 21-29.

Example: A station requires TNUTL and IONTR samples along with replicates and equipment blanks. The following table illustrates acceptable values for sample tags.

	Replicates		Blanks
Blank/Dups field:	S1	S2	EB
TNUTL **container #**	1	11	21
IONTR **container #**	2	12	22

2.5 Muffling Sample Filters

Most samples covered under this SOP manual do not use muffled glass fiber filters that remove trace contaminants like carbon. If samples require muffled filters, the WQM program uses the muffling procedure found in the Chesapeake Bay Program Tidal SOP manual at https://www.deq.virginia.gov/our-programs/water/water-quality/monitoring/chesapeake-bay-monitoring.

2.6 Chemical Preservatives and Reagents

Each regional office is responsible for maintaining an adequate supply of chemical reagents to preserve samples and clean equipment. Expired or tainted chemicals can result in inadequate preservation and sample contamination.

Note: While the below information is helpful, please refer to the DEQ Chemical Hygiene Plan at https://covgov.sharepoint.com/sites/DEQ-Health/SitePages/Resources.aspx or speak with the regional Chemical Hygiene Officer for more information regarding chemical handling, storage, and disposal. **Section 7.3** contains additional information on chemical safety and disposal.

- Write the date the bottles were first opened on the bottle to ensure they are consumed quickly.
- When not in use, store chemicals in the appropriate storage cabinet. Do not store clear or amber colored reagent bottles in the open as light may degrade the chemical. Chemicals in opaque bottles may be stored on a shelf or laboratory cabinet if they are not overly toxic or harmful. Otherwise, store reagents in the proper chemical storage cabinet.
- Whenever handling chemicals of any kind, always follow safe laboratory techniques including the use of eye protection, gloves and aprons and wash hands after handling. **Section 7** contains general information on handing routinely used reagents.

2.6.1 Chemical Preservatives and Reagents Disposal

- Soap solutions and waste tap or lab grade water can be poured down the drain.
- Diluted solvents and acids used in cleaning may be poured down the drain after neutralization and additional dilution with tap water.
- High strength solvent and acid waste is to be handled as hazardous waste and must be properly collected and disposed of according to federal, state, and local regulations. Consult the regional Chemical Hygiene Officer for guidance on handling and disposing high strength chemicals or waste products.

Chemical hygiene information

List of Regional Chemical Hygiene Officers: https://covgov.sharepoint.com/sites/DEQ-Health/SitePages/Committee-Members.aspx

DEQ Chemical Hygiene Plan: https://covgov.sharepoint.com/:w:/r/sites/deqnet/Shared%20Documents/Health%20%26%20Saftey/Resources/2022_Chemical_Hygiene_Plan.docx?d=wd4bd82a7671c4bc2a13f82abfa557d63&csf=1&web=1&e=k5F3pp

Table 2-1: Reagent shelf life and storage

Compound Type	Name of Reagent	Shelf Life	Recommended Storage Area	Discard prior to expiration if:
Acid	Concentrated acetic acid	3 years	Acid cabinet	Cloudy and/or solids observed in the container.
	Conc. hydrochloric acid			
	Conc. sulfuric acid			
	Conc. nitric acid		Oxidizer or acid cabinet. Not with organics.	Nitric acid has strong yellow/orange color.
Base	Conc. sodium hydroxide or pellets	5 years	Base (Alkaline) cabinet. Pellets may be stored on a closed container on a laboratory shelf	Liquid is cloudy, discolored, or solids observed. Pellets clump together and cannot break apart easily.
Solvents/ Organics	Acetone	5 years	Flammable cabinet	Solution turns cloudy or solids observed in the container.
	Conc. ethanol or methanol			
	Formalin (formaldehyde)	3 years		
Solid Chemicals	Potassium chloride crystals Sodium thiosulfate crystals	5 years	Laboratory shelf away from light (if bottle is not opaque)	Powder clumps do not break apart from shaking container.
	Magnesium carbonate			
	Sodium chloride			
Buffers	pH Buffer	12-18 months	Laboratory shelf or storeroom	Cloudy or suspended solids
Dye	Rhodamine WT	1 year	Laboratory shelf away from light	Discoloration or cloudy
Diluted Reagents	Any of the above compounds diluted ≤50%	1 month to 1 year	Laboratory shelf away from light	Discoloration, suspended solids, insufficient strength

Note: The DEQ Safety page https://covgov.sharepoint.com/:f:/r/sites/deqnet/Shared%20Documents/Health%20%26%20Safety contains a list of chemicals and storage locations used in each region

To dilute a solution to a desired concentration, follow the dilution equation:

$$M_1V_1 = M_2V_2$$

Where:

- M_1 = initial concentration (or molarity)
- V_1 = initial volume
- M_2 = final concentration (or molarity)
- V_2 = final volume

2.7 Laboratory Glassware Cleaning

After use, all glassware used to prepare or handle chemicals must be cleaned using lab grade soap and water. Precise volumetric flasks and pipette glassware may require additional acid wash cleaning. Acid washing should be performed if water droplets are seen inside the volumetric glassware after adding lab grade water.

Note: If handling high strength acids, consult the regional Chemical Hygiene Officer.

1. Before starting the acid washing process, clean the glassware.
    a. Add a small amount of phosphate-free lab soap such as Liquinox and lab grade water into the empty glassware. To wet the entire inner surface with the soap solution, use a clean bottle brush or cap the opening with a stopper and invert repeatedly. Pipettes can be cleaned by placing in a pipette cleaner or by hand washing.
    b. Dump the soapy water and rinse with lab grade water six times.
2. **For non-volumetric glassware, skip to step 9**. If cleaning volumetric glassware, determine if water droplets form on the inner surface. **If no droplets are observed, proceed to step 9. If droplets are seen, proceed to step 3.**
3. Ensure the fume hood is on and operating normally. While under the fume hood, pour a small amount (usually 10 to 20 mL) of 50% or concentrated sulfuric acid into a beaker. Use the beaker to pour into the flask or draw up into a pipette.
4. Allow the acid to slowly coat the glassware inner surface by capping and rotating/inverting flasks to wet the entire surface. For pipettes, fill to at least 1 inch above the volumetric line.
5. The acid is finished cleaning when the liquid coating the surface flows smoothly (no ripples). Repeat steps 3 to 5 until the acid coating the bottle flows smoothly.
6. Slowly pour out the acid wash into a beaker to reuse for a second piece of glassware. Discard acid washes in an acid waste container or neutralize in a bucket containing a solution of water and baking soda or sodium hydroxide. If neutralizing, add excess sodium hydroxide or baking soda until bubbles stop forming or check the pH using litmus paper. Do not dump contents down the sink until neutralized (no bubbles) and pH is above 4.00.
7. Rinse the glassware using three successive 20-50 mL rinses of lab grade water. Pour the rinses into the waste container or neutralizing bucket. For pipettes, use a clean squirt bottle with lab grade water and do three rinses through the top hole of the pipette.
8. Observe the glassware to determine if water spots form. If so, repeat steps 3-7.
9. Allow the glassware to dry completely. For volumetric flasks, cap using a plastic flask cap or foil to prevent dust from entering the cleaned container while drying and in storage. **Do not cap flasks with ground glass stoppers as they can become stuck.** Pipettes can be wrapped in foil. Store glassware in the glassware cabinet or pipette drawer until needed.

2.8 Analytical Scale Calibration

Analytical scales that are used to measure reagents must be properly calibrated as follows:

1. Turn the scale on and allow it to warm up for at least 15 minutes. While warming up, use a soft brush to clean the weighing pan and close all scale doors.
2. Level the scale by adjusting the feet and using the provided level bubble indicator.
3. If calibration weights have dust or foreign material present, gently clean them using a soft cloth or lint free tissue. DO NOT pick up or handle weights with bare hands.
4. Once the scale has warmed up, tare the scale so the readout displays 0.0000 grams.
5. Following the scale manufacturer manual, set the scale to calibrate mode. In calibration mode, the scale will usually display the needed weight to calibrate.
6. Using a lab tissue or weight tongs, place the necessary weight(s) on the center of the scale weighing pan and gently close the door.
7. The scale will indicate calibration is complete and automatically exit calibration mode.
8. Remove weights and allow the scale to report a stable reading. Tare the scale to 0.0000.
9. To ensure the calibration accuracy. Place the calibration weight(s) back onto the scale to confirm readings are within 0.0005 grams of the weight(s). If not, repeat steps 6-9.

Note: If the scale must be moved, move the scale to a flat and stable surface, ensure that the scale is level, and check with reference weights to determine if recalibration is necessary.

2.9 Lab Standard Preparation

To ensure accurate standard preparation, use the guidelines outlined in the following subsections.

2.9.1 General Guidelines

1. Refer to **Table 2-1** to confirm reagents are not expired and in good condition.
2. If using unexpired but clumpy powder reagent, it must be dried to ensure accuracy.
   a. Place reagent into a clean weighing pan or crucible.
   b. Place the pan into a drying oven set at 100-110° C and heat for at least 3 hours.
   c. Remove the pan from the oven and place in a desiccator that has activated desiccant (usually blue color indicates activated desiccant) until ready for weighing. Allow at least 15 minutes for reagent to cool in the desiccator before weighing.
   d. Before weighing, use a clean lab spatula to confirm powder no longer clumps.
3. Only use lab grade water to prepare reagents. Contact the QA Coordinator if there may be problems with the water purification system.
4. Use analytical scales and Class A volumetric glassware to measure stock reagents.

Table 2-2: Preparation of commonly used stock solutions per liter.

Solution	Uses for	Powder Reagent	Liquid Reagent	Dilute To
50% H_2SO_4	Preservative, cleaning agent	N/A	500.0 mL concentrated H_2SO_4. **First add 300 mL water to volumetric flask!**	Bring to 1.0 L with lab grade water
70 % HNO_3	Preservative	N/A	**Use undiluted 70% HNO3** to preserve samples.	
10% HCl	Cleaning agent	N/A	100.0 mL concentrated HCl. **First add 300 mL water to volumetric flask!**	
1 M KCl	Conductivity stock	74.551 g KCl	500.0 mL of 2 M stock.	
0.1 M KCl	12,880 µS/cm standard	7.455 g KCl	100.0 mL 1 M KCl	
0.01 M KCl	1,413 µS/cm standard	0.7455 g KCl	100.0 mL 0.1 M KCl or 10.0 mL of 1 M KCl	
10 g/L $MgCO_3$	Chlorophyll a filter preservative	10.0 g $MgCO_3$	N/A	
Rhodamine WT 125 mg/L Stock	Chlorophyll and blue green Stock	N/A	5.0 mL 2.5% Rhodamine WT	
625 ug/L Rhodamine WT	Chlorophyll and blue green standard	N/A	5.0 mL of Rhodamine WT stock	
1000 mg/L NaCl	Chloride sensor	1.655 g NaCl and 0.5g $MgSO_4$	N/A	
10 mg/L NaCl	Chloride sensor	0.5g $MgSO_4$ and	10.0 mL 1000 mg/L NaCl	

2.9.2 Standard Preparation: Powder Reagents

If using an analytical scale to measure powder reagents, use the following procedure:

1. Turn on and calibrate the scale as outlined in **Section 2.8** of this manual.
2. After verifying the accuracy of the scale, place a clean, empty weighing dish or crucible onto the scale and close the scale door.
3. After the scale stabilizes, press the 'Tare' or 'Zero' button. The display should show a reading of 0.0000 g. Remove the dish after zeroing the scale.
4. Using a clean beaker, measure out an approximate amount of powdered reagent needed.
5. With a clean spatula, transfer the reagent from the beaker into the weighing dish. Place the dish back onto the scale and allow the reading to stabilize. When close to the desired weight, close the scale door after adding or removing additional reagent to ensure accuracy. **DO NOT pour unused reagents back into the reagent bottle.**
6. When the weight is correct, remove the weighing dish containing the reagent and carefully pour into a clean volumetric flask using a clean funnel. Rinse all residues from the pan and funnel into the flask using lab grade water. Discard any unused reagent according to **Section 2.6.1**, taking care to follow manufacturer's instructions and state and federal regulations. Do not dump unused reagent back into the reagent container.
7. Proceed to **Section 2.9.5** for mixing the reagent using a volumetric flask.

2.9.3 Standard Preparation: Liquid Reagents and Flask

If using volumetric glassware to measure liquid reagents, use the following procedure:

1. Determine if the volumetric flask is clean by adding ≈ 10 mL of lab grade water to see if spotting on the stem of the flask occurs. Discard this rinse down the drain.
    a. If spotting is observed, use new flask or go to **Section 2.7** to acid wash the flask.
2. Fill the flask with the reagent so the bottom of the meniscus (U-shaped depression) rests on the etched line of the flask stem. Discard any excess down the drain using a clean pipette.
3. Drain the entire flask contents into the larger preparation volumetric flask. Rinse the smaller flask with three, 10-20 mL rinses of lab grade water and drain into the larger flask. Ensure that rinses cover the entire inner surface of the smaller flask.
4. Proceed to **Section 2.9.5** for mixing the reagent using a volumetric flask.

2.9.4 Standard Preparation: Liquid Reagents and Pipette

If using a volumetric pipette to measure reagents, use the following procedure:

1. Ensure the pipette is clean by filling the pipette to the printed measurement line with reagent. Drain the contents into a waste container or sink and check for droplets on the inside of the pipette. If it is dirty, obtain a new pipette or clean following **Section 2.7**.
2. If the pipette is clean, fill again with the stock solution to the printed measurement line and drain into the volumetric flask for the lab working solution.
3. If the pipette has a TC (To Contain) mark, blow out any residue into the flask and rinse the inside with lab grade water into the flask. If using a TD (To Dispense) pipette, do not blow out contents or rinse.
4. Proceed **Section 2.9.5** for mixing the reagent using a volumetric flask.

2.9.5 Proper Filling and Mixing: Volumetric Flasks

1. Fill the volumetric flask containing the reagent and rinses to the neck with lab grade water.
2. Tightly cap the flask using a cap and invert ten times or until the powder/crystals dissolve.

   Note: Magnesium carbonate will not fully dissolve.
3. Remove the cap. Using a squirt bottle, add additional lab grade water to the etched line on the flask. The bottom of the meniscus (U shaped depression) should rest on the etched line. If the flask is overfilled, discard the solution and restart.
4. Cap and invert the flask a least 20 times to ensure proper mixing. Label the container that will hold the standard with:
   a. Standard strength/concentration
   b. Date of preparation
   c. Preparer initials

3 FIELD PROBE CALIBRATION AND MAINTENANCE

This section covers the calibration and maintenance of electronic field meters. Although different regions and programs may use different field probes, the same general procedures apply unless stated otherwise. Always follow instructions provided in probe-specific manufacturer user manuals. Ensure that manufacturer user manuals are readily available in appropriate locations (i.e., in regional office labs).

3.1 FIELD PROBES: STORAGE AND TRANSPORT

To ensure sensor performance and accuracy, transport and store probes in the following manner:

- **Short-term storage (daily, weekly, biweekly use):** Ensure that the sonde, probes, sensors, and junctions are clean and free of sediment and/or biofilms. Attach the calibration cup or equivalent probe container with a small amount (about 1-cm) of tap water or a moistened sponge. Do not submerge the sensors in the solution. Store probes inside the regional office or other temperature-controlled area while not in use.
- **Long-term storage (e.g., over winter, end of sampling season):** Ensure that the sonde, probes, sensors, and junctions are clean and free of sediment and/or biofilms. Remove and store individual sensors independently according to sensor-specific guidelines found in the probe-specific user manual. Plug open ports according to manufacturer's instructions. Remove batteries if sonde was deployed for continuous monitoring.
- **During transport:** Turn off probe and display. If possible, keep equipment in a temperature-controlled environment, such as the vehicle passenger compartment while traveling. Keep sensors in a moist environment according to short-term storage guidelines. When traveling between stations, sample water may be used to keep sensors moist.

3.2 PREPARATION FOR FIELD USE

Prior to departing the lab or office for field monitoring, ensure the following:

- Calibrate field meters according to the calibration schedule described in **Section 3.3.3**.
- Use a multiprobe communication cable of sufficient length to sample all sites on the run.
- Prior to leaving the office and between station visits, ensure that the sensors are kept moist by following the guidelines in **Section 3.1**.
- At the sample site, remove the storage cup and ensure that the guard is attached before deploying.
- Between sample sites, either immerse the sensors in a container of sample water or install the calibration cup with tap or sample water to keep sensors moist.

3.3 MULTIPROBE CALIBRATION AND REFERENCE CHECKS

The following guidelines apply generally to multiprobe sondes (e.g., YSI EXO, Hydrolab HL4, In-Situ TROLL). For manufacturer-specific information refer to manufacturer user manuals.

Note: The procedures below assume familiarity with the basic operation of multiprobe displays, including accessing calibration and diagnostic menus. Refer to manufacturer user manuals for probe-specific instructions or to troubleshoot or accomplish tasks not outlined below.

General guidelines:

ALWAYS

- Use fresh, unexpired standards to calibrate or verify. Old standards may only be used for pre-calibration rinses.
- Calibrate/verify using standards closest to expected field values.
- Record information from calibration, end of day checks, and maintenance notes in the calibration logbook.
- Ensure that sensors are in an upright position during calibration by securing the multiprobe with a lab stand and clamps/support rings.
- When handling the sonde, hold near the cable connection to minimize temperature fluctuations.
- Tag and remove from rotation any sondes that require maintenance due to expired sensors or failed reference checks.

NEVER

- Accept a calibration or verification if a warning or probe failure message is displayed. Service and recalibrate the unit prior to use.
- Turn off the display prior to completing calibrations.

3.3.1 Controlled Environment

When possible, calibrate sensors in a temperature-controlled environment. Allow the probe to stabilize before calibrating. A probe is considered stable if the readout indicates it is stable or does not significantly change (≈ ±0.01 units) within ten seconds.

3.3.2 Data and Records Management

All results of calibration, post sampling verification, and field data sheets must be documented and kept in a safe place for five years. Record temperature, DO, and pH to the hundredth place, and specific conductance to the tenth place and enter data into CEDS as such. Enter calibration data in an organized logbook. Submit calibration data for all probes to the QA Coordinator quarterly.

3.3.3 Weekly Multiprobe Calibration Schedule

Sondes must be calibrated regularly according to the schedule outlined in this section. Calibration frequency is parameter-specific and may depend on the results of a previous day's post-calibration check. See **Table 3-1** for a summary of the weekly calibration schedule.

Beginning of the week:

- Calibrate sonde sensors for all planned sampling parameters prior to departing the office for a sampling run.
    - Follow parameter-specific calibration guidelines in this section and/or using the manufacturer's instructions.
    - Parameters such as depth must be calibrated at the sampling site, not at the office.

During the week:

- Mid-week calibration requirements are parameter specific. Refer to **Table 3-1** to determine when to calibrate.
    - If the parameter requires checking the previous day's post-calibration check, ensure that the logbook indicates that the post-check values are within the calibration tolerance listed in **Table 3-2**.
    - If a previous day's post-calibration check was outside the calibration tolerance limits, recalibrate prior to sampling using a **factory reset calibration**.
    - If there was no sampling or post-calibration check on the previous day, recalibrate all parameters.

<table>
<tr><th rowspan="2">Parameter</th><th rowspan="2">Beginning of Week</th><th colspan="3">During the Week</th></tr>
<tr><th>Do Not Recalibrate</th><th>Factory Reset Recalibration</th><th>Service Required</th></tr>
<tr><td>pH</td><td rowspan="2">Calibrate prior to sample run at start of week</td><td rowspan="2">Previous day end of day check within calibration tolerance</td><td rowspan="2">Previous day end of day check within end of day check tolerance</td><td rowspan="4">Previous day end of day check outside end of day check tolerance</td></tr>
<tr><td>Specific Conductance</td></tr>
<tr><td>Barometric pressure</td><td colspan="3">Check daily prior to DO calibration</td></tr>
<tr><td>Dissolved oxygen</td><td colspan="3">Calibrate daily</td></tr>
<tr><td>Depth</td><td colspan="4">Calibrate at each site</td></tr>
<tr><td>Others</td><td colspan="4">Consult manufacturer's instructions and/or program specific QAPP/SOP</td></tr>
</table>

Table 3-1. Calibration schedule summary of common multiprobe parameters.

Table 3-2. Summary of calibration and end of day reference check acceptance criteria.

<table>
<tr><th rowspan="3">Parameter</th><th rowspan="3">Standard</th><th colspan="4">Acceptance Criteria</th></tr>
<tr><th colspan="2">Calibration</th><th colspan="2">End of Day Check</th></tr>
<tr><th>Tolerance</th><th>Range</th><th>Tolerance*</th><th>Range</th></tr>
<tr><td>Barometric pressure (mmHG)</td><td>Lab barometer or local weather station</td><td colspan="4">± 5 mmHG from reference</td></tr>
<tr><td>Diss. oxygen (mg/L)</td><td>Theoretical DO** based on BP and temperature</td><td colspan="2">± 0.10 from theoretical</td><td colspan="2">Maintenance threshold: ± 0.20 from theoretical
Data entry threshold: ± 0.30 from theoretical</td></tr>
<tr><td rowspan="3">pH (SU)*** (at ≈20 °C)</td><td>4.0</td><td rowspan="3">± 0.1</td><td>3.9 - 4.1</td><td rowspan="3">± 0.2</td><td>3.8 - 4.2</td></tr>
<tr><td>7.0</td><td>6.9 - 7.1</td><td>6.8 - 7.2</td></tr>
<tr><td>10.0</td><td>9.9 - 10.1</td><td>9.8 - 10.2</td></tr>
<tr><td rowspan="2">Spec. cond. (µS/cm)</td><td>1,413</td><td rowspan="2">± 2.0%</td><td>1,385 - 1,441</td><td rowspan="2">± 5.0%</td><td>1,342 - 1,483</td></tr>
<tr><td>12,880</td><td>12,622 - 13,138</td><td>12,236 - 13,524</td></tr>
<tr><td>Depth (m)</td><td>0****</td><td>± 0.3</td><td colspan="3" rowspan="4"></td></tr>
<tr><td>Turbidity</td><td rowspan="3">Consult program SOP/QAPP</td><td>± 5%</td></tr>
<tr><td>Chlorophyll</td><td>± 20%</td></tr>
<tr><td>Chloride</td><td>± 10%</td></tr>
<tr><td>Others</td><td colspan="5">Consult manufacturer’s instructions and/or program specific QAPP/SOP</td></tr>
</table>

*If end of the day checks meet or exceed tolerance range, do not enter associated field data into CEDS.
** Calculate theoretical DO values using **Appendix B**.
***pH is temperature dependent. Values in table are consistent with an ambient temperature of ≈20 °C.
****Calibration value for depth is instrument specific. YSI EXOs are calibrated at 0 m.

3.3.4 Factory Reset Calibration

Note: Information in this section is consistent with YSI EXO models. Follow manufacturer’s instructions for factory reset calibrations.

If a previous day’s end of day QA check produces values outside of calibration tolerance limits, perform a factory reset calibration. This process will reset sensor gain and offset to factory defaults. Follow all factory reset calibrations with a normal calibration according to this SOP and manufacturer’s instructions.

1. Navigate to the calibration screen. Select the desired parameter.
2. Select **‘Restore Default Cal’**. Select ‘**Yes**’ to confirm.
3. Calibrate parameter according to normal calibration procedures.

3.3.5 Multiprobe End of Day Checks

After sampling is completed for the day, teams must verify field probe accuracy by performing an end of day check. ***The end of day check is not a calibration***. The probe is verified by checking against standards in a controlled environment. **If the end of the day check meets or exceeds the tolerance ranges outlined in Table 3-2**, **do not enter associated field data into CEDS**.

The following sections provide parameter-specific information on calibration steps and end of day checks for multiprobes.

Note: A probe at room temperature will stabilize faster and reduce error during the end of day check. If probe temperature drifts strongly (> 0.20° C in 10 seconds) during a check, set up a room temperature water bath and submerge the probe for at least 15 minutes.

3.3.6 Multiprobe Calibration & Checks: *Temperature*

Sonde thermistors do not require calibration and instead rely on an initial factory calibration followed by user validation checks against a NIST-traceable thermometer. While thermistors installed on multiprobe sondes are generally very stable, as the thermistors age, temperature values will eventually begin to drift. It is important to ensure that sondes are checked regularly; sondes may need to be checked more frequently as thermistors age and approach their expected end of life (≈ 5 years).

Thermistors that differ from NIST-traceable thermometer values by ± 0.5° C or more should not be used for monitoring, require replacement, and possibly warrant flagging associated monitoring data. **Periodically compare the field probe temperature reading to a laboratory thermometer of known accuracy**. Record both readings on the log sheet. **Notify the QA Coordinator if the temperature difference is > 0.5 °C.**

3.3.7 Multiprobe Calibration & Checks: *Barometric Pressure*

Note: Barometric pressure is factory calibrated and should rarely need to be recalibrated

1. Turn on the display to view the main readout screen.
2. Compare the barometer reading to the laboratory barometer or use **Appendix B** to calculate local barometric pressure from the nearest National Weather Service (NWS) station.
3. If the two readings are off by 5 mmHg or more, calibrate the multiprobe barometer according to manufacturer's instructions.

Note: A laboratory barometer will display the uncorrected ("true") barometric pressure, which is required for checking sonde barometric pressure. NWS barometric pressure readings have been corrected to sea level. The equation in **Appendix B** converts the NWS reading to the uncorrected values required for calibration.

3.3.8 Multiprobe Calibration & Checks: *Specific Conductance*

Note: Some sensors require two-point calibration with a zero-calibration step (e.g., Hydrolab HL4, In-Situ TROLL), while others (e.g., YSI EXO) only require a one-point calibration with a known standard. For sensors that do not require a zero calibration, periodically verify a zero (or very close to zero) reading using the procedures described below, but without a calibration step.

Calibration

1. Inspect the conductivity sensor to ensure that the electrode channels are clean and free of deposits.
2. If needed, use a wet soft-bristle brush to gently scrub the sensors until clean. If a brush does not remove deposits, use a mild dish soap solution and repeat.
3. Rinse probes with the appropriate conductivity standard based on the expected field values.
    a. 1,413 µS/cm for freshwater
    b. 12,880 µS/cm for bay water
4. Fill the calibration cup with enough fresh standard to submerge the thermistor and conductivity sensor. If air bubbles are observed in the conductivity sensor gap, tap the side of the cup to dislodge the bubbles.
5. Allow temperature and specific conductance readings to stabilize. A reading is stable when the smallest displayed digit does not change more than one unit in ten seconds. This will likely take about a minute. Record the observed specific conductance reading on the calibration log sheet.
6. Navigate to the calibration menu on the display to calibrate for specific conductance.
7. Enter the appropriate calibration standard value using the keypad. Follow the prompts on the display to complete the calibration and record the displayed specific conductance value on the log sheet.
8. The specific conductance value must be within ±2% of the standard used.

Zero-Calibration/Verification

1. Rinse the conductivity sensor twice with lab-grade water and dry sensor gap with a clean tissue.
2. For sondes requiring a zero-calibration, continue with a two-point calibration step according to manufacturer's instructions.
3. For sondes that do not require a zero-calibration: ensure that the meter reads near zero (0-2 µS/cm) and proceed to a one-point calibration with a known standard.

End of Day Check

1. Rinse the conductivity probe with lab grade water and blot dry. Ensure the reading is 0 µS/cm (or 0 mS/cm). This verifies the sensor is not giving a false positive reading.
2. Rinse the sensor and calibration cup with conductivity solution of the same strength used to calibrate the probe. Refill the cup with fresh conductivity solution. Dislodge any air bubbles on the sensor by shaking or gently swirling the cup.
3. Allow the conductivity readings to stabilize. This may take up to minute or two.
4. Record the reading in the appropriate section of the calibration log sheet.
    a. Determine if the values are within the acceptable range (**Table 3-2**).

3.3.9 Multiprobe Calibration & Checks: *Optical Dissolved Oxygen*

Note: These guidelines apply to optical DO sensors only. For Clark Cell DO sensors information, see **Appendix G**.

Calibration

1. Inspect the optical surface of the DO sensor cap to ensure that it is clean and free of scratches.
    a. If needed, flush the sensor with water and gently wipe optical surface clean with a lint-free, clean, non-abrasive cloth or lab-tissue.
    b. If the DO sensor is scratched, replace the DO sensor cap.

Note: Room or ambient temperature water will reduce temperature equilibration time.

2. Rinse sensors and calibration cup twice with lab grade water.
3. Fill the calibration cup with ≈ 1/8 inch of water and loosely replace the calibration cup cap (do not tightly seal, keep loose to allow venting).
4. Allow temperature and DO readings to stabilize (± 0.01 units in 10 seconds). This step may take 10-15 minutes. Record the initial DO and temperature readings in the calibration logbook.
5. Calculate the theoretical DO value using the Dissolved Oxygen Calibration Table in **Appendix B** of this document. Record theoretical value in the calibration log sheet.
6. Navigate to the calibration menu on the handheld display or via associated software. Select **optical dissolved oxygen % saturation** (e.g., on a YSI EXO display, navigate to **ODO**, then select **DO%**.)
7. Confirm that the barometric pressure is accurate or enter the correct value.
8. After confirming that DO and temperature are stable, follow screen prompts to calibrate (e.g., on a YSI EXO display, select Accept Calibration).
9. The optical DO (mg/L) reading must be within ± 0.10 mg/L of the calculated theoretical level. Record the calibrated DO in mg/L on the log sheet.
10. If the reading is not acceptable, verify the barometer reading and re-examine the DO sensor cap. Clean and/or replace the sensor cap as needed and recalibrate.

End of Day Check

1. Follow **steps 1-7** of the calibration instructions above.
2. After confirming that DO and temperature are stable, record the reading in the appropriate section of the calibration log sheet.
    a. Determine if the values are within the acceptable range (**Table 3-2**).
    b. If the DO reading is 0.2 to 0.3 mg/L off from the theoretical DO, perform necessary maintenance.

3.3.10 Multiprobe Calibration & Checks: *pH*

Note: When calibrating/verifying pH sensors, it is generally best to conduct a 3-point calibration (4, 7, 10 pH buffer solutions), but staff can use the two pH buffers that most closely bracket the expected field values (**4 and 7** *or* **7 and 10** pH buffer solutions).

Calibration

1. Rinse the calibration cup and sensors twice with lab grade water.
    a. If the sensors are clean and free of obstruction, proceed to calibration.
    b. If the sensors require further cleaning due to fouling, ***do not*** physically scrub or swab the glass bulbs. Follow the manufacturer's instruction manual on cleaning the pH sensor, summarized in **Table 3-5**.

Note: Used pH buffer solutions from previous calibrations may be used for rinses only. **Always use fresh pH buffer solution for calibration.**

Note: The following instructions begin with pH 7. Consult manufacturer's instruction manual to determine the model-specific calibration order of pH buffer solutions.

2. Rinse the sensors twice with a small amount of 7.0 pH buffer solution. Discard rinses down the drain.
3. Fill the calibration cup with fresh pH buffer solution sufficient to cover the pH and temperature sensors by at least 1 cm.
4. Allow pH and temperature readings to stabilize.
5. Enter the calibration menu. Select 2-point (or 3-point) calibration if prompted (may vary depending on model; see manufacturer's instruction manual).
6. Record the displayed pre-calibration pH and mV values on the log sheet and follow screen prompts to calibrate the buffer value.
7. When readings stabilize, accept the calibration and record the final calibration value.
8. Pour the used pH buffer into a labelled storage bottle for use in future rinses and post-calibration checks.
9. Flush the calibration cup and sensors twice with lab grade water.
10. Complete steps 1-8 with pH 4 and/or pH 10 buffer solutions.

End of Day Check

1. Rinse the pH probe with tap or lab grade water, then rinse with fresh or used 7.0 buffer.
2. Fill the calibration cup (or appropriate container) with fresh 7.0 buffer.

3. Allow the pH readings to stabilize (±0.01 units in 10 seconds).
4. Record the reading in the appropriate section of the calibration log sheet. If the probe can display millivolt (mV) readings, record this as well.
5. Repeat steps 1 through 3 for pH 4.0 and/or 10.0 buffer. Use the same strength standards used during the morning calibration and any covering the values encountered in the field.
    a. Determine if the values are within the acceptable range (**Table 3-2**).

Table 3-3. Temperature dependent pH values of commonly used pH reference standards.

Temperature	0 °C	5 °C	10 °C	15 °C	20 °C*	25 °C	30 °C
pH 4.0 standard	4.00	4.00	4.00	4.00	4.00	4.00	4.01
pH 7.0 standard	7.12	7.09	7.06	7.04	7.02	7.00	6.99
pH 10.0 standard	10.31	10.23	10.17	10.11	10.05	10.00	9.95

*Approximate temperature of typical RO lab environment.

3.3.11 Multiprobe Calibration: *Turbidity*

Calibration

1. Rinse the calibration cup and sensor three times.
2. Ensure that the sensor is clean and free of any debris after rinsing with lab grade water.
    a. If needed, gently wipe optical surface clean with a lint-free, clean, non-abrasive cloth or lab-tissue.
3. If the sonde is being deployed with a wiper, ensure that the wiper is clean and free of debris after flushing with water.

Note: Always calibrate turbidity **with the guard on**.

Note: Used turbidity standards from previous calibrations may be used for rinses only. **Always use fresh turbidity standard for calibration.**

11. Slowly fill the calibration cup with 0 FNU standard or lab grade water to submerge the turbidity sensor. Fill carefully and slowly to avoid adding air bubbles.
12. Gently immerse the sonde (with the guard attached) into the calibration cup with sensors facing down and loosely attach the cup with one turn to allow venting.
13. Navigate to the turbidity calibration menu on the display or associated software.
14. Enter 0.0 as the first calibration value.
15. While the sonde is immersed and equilibrating, activate the brush to dislodge bubbles.
16. When readings have stabilized, apply/accept the calibration. Record initial and calibrated values on the log sheet.
17. Continue to the second calibration point by following display/software prompts.
18. Rinse the sensor and calibration cup with used turbidity standard and follow steps 1-7 for the second and/or third calibration points as necessary with fresh standard.
    a. After calibration, pour standards into labelled containers to store for future rinses.

3.3.12 Multiprobe Calibration: *Chlorophyll*

Note: These instructions apply only to YSI EXO Total Algae sensors.

The EXO Total Algae (TAL) sensors include two channels. One measures **chlorophyll** and the other measures **phycocyanin (PC)** or **phycoerythrin (PE)**, depending on the sensor installed. Each must be calibrated independently. This section will focus on chlorophyll and PC. For PE sensors, follow manufacturer's instructions.

Two procedures are described below:

1. **Two-point calibration**: To calibrate a TAL sensor, use a two-point calibration process including a zero point with lab grade water and a second point with a Rhodamine WT solution of known concentration.
    a. The calibration value for the Rhodamine WT standard is temperature dependent. Use **Table 3-4** to determine the temperature-compensated calibration value to enter for the second point.
2. **Re-zeroing** (previously called a one-point calibration): To reset the zero value, only lab-grade water is used. This process will address drift error that has accumulated at values near zero. Drift error at higher values will continue to accumulate. As such, this process only addresses accuracy in water with near-zero pigment.

Table 3-4: Temperature-compensated standard solution values for TAL sensors. Use this table to determine the second calibration point for TAL parameters.

	Chlorophyll 0.625 mg/L Rhodamine	**Phycocyanin** 0.625 mg/L Rhodamine	**Phycoerythrin** 0.025 mg/L Rhodamine
Temp	**Chl µg/L**	**PC µg/L**	**PE µg/L**
8	83.8	22.6	170.0
10	81.2	22.2	163.0
12	78.6	21.2	157.0
14	76.0	20.1	150.0
16	73.5	19.1	144.0
18	70.8	17.5	138.0
20	68.4	17.1	132.0
22	66.0	16.0	126.0
24	63.5	15.0	120.0
26	61.3	14.1	115.0
28	58.7	13.1	109.0
30	56.5	11.4	104.0

Note: Chlorophyll and phycocyanin (or phycoerythrin) must each be calibrated separately. For a two-point calibration, perform a two-point calibration for one parameter (e.g., chlorophyll), then start again and perform a two-point calibration for the second parameter (e.g., phycocyanin or phycoerythrin).

Pre-calibration

1. Ensure the sensor face is clean and free of debris. If needed, gently wipe the surface with a clean, non-abrasive lint-free cloth or lab tissue.

Chlorophyll (µg/L) two-point calibration

1. Rinse the sensor and calibration cup three times with lab grade water.
2. Fill the calibration cup with lab grade water to submerge the sensor. Check to ensure that no air bubbles are present.
3. Navigate to the calibration menu to select chlorophyll (chl), and then the units (µg/L). Select **2-point**.
4. When prompted to enter a standard value, **enter 0** for the first point.
5. When prompted to enter the second value, use the temperature displayed on the sonde display and use **Table 3-4** to determine the correct calibration point (e.g., for 22° C, enter 66 µg/L).
6. When readings are stable, click **Apply** to accept the 0 calibration.
7. Discard the water and rinse twice with 0.625 mg/L Rhodamine WT standard and fill the calibration cup to the first line with the 0.625 mg/L Rhodamine WT standard.
8. Submerge the sensors and ensure that there are no air bubbles.
9. Click **Proceed** on the display and observe the readings. When the readings stabilize, click **Apply** to accept the calibration.
10. Click Complete and review the calibration summary. Record readings on a log sheet.
11. Exit the calibration menu and rinse the sensor and calibration cup three times with lab grade water.

Phycocyanin two-point calibration

Note: Phycocyanin and phycoerythrin require different Rhodamine WT concentrations. This section focuses on Phycocyanin calibration.

1. Rinse the sensor and calibration cup three times with lab grade water.
2. Fill the calibration cup with lab grade water to submerge the sensor. Check to ensure that no air bubbles are present.
3. Navigate to the calibration menu to select phycocyanin (PC), and then the units (µg/L). Select **2-point**.
4. When prompted to enter a standard value, **enter 0** for the first point.
5. When prompted to enter the second value, use the temperature displayed on the sonde display and refer to **Table 3-4** to determine the correct calibration point (e.g., for 22° C, enter 16 µg/L).
6. When readings are stable, click **Apply** to accept the 0 calibration.
7. Discard the water and rinse twice with 0.625 mg/L Rhodamine WT standard and fill the calibration cup to the first line with the Rhodamine WT standard.
8. Submerge the sensors and ensure that there are no air bubbles.
9. Click **Proceed** on the display and observe the readings. When the readings stabilize, click **Apply** to accept the calibration.

Re-zero chlorophyll and phycocyanin

Note: As with a two-point calibration, each parameter (chlorophyll and phycocyanin) will need to be re-zeroed independently. To re-zero chlorophyll and phycocyanin, follow this procedure for each.

1. Follow steps 1-2 from the two-point calibration instructions for each parameter.
2. Navigate to the calibration menu to select chlorophyll (chl) or phycocyanin (PC) and then the units (µg/L). Select **1-point**.
3. When prompted to enter a standard value, **enter 0.**
4. When readings are stable, click **Apply** to accept the calibration.

3.3.13 Multiprobe Calibration: *Chloride*

Note: Below instructions apply only to YSI EXO Chloride ISE sensors

Sensor Drift: ISE sensors are prone to sensor drift. For short term deployments (<3 days) sensor drift should not be significant. For longer deployments, periodic grab samples for laboratory analysis or compare readings to recently calibrated ISE sensor are recommended.

Pre-calibration

1. The night before sampling, remove the chloride sensor and soak in 1000 mg/L chloride solution. Insert the sensor plug to the sonde to allow calibration of other parameters. If this is not done, calibration of the chloride sensor may take 30 minutes or longer to obtain stable readings.

Note: **Calibrate other parameters prior to removing the plug and attaching the chloride sensor.** The chloride sensor should not be exposed to high conductivity standards.

Note: Chloride calibration is dependent on accurate pH readings. As such, **the pH sensor must be calibrated before the chloride sensor**.

Note: **Do not use any coarse materials (including paper towels) to wipe the sensor**. If lab grade water does not remove deposits or debris, consult the manufacturer's instructions.

Note: If performing a 3-point calibration, the first two points should use standards at ambient temperature. The **third point requires a standard at a different temperature**. For the instructions below, use **chilled 10 mg/L standard**. The temperature should be at least 10° C below the ambient temperature.

Calibration

1. After completing pH and other calibrations of the sonde, remove the sensor plug and install the chloride sensor. Rinse the chloride sensor with lab grade water.
2. In the **Calibrate** menu, select **ISE**, then select **Chloride.**
3. Click **2 point** (for day runs) or **3-point** (continuous monitoring). For the first two calibration points enter **10 mg/L** and **1000 mg/L**. For the third calibration point, enter **10 mg/L**.
4. Rinse and fill the calibration chamber to the marked line with the calibration standard. Rinse the chloride sensor with lab grade water and dry. Insert into the calibration chamber. The sensor tip should be at least 1 cm in the solution. Remove any air bubbles. Allow the sensor to adjust to the temperature of the standard before proceeding.
5. Observe the readings under **Current** and **Pending** data points. When readings are stable (no significant change after 40 seconds), click **Apply** to accept the calibration point.

Confirm the **Pending** data value is close to the **Setpoint** value. Click **Proceed** to go to the next calibration point.

6. Repeat steps 5 and 6 for the second standard (1000 mg/L) and third standard (10 mg/L of a different temperature).
7. Click **Complete** and view the **Calibration Summary** and **QC Score**. Enter data into the log sheet and return to the calibration menu. Rinse the sensors and calibration chamber with lab grade water.

3.3.14 Multiprobe Calibration: *Depth*

Note: Calibration should be done at the sample site.

Note: Depth calibration varies by make and model. Consult manufacturer's instructions. The following instructions apply to YSI EXO models.

Calibration

1. At the sampling site, navigate to the calibration menu and select depth. Enter 0 as the calibration value (this is the only acceptable value for YSI EXO models, other models may require a depth of 1 m).
2. While ensuring the sonde is held still and is not immersed in any solution, observe the pre-calibration value readings, and click Apply when readings are stable.

3.4 MULTIPROBE GENERAL MAINTENANCE

If maintenance is required for a multiprobe sonde, consult the quick reference table below. For instrument specific, detailed instructions, consult the user manual of the specific device.

Table 3-5. Multiprobe sonde general maintenance information.

Sensor Type	Item	Procedure
Optical DO Sensor	**Cleaning sensor** Whenever there is dirt, algae, or mold on the sensor housing or membrane.	1. Flush the entire sensor with clean, fresh water. 2. Inspect the membrane cap. Use a lint free lab tissue and gently wipe away any foreign material on the sensor cap. 3. If rinsing does not work, gently wash with warm water and dish soap and rinse with fresh lab grade water. **DO NOT clean with alcohol or organic solvents. It will destroy the membrane.** **DO NOT remove the membrane cap unless replacing with a new cap.**
	Replacing membrane Damaged membrane, LED light seen through scratches (≥1mm), calibration failure	1. If wiper is attached, remove wiper with supplied tools. 2. Unscrew and discard the old membrane cap and any O-rings. 3. Use a lint free tissue to remove any water or deposits on the sensor. 4. Place the new O-ring and cap seal at the appropriate locations of the optical sensor. **DO NOT add grease to the O-ring or cap seal**. 5. Screw in new membrane cap to the sensor. Tighten to finger tightness. 6. Do not touch the inner or outer membrane surface with ungloved fingers. 7. Some probes like YSI require updating software or entering calibration constants. Do so following information provided with the DO membrane kit.
	Rehydrate optical membrane If sensor is not kept in a 100% humid environment longer than 2 hours	1. Attach the calibration/storage cup and add room temp tap water until it covers the optical membrane without touching the pH sensor. 2. Place the sonde in a location and orientation that ensures the optical membrane is submerged without submerging the pH sensor. 3. Allow the sonde to maintain the position for at least 24 hours. 4. Recalibrate and confirm sensor is working properly. If so, remove excess water and follow normal storage protocol.
Temp/ Conductivity Sensor	**Sensor cleaning** As needed	1. Using the provided cleaning brush, clean the sensor ports of hardened foreign material with clean water. 2. If deposits were not removed, repeat with warm water and dish soap. 3. Rinse channels with clean water. 4. If needed, sensor can be soaked in white vinegar prior to cleaning.
pH sensor	**Sensor cleaning** Slow readings, when obviously coated with foreign material or the glass sensor is scratched	1. If possible, remove the sensor from the multiprobe housing. 2. Soak pH sensor in warm water with mild detergent for 30 minutes. 3. If ineffective or the sensor shows slow response, soak for about 30 minutes with 10% HCl. 4. If ineffective, gently clean glass bulb sensor with a methanol-soaked swab. 5. After cleaning, rinse three times with clean water and blot dry. 6. Reattach sensor to the sonde and grease the sensor port O-rings if needed.

Sensor Type	Item	Procedure
pH Reference Electrode	**Changing reference solution (Hydrolab and In-Situ)** Erratic/slow pH response, electrode solution appears low or cloudy.	1. Unscrew the Teflon reference junction. 2. Discard the old electrolyte from the reference sleeve. 3. If Teflon cap is darker than off white, replace with a new one. 4. Drop two KCL salt tablets into the reference sleeve. 5. Refill the sleeve to a positive meniscus with fresh electrolyte. 6. Screw on the Teflon junction Bubbles and some solution should escape through the Teflon cap indicating it is functioning. 7. Rinse the junction and sensors with tap or lab grade water.
ISE Sensor	**Sensor cleaning**	1. If rinsing with tap water does not remove deposits, soak and rinse sensor tip with alcohol. 2. Gently polish with fine emery paper using a circular motion to remove hardened deposits (**do not use paper towels**). 3. Rinse sensor with lab grade water.
Turbidity and Total Algae	**Cleaning**	1. Use a lint free cloth to gently wipe the sensor tip.
General	**Sonde housing O-rings** Yearly or as needed	1. Check O-rings to the sensor guard, battery compartment, sensor ports, and cable junction for wear. 2. Replace worn O-rings with new ones supplied by the manufacturer. Some O-rings require applying grease. 3. Follow manufacturer directions and use specified grease. Typically, use just enough grease so the O-ring has a slight shine and feels smooth with no visible grease deposits.
	Short term storage (<1 month)	Place a small amount of clean tap water in the storage cup and securely attach to the sensor end of the unit. Be sure the water does not directly contact with any of the sensors.
	Long term storage (>1 month)	4. Remove batteries (size AA, C, rechargeable) from sondes and displays. Do not remove the lithium battery (silver disk) from the sonde housing as it maintains the internal clock. 5. If possible, remove the pH sensor from the unit and place the glass bulb end into the provided pH storage bottle with pH electrode storage solution or 4.0 buffer. Cap the exposed pH port with a provided sensor plug. 6. Remove ISE sensors and submerge the sensor tip in tap water. 7. Install sensor plugs to open ports to avoid damaging connections. 8. Add ½ inch of lab grade water to the calibration/storage cup and securely attach to the sonde. Check periodically (≈ every 30 days) to ensure water has not evaporated or become contaminated.

Table 3-5. (continued) Multiprobe sonde general maintenance information.

3.5 Equipment Performance Verification

Electronic equipment will degrade due to age and general wear and tear. To limit data loss due to faulty readings, field and central office staff perform the following verification checks.

3.5.1 Field Probe Equipment Verification

At least once every 6 months, the following procedures are performed to verify the accuracy and performance of field probes.

Note: For the most accurate readings, circulate water with a large spoon or similar method.

1. Calibrate at least three probes for the same parameters.
2. Place the calibrated probes in a container of tap water so that all sensors are submerged.
3. Turn on displays and allow readings to stabilize.
4. Once all readings have stabilized, record temperature, dissolved oxygen, pH, and specific conductance on the verification sheet found in **Appendix F**.
5. Calculate the average readings for each parameter to compare against individual readings. See Error! Reference source not found. for any needed corrective actions.
6. Submit the completed verification to the QA Coordinator for review.

Note: An optional verification step involves checking DO readings by Winkler titration and using a reference pH solution. **Appendix E** contains procedures to conduct such checks.

Table 3-6. Probe Check: variance from average value and associated corrective action.

Parameter	DO Variance	pH Variance	Temperature Variance	Sp Cond Variance	Corrective Action Required
units	(mg/L)	(SU)	(˚C)	(µs/cm)	
Acceptable variance	< 0.30	< 0.10	< 0.50	< 2.0 %	No corrective action needed.
Service required	0.30 - 0.60	0.10 - 0.20	N/A	2.0 % - 5.0 %	Service affected probes.
Fail verification	≥ 0.60	≥ 0.20	≥ 0.50	≥ 5 %	Contact QA Coordinator, data may need flagging. Tag unit out of service until serviced and checked.

3.5.2 Lab Barometer Verification

At least quarterly, regions should check the laboratory reference barometer to the nearest National Weather Service (NWS) station. The most accurate NWS stations are at major airports.

1. Using **Appendix B**, locate the nearest NWS station and adjust the reading based on the elevation of where the reference barometer is stored.
2. Record the elevation-corrected NWS and reference barometer reading on the calibration log sheet.
3. If readings between the elevation-corrected NWS and lab barometer are greater than 5 mmHg, contact the QA Coordinator

3.5.3 Probe and Reference Thermometer Verification

At least annually, Central Office personnel will check water quality sensors and reference thermometers using a NIST-validated master thermometer according to the following protocol.

1. Make three water baths within the following temperature ranges (these can be made one after the other in a single cooler):
    a. Ice bath (1-5 °C)
    b. Room temperature (18-23 °C)
    c. Warm water (30-35 °C)
2. Place all regional office meters with the NIST-traceable reference thermometer in each water bath. Record temperature readings of all regional equipment and the reference thermometer on the 'Multiprobe Thermistor Check' worksheet in **Appendix F**.
3. Compare readings from regional meters (multiprobes, thermistors, regional reference thermometers) with the NIST reference thermometer. If any of the regional meters differ by ≥ ±0.5 °C from NIST thermometer readings, flag the meter and ensure that it is not used. Any affected units will be evaluated for possible QA failure and flagging of associated monitoring data.

Note: Muffle furnaces are checked at their set operating temperature (typically 500 °C) against a master thermistor unit rated for the operating temperature. Muffle furnaces readings should be within 500 ±5 °C.

3.5.4 Analytical Scale and Weight Verification

At least annually, Central Office personnel will verify the accuracy of analytical scales and calibration weights used by the Regional Offices. This check uses NIST verified weights to check the scale at three reference points across the expected weighing range and the regional calibration weight(s). For analytical scales and weights typically used to weigh out chemical reagents covered in this SOP manual, the maximum allowable error is ±0.0005 g. The verification procedure is as follows:

1. As outlined in **Section 2.8** of this document, clean the scale of dust, allow to warm up, balance, and tare to zero (0.0000 g).
2. Calibrate the scale using the NIST-validated weights maintained by Central Office.
3. Verify scale accuracy using the three NIST verified weights maintained by Central Office. Readings must not differ by greater than 0.0005 g from the verified weight value.
4. Recalibrate the scale if it fails verification using steps 1-3.
5. If the scale again fails verification, reset to factory default settings, recalibrate, and check using steps 1-4.
6. Record final weights on the Analytical Balance and Weight Verification form.
7. If scale still fails, tag it out of service until serviced by a professional company.
8. If scale passes verification, check Regional Office calibration weight(s) and record weights on the form. If the calibration weight(s) are off by more than 0.0005 g, do not use until evaluated by a professional company or replaced with a NIST-verified set.

3.6 DATA LOGGING

Manufacturers use different protocols to log and export probe data collected during a sample run or unattended continuous monitoring deployment. Below are general steps to set up and download logged data. If available, use dedicated software associated with sondes (e.g., Kor Software for YSI EXO) to set up sondes for unattended continuous monitoring deployments. Deployments can also be configured on handheld displays. For detailed, step-by-step instructions, see manufacturers' instructions.

3.6.1 Setting Up a Log File

Connect the sonde to a computer, device, or handheld display.

Use associated software (e.g., Kor) or handheld keypad to enter the deployment screen or logging menu.

Follow screen prompts to prepare the sonde for data logging. This may include:

a. **Deployment start time**: Sonde may be programmed to start at a user-defined date and time.
    i. Next interval (interval specified by user)**.**
    ii. Now (immediately).
    iii. Custom: User sets a date and time to start logging.
b. **Template name**: a template may be used for frequently used deployment intervals and metadata.
c. **File name**: name of the logged data file.
d. **Logging interval**: frequency that sonde will log data (program-specific).
e. **User name**
f. **Site name**
g. **Parameter selection**: Choose parameters for continuous monitoring.
h. **Available memory**: Ensure sufficient memory is available for deployment. May be viewed in status bar in software program or handheld display menu.
i. **Battery life**: Ensure there is sufficient battery life for length of deployment. May be viewed in status bar in software program or handheld display menu.

3.6.2 Deploying Sonde for Unattended Sampling

1. If the start date/time was not configured in an earlier set up configuration step, enter the logging menu to start unattended sampling.
2. Prepare the sonde for unattended sampling:
    a. Disconnect sonde from display if connected.
    b. Ensure the unit is operating by checking indicator lights (YSI EXOs have a red indicator light that flashes every 10 seconds while in deployment mode).

c. Attach sensor guard. Use an antifouling guard in marine or extended deployments.

d. Secure cable port with waterproof plug.

e. Secure the sonde to the monitoring station, structure, or well-rooted object.

f. Lower sonde into the water and record the time deployed on the log sheet.

3. The unit is now in place and will continuously record data until it reaches the entered logging end date/time or when reconnected to the display and logging is terminated.

3.6.3 Retrieve Logged Data

Data from unattended deployments are stored in in a sonde's internal memory. Upon retrieving sondes after the deployment period has ended, data may be transferred to a computer via the sonde's dedicated software program or to the handheld display, which can then be transferred to a computer.

Note: The following instructions are consistent with YSI EXOs, for detailed instructions on sonde-specific processes, follow manufacturers' instruction manuals.

Note: If connecting to a deployed multiprobe currently logging, be sure to end the logging event before proceeding.

3.6.3.1 Copy Logs to Handheld Display

1. Use the display keypad to navigate to the **Data** menu.
2. Select **Transfer Sonde Data** to transfer the logged data from the sonde's internal memory to the handheld display.

3.6.3.2 Copy Logs to Computer

1. Open the sonde-associated software program on the computer.
2. Connect the sonde or handheld display a computer with data cable (connecting directly to the sonde may require an adaptor).
3. Navigate to the connected sonde and select **Start Download from Device**.
4. Navigate to the **Recorded Data** menu and select **Export to CSV** to save the logged data to the computer.

4 FIELD SAMPLING PROCEDURES

The section details the collection of water and sediment samples covered by the Water Monitoring and Assessment Program as well as affiliated programs such as Pollution Response and Facility Inspection. Staff should use other agency approved SOP materials where such a document is more specific or appropriate to the monitoring activity being performed.

4.1 USE OF PROTECTIVE GLOVES

Gloves serve a dual purpose:

1. Protecting the sample collector from pathogens and other harmful substances
2. Minimizing accidental contamination of samples by the collector.

Wearing protective gloves while sampling is recommended and sometimes required, however, it is not mandatory if:

1. The sample source is considered non-hazardous.
2. The samples do not involve trace analysis (e.g., concentrations of pg/L, ng/L).
3. The program-specific SOP or SOP section does not explicitly require gloves.

Note: Staff must wear a **fresh pair of gloves at each site** for collecting sediment by scoop and pan (wading), PCB, clean metals, PFAS, and any other program that explicitly requires gloves for the purpose of minimizing contamination.

Note: If a program requires gloves, ensure that the gloves meet any specific guidelines (e.g., powder-free nitrile gloves)

4.2 EQUIPMENT RINSE

Except for trace samples, bacteria samples, and any programs that explicitly proscribe it, rinse all collection equipment at least once with water from the sample site before sample collection.

Sample Bucket: Fill the bucket approximately half-full of water from the sample site. Swirl the collected water around and dispose the rinse away from the sampling site.

Sample Wand, Dredge, etc.: Rinse the device inside and out by dipping the device into and out of the sample site water or otherwise sufficiently flushing with sample site water. Do so downstream or otherwise away from the final sampling location to avoid sampling rinses.

Pump and Hose: Follow the Chesapeake Bay Program SOP manuals, located here: https://www.deq.virginia.gov/our-programs/water/water-quality/monitoring/chesapeake-bay-monitoring.

Note: Do not rinse equipment with sample water for PCBs, trace metals, or any program that explicitly proscribes it. Equipment for such programs is typically cleaned prior to arriving at the site; rinsing may unnecessarily introduce contamination.

4.3 WATER SAMPLING

4.3.1 General Sampling Procedures

1. Conduct sampling with the proper safety equipment and in a manner to pose the least risk to field personnel. When necessary, use vehicle amber lights, safety vests, and related traffic safety equipment. Additional sampling safety information is in **Section 7**.
2. Monitoring staff are responsible for determining if sites are safe for sampling. If access is needed on private property, obtain permission from landowners prior to sampling.
3. If collecting water and sediment samples at the same location, collect water samples first to avoid disturbing sediment that could contaminate the water sample.
4. Whenever possible, collect field measurements (DO, pH, temp, etc.) directly from the sample site. If field measurements need to be collected from a bucket, collect water quality samples (nutrients, etc.) first.
5. When recording field parameters, truncate values (temp, DO, pH, sp. cond.) at the hundredths place where available (record to two decimal places or to the end of the displayed value when fewer than two decimal places are displayed).
6. If utilizing specialized or non-standard sampling equipment, follow the manufacturer's instructions for maintenance, cleaning, and use.
7. Do not collect samples or field readings at a site with obvious standing pools of water during low or no flow conditions. Note it on the field sheet and include a remark in CEDS in the comment field explaining the site conditions.
8. Prior to sampling, rinse empty, unsterilized sample bottles with a small amount (about 10% of the sample container) of sample water **three times with the lid on**. Dump rinse water away from the sampling location and bucket. **Never rinse bacteria sample containers or sample bottles that have prefilled preservatives.**
9. Cubitainers may be opened for filling either by removing the cap and pulling open (compliance samples), or by removing the cap and blowing them open (ambient samples). **Always rinse sample containers with sample water three times** prior to filling.
10. When collecting bacteria samples:
    a. Never use an unsterilized sample container.
    b. Do not collect composite bacteria samples.
    c. Do not rinse or touch the interior bottle surface or cap.
    d. Fill bacteria bottles between the 100 mL mark and bottom shoulder. **Do not overfill bacteria bottles**, otherwise samples are rejected.
    e. Securely cap and label the container.

Figure 4-1. Bacteria sample fill range

Note: If samples are from waters with known or suspected chlorine is present, use a bacteria bottle with sodium thiosulfate. Note the preservative on the sample tag in the comment field.

11. Except for specific, non-routine samples such as VOC or mercury samples, do not fill sample bottles completely. An air space is necessary to ensure proper mixing by the laboratory. Filling to the bottom of the bottle shoulder is typically sufficient.
12. When preserving samples with acid solutions, carefully add to the sample with a dropper or squeeze bottle. Avoid any direct contact with the acid. See **Section 7** for additional safety information. Cap the acid container.

Note: A cubitainer "shoulder" is where the mouth meets the flat top of the container.

4.3.2 Bridge Sampling

Many samples collected by staff are from bridges as they allow easy and relatively safe access to the mainstem of many riverine segments. **Section 7** of this document contains important safety information including working along roadways.

1. Lower the bucket into the center of main flow facing into the current and fill ¼ full. Raise the bucket and rinse the bucket interior by using a swirling motion. Dump rinse on the roadway or well away from the sampling point.
2. Inspect the bucket after rinsing. Repeat rinsing if needed.
3. To collect bacteria samples:
   a. **Bucket**: attach bacteria bottles to the rinsed bucket interior using rubber tubing and remove the lid.
   b. **Bacteria sampler device**: Place the bottle in the sampler. Remove the bottle lid and secure to the retaining clips using a rubber band if using retaining clips.
4. If using a clip to assist in filling the bucket, place the rope through the clip located on the side of the bucket or sampler.
5. Slowly lower the bucket or sampler into the center of main flow. Fill the bucket with sample water (if not using a clip, this may require manipulating the rope to tip the bucket) and retrieve the bucket and/or bacteria sampler.
   a. If using a clip: Once the bucket has a sufficient sample, jerk the rope to free the rope from the clip and retrieve the bucket.
6. Remove the bacteria sample bottle(s) from the rubber tubing or sampler. Pour off any excess so the water is at or barely above the line and securely cap and label the bacteria bottle(s). If the bacteria bottles do not contain enough water, repeat using a new bottle. **Do not add additional water from a sample bucket into bacteria sample bottles.**
7. Place the bacteria sample into the mesh bag and surrounded with wet ice.
8. If collecting a chlorophyll sample, collect water and follow the steps described in **Section 4.5** prior to collecting any further samples. If using the delayed filtering method described in **Section 4.5**, the remaining samples may be collected prior to filtering.

9. Rinse the remaining (non-sterile) sample containers **three times** with sample water.
10. Fill remaining sample containers by pouring from the bucket and cap them. Leave approximately one inch of air space in the bottles.
11. Add appropriate preservatives as described in CEDS and printed on the sample label.
12. Place all other sample containers in the cooler up to the neck of the bottle with wet ice.

4.3.3 Wading and Streambank Sampling

In cases like pollution response, biological monitoring, or probabilistic sampling, sampling by wading in the stream or at the streambank may the only option. In such cases and whenever possible, wade into the stream to collect the sample. If the streambank is too steep or water flow is unsafe to wade in as outlined in **Section 7**, sample from the streambank.

When sampling from the streambank, try to sample from the bank that most closely represents the entire stream where the greatest flow occurs and away from stagnant pools or eddies.

Note: If all samples are obtained directly in the sample bottles, add preservatives after collecting the sample as pre-preserved bottles can wash out while filling.

4.3.3.1 Instream Sample Collection

1. Enter the stream and wade upstream to the sample site. Ensure that no sediment or debris disturbed from the wading are present where the sample will be collected.
2. Collect the bacteria sample first.
    a. Submerge the bacteria bottle neck first into the water. The mouth of the bottle should be below the water surface approximately 3-6 inches.
    b. Invert the bottle so the neck is upright and pointing into the water flow.
    c. Move the bottle forward away from the body for at least six inches.
    d. Return the filled container quickly to the surface. Pour off any excess water and cap.
3. Rinse the remaining sample containers **three times** with sample water, discarding rinses downstream or away from the sample location. Collect the remaining samples. If using a bucket, rinse the sample bucket twice with stream water. Pour rinses away from the sampling area. Fill the bucket and return to shore to fill the remaining containers.
4. Place the bacteria sample into the mesh bag and surrounded with wet ice.
5. If collecting a chlorophyll sample, collect water and follow the steps described in **Section 4.5** prior to collecting any further samples. If using the delayed filtering method described in **Section 4.5**, the remaining samples may be collected prior to filtering.
6. Pour the remaining samples directly from the bucket into any additional containers to be collected and cap them. Fill to the shoulder of sample containers.

7. Add appropriate preservatives as specified in CEDS and printed on the sample label.
8. Place all other sample containers in the cooler up to the neck of the bottle with wet ice.

4.3.3.2 Streambank Sample Collection

Note: If the sample site will involve collecting from the streambank, consider using a sample wand that can hold the sample bottle(s) rather than using the toss bucket method outlined below. Using a sample wand for bacteria samples is especially recommended.

1. If wading to the sample site is not possible, toss or swing the bucket into the most representative point of the stream that is accessible while taking care to keep ahold of the rope attached to the bucket. Allow the bucket to partially fill and retrieve using the rope.

Note: If the sample bucket drags across the bottom sediment while retrieving, instream sampling may be necessary**. Sample buckets should not contain sediment from dragging along the bottom.**

2. Rinse the sample bucket with the collected water and discard rinses away from the sample area to avoid disturbing sediment. Repeat rinse one more time.
3. After rinsing twice, toss the bucket to the sample location most representative of the stream and allow filling. Carefully retrieve the bucket by rope to avoid disturbing the sediment to the point it may enter the bucket.
4. After retrieving the bucket, collect the bacteria sample bottle first. **Note on the log sheet and in CEDS if a bacteria sample had to be collected from the bucket.**
    a. Wearing a clean pair of latex or nitrile gloves, use a U motion to fill the sample bottle by moving the bottle from one side of the bucket to another.
    b. Pour out any excess water away from the bucket and cap.
5. Place the bacteria sample into the mesh bag and surrounded with wet ice.
6. If collecting a chlorophyll sample, collect water and follow the steps described in **Section 4.5** prior to collecting any further samples. If using the delayed filtering method described in **Section 4.5**, the remaining samples may be collected prior to filtering.
7. Rinse the remaining (non-sterile) sample containers **three times** with sample water.
8. Pour the remaining samples directly from the bucket into any additional containers to be collected and cap them. Leave approximately one inch of air space in the bottles.
9. Add appropriate preservatives as specified in CEDS and printed on the sample label.
10. Place remaining sample containers in the cooler up to the neck of the bottle with wet ice.

4.3.4 Sampling by Boat

1. Use a GPS to ensure sampling location accuracy. If possible, anchor the boat.
2. Collect all samples as far as possible away from the propeller and prop wash area as possible. If possible, collect in the direction of the current.
3. Collect all water samples before collecting sediment samples.
4. Collect bacteria samples before all other water quality samples. Do not collect bacteria samples using a pump and hose. Do not contaminate the sterile bottle by touching the inner surfaces of the bottle or cap. Place the collected bacteria sample into the mesh bag and surrounded with wet ice.
5. If collecting a chlorophyll sample, collect water and follow the steps described in **Section 4.5** prior to collecting any further samples. If using the delayed filtering method described in **Section 4.5**, the remaining samples may be collected prior to filtering.
6. Rinse the remaining (non-sterile) sample containers **three times** with sample water.
7. For pump and hose samplers, ensure the apparatus has accurate marks for the hose intake depth.
8. Pour remaining samples directly from the bucket or hose into any additional containers to be collected and cap them. Fill sample bottles to the shoulder, leaving approximately one inch of air space.
9. Add appropriate preservatives as described in CEDS and printed on the sample label.
10. Place all other sample containers in the cooler up to the neck of the bottle with wet ice.

4.3.5 Collection of Samples with a Pump and Hose

Pump and hose sampling is required when depth-specific samples are needed in addition to the standard 0.3 m depth surface sample.

If sampling using pump and hose, refer to the Chesapeake Bay Program SOP manual at:

https://www.deq.virginia.gov/our-programs/water/water-quality/monitoring/chesapeake-bay-monitoring

4.3.6 Secchi Disk Measurements

Note: Check the accuracy of Secchi disk lines with a measuring tape each year. Do not wear sunglasses while obtaining Secchi readings. Record Secchi depth readings in CEDS at first depth reading where field parameter readings are collected.

1. Use a 20 cm Secchi disk attached to a line marked in 0.1 m increments with paint or tape.
2. On the shaded side of the boat, lower the Secchi disk into the water until the black and white quadrants are no longer distinguishable.
3. Note the depth where the line meets the water. Raise the disk several increments and slowly lower until the quadrants are no longer visible. Note the depth.
4. Record the final Secchi depth as the average of the two depths to the closest 0.1 m.

4.3.7 Light Attenuation (LICOR Measurements)

If LICOR measurements are required, refer to Chesapeake Bay Program SOP manual at:

https://www.deq.virginia.gov/our-programs/water/water-quality/monitoring/chesapeake-bay-monitoring

4.4 Chlorophyll *a* Vacuum Filtration Method

If using an electric pump, follow the appropriate procedure outlined in the Chesapeake Bay Program SOP manual.

Hand pump method:

1. Rinse the filter holder, funnel, and graduated cylinder with lab grade water.
2. Open the filter holder and remove the rubber O-ring. Using clean forceps, place a GF/F filter on the holder. Replace the O-ring and close the filter housing.
3. Measure 250 mL of sample water with a graduated cylinder and pour into the funnel and cap.
4. Pump the sample water through the filter. Do not exceed 7 inches HG (3.44 psi) of pressure.
   a. If 250 mL of sample water does not pass through the filter, change the filter, rinse the apparatus, and repeat the procedure with 100 mL of sample water.
   b. Observe the filter for color. If there is visible color, proceed to the next steps. If color is not observed, repeat steps 3 and 4 until color is visible or a maximum of 2000 mL have been filtered.
5. If sample water has a pH less than 7.00 SU:

a. Pump sample water from the funnel until about 10 mL remains.

b. Remove the funnel cap.

c. Shake the magnesium carbonate bottle and add 1 mL to the sample water in the funnel.

d. Reattach the cap and finish pumping to add magnesium carbonate solution to the filter.

6. Record the final volume filtered on the field data sheet and the sample tag comment field.

7. Remove the filter holder from the pump apparatus and open the holder. Using clean forceps, remove the O-ring. Using clean forceps, carefully fold the filter in half to keep the pigment inside and remove from its holder.

8. Place the folded filter in the center of 4”x4” aluminum foil. Gently fold the foil to protect the filter and attach the sample label to the foil to prevent it from unwrapping.

9. Place the labeled foil in a Ziploc bag and store in the cooler on top of wet ice. Make sure the opening of the bag hangs out of the cooler when the lid is lowered.

Note: Place the closed Ziploc bag opening through the hinge side of the cooler. This helps the lid close and keep the bag opening from falling into meltwater which can foul the filters.

10. Thoroughly rinse the filter holder, funnel, and graduated cylinder twice with lab grade water. Inspect the filter holder; continue to rinse until the apparatus is clean before filtering the next sample.

11. After returning from the field, enter the volume filtered into CEDS along with field data.

4.5 Chlorophyll *a* Syringe Filtration

The syringe method is useful if it is not practicable to bring the vacuum filter rig. The method uses a 150cc polypropylene syringe to filter a sufficient sample (usually 300 mL).

1. Rinse the filter holder with lab grade water.

2. Open the filter holder and remove the rubber O-ring. Using clean forceps, place a GF/F filter on the holder. Replace the O-ring and close the filter housing.

3. Rinse the syringe with sample water by pulling the plunger back to the 100 mL mark and drawing up 50 mL of sample water. The plunger should be at the 150 mL mark. Shake the syringe to wet the entire inner surface. Depress the plunger to remove all water and air.

4. Fill the syringe past the 150-cc mark (Usually it is the middle of “Y” on the syringe). Holding the syringe upward, tap on the side to eliminate as many air bubbles as possible. Depress the plunger until the first ridge of the plunger aligns with the 150-cc mark.

5. Attach the syringe to the filter holder and gently depress the plunger. The goal is to filter 300 mL of sample or until the filter paper clogs and there is a green color on the filter.
   a. If the first 150-cc filtered easily, detach filter and repeat steps 4 and 5 to filter 300 mL.
   b. If the filter becomes clogged (e.g., difficult to depress the plunger), stop filtering and note the volume filtered on the sample tag or attach a new filter and continue filtering.
6. If sample water has a pH less than 7.00 SU:
   a. Push all sample water out of the syringe.
   b. Detach the syringe from the filter assembly.
   c. Pull the plunger back an inch or so.
   d. Shake the magnesium carbonate bottle and add 1 mL to the syringe.
   e. Reattach the filter and apply gentle pressure to add magnesium carbonate solution to the filter.
7. Record the final volume filtered on the field data sheet and the sample tag comment field.
8. Remove the filter holder from the syringe and open the holder. Using clean forceps, remove the O-ring. Using clean forceps, carefully fold the filter in half to keep the pigment inside and remove from its holder.
9. Place the folded filter in the center of 4”x4” aluminum foil. Gently fold the foil to protect the filter and attach the sample label to the foil to prevent it from unwrapping.
10. Place the labeled foil in a Ziploc bag and store in the cooler on top of wet ice. Make sure the opening of the bag hangs out of the cooler when the lid is lowered.

Useful Tip: Place the closed Ziploc bag opening through the hinge side of the cooler. This helps the lid close and keep the bag opening from falling into meltwater which can foul the filters.

11. Thoroughly rinse the filter holder and syringe twice using 20 to 50 mL lab grade water. Inspect the filter holder; continue to rinse until the apparatus is clean before the next sample.
12. After returning from the field, enter the volume filtered into CEDS along with field data.

4.6 SEDIMENT SAMPLING

Deep water sediment samples are usually collected with a sample dredge (e.g., 6”x6” Petite Ponar). In shallow water, sediments may be hand-sampled using a scoop and pan method.

Note: This method applies for most sediment sampling protocols including trace metals, PCB, toxicity, and similar analyses. For projects that follow a separate SOP and/or QAPP (e.g., benthic samples for coastal probabilistic monitoring), the project-specific SOP/QAPP takes precedence.

4.6.1 Sampling Location and Substrate Selection

When sampling from a boat, samples must be collected away from the propeller wash whenever possible. When sampling in shallow streams, collect samples from the submerged streambed. The most representative samples are from recently deposited sediments containing fine particles with high organic content. Sediment with high organic content will appear dark brown or black.

4.6.2 Collecting Sediment with Sampling Dredge

Prior to use, the dredge and all associated sampling equipment must have been thoroughly cleaned and properly stored to prevent contamination as outlined in **Section 2.2.2**.

Note: Sediment conditions are variable; it may not be possible to get an ideal grab sample. If after a couple of attempts an ideal grab is not collected, use best professional judgment to obtain a suitable sample. If the sediment condition is not ideal, note it on the field sheet and in CEDS.

1. Collect water samples and field probe readings prior to performing sediment sampling.
2. Put on fresh, powder-free nitrile gloves before collecting the samples.
3. Check the rope and knot attaching the dredge is secure.
4. Rinse sediment dredge equipment with sample site water.
5. Open the jaws of the dredge and engage latch mechanism or insert spring-loaded pin so the dredge remains open.
6. Hold the dredge over the edge of the boat or bridge and lower it straight into the water. Once in the water, lower at a rate of about one foot per second to minimize disturbance.
7. Once the dredge rests on the sediment, give the rope some slack, then pull up to activate the spring to close the dredge.
8. Raise the dredge at a rate of about one foot per second to avoid disturbing the sample.

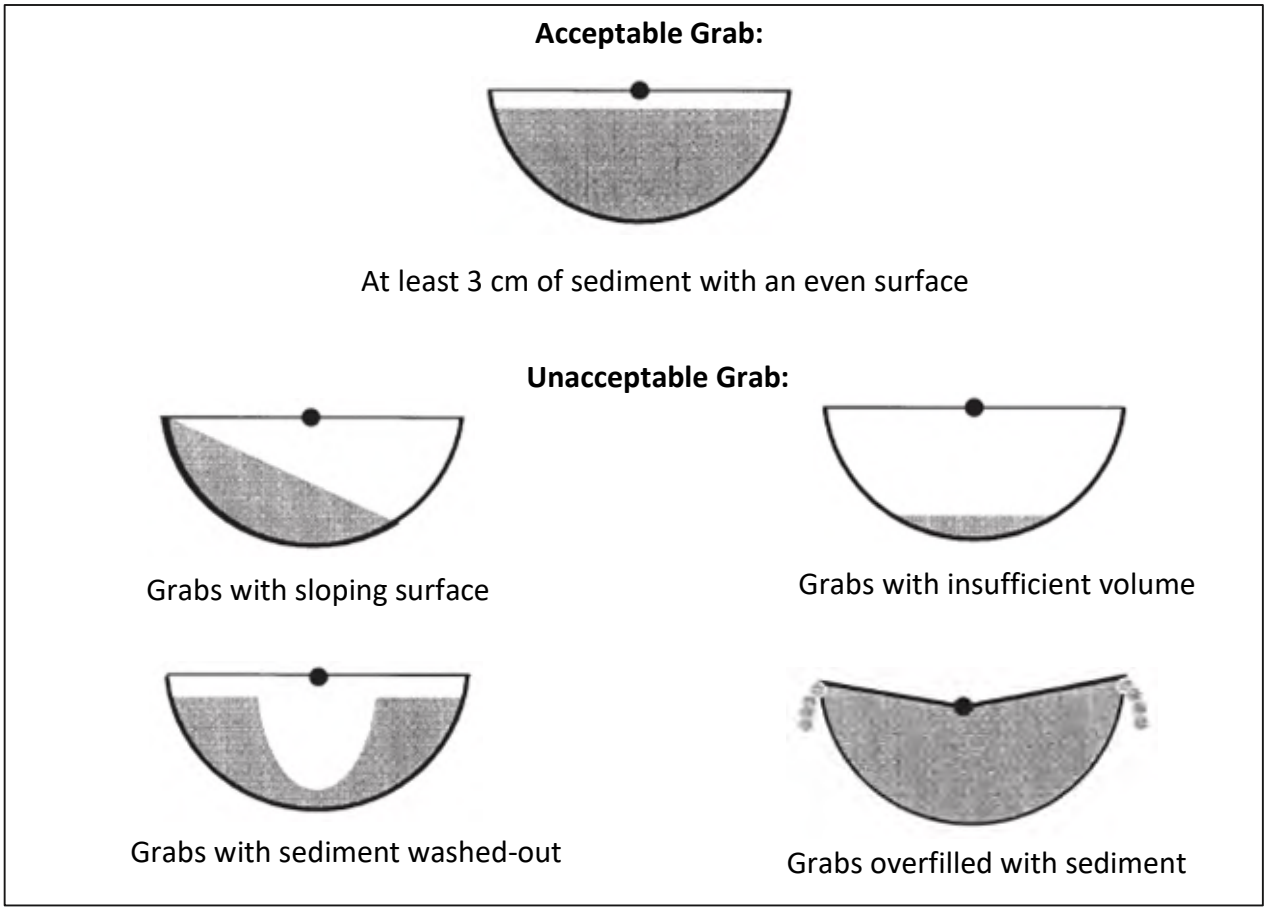


Figure 4-2. Illustration of acceptable and unacceptable dredge samples.

9. Slide the dredge viewports to inspect the sample (see **Figure 4-2**). The sample is suitable if there is:

- **a.** Complete closure of the dredge jaws.
- **b.** No evidence of sediment washout through the dredge jaws or top.
- **c.** An even distribution of the sediment in the dredge.
- **d.** Minimum disturbance of the sediment surface.

10. Carefully drain the overlying water from the dredge, taking care to avoid loss of fine sediments. Place the dredge in a clean stainless-steel pan and open the top access doors of the dredge.

11. Use a clean stainless-steel scoop to remove the top 2cm of the sediment from the dredge and place into a second clean stainless-steel pan.

12. Remove any undesired materials (e.g., shells, leaves, stones) using clean stainless-steel forceps. The sediment should be thoroughly stirred with a clean stainless-steel scoop until it is uniform in texture, color, and moisture and place in the sample container.

13. Dump the remaining sediment away from subsequent Ponar grabs.

14. Repeat steps 4-12 at least two more times or until enough sediment is collected for the sample. The container containing composited sediment should remain covered with a stainless-steel top or a sheet of aluminum foil until a sufficient volume of sediment is obtained. Leave at least 1 inch of airspace in the sample container to prevent breakage if the sample freezes during storage.
15. Pour off any remaining water in the sample while avoiding losing fine sediment.
16. Cap and label the container and place in a cooler containing wet ice.

4.6.3 Collecting Sediment by Scoop and Pan Method

Prior to use, all associated sampling equipment must have been thoroughly cleaned and properly stored to prevent contamination as outlined in **Section 2.2.2**.

1. Collect water chemistry and field probe samples prior to performing sediment sampling.
2. Put on fresh, powder-free nitrile gloves before collecting the samples.
3. Rinse all sediment sampling equipment with site water prior to sampling.
4. Generally, the sampler will need to wade to the sample site to obtain a scooped sample. If wading, the sampler should approach the sample site from the downstream direction and walk upstream, against the current to the sampling point. Allow any sediment or debris disturbed from wading to move downstream prior to sampling.
5. Do not disturb the sediment at the sampling location prior to collecting the sample.
6. Scoop the sample in an upstream direction, against the flow. Slow movement during scooping will prevent excess sediment from washing off the scoop.
7. Scoop a sample from the top 2-3 centimeters of the sediment. Transfer scooped material into a pre-cleaned stainless steel compositing tray. Collect three to five scoops of sediment of approximately equal volumes from different areas of the sample site for compositing. Cover the container containing composited sediment with a stainless-steel top or a sheet of aluminum foil until a sufficient volume of sediment is obtained.
8. After the sediment settles, siphon off as much water as possible. If sufficient sample volume was not collected with the initial scoops, collect an additional three to five scoops of sediment until the required amount of sediment is obtained.
9. Remove undesired materials (e.g., shells, leaves, stones) using clean, stainless-steel forceps.
10. Thoroughly mix the sediment with a clean stainless-steel scoop until uniform in texture, color and moisture and place in the sample container.
11. Leave at least 1 inch of airspace in the container to prevent breakage if the sample freezes during storage.
12. Pour off any remaining water in the sample while avoiding losing fine sediment.
13. Cap and label the container and place in a cooler containing wet ice.

4.7 PREP OR UNCOMMON SAMPLING PROCEDURES

In some cases, various DEQ monitoring programs such as Pollution Response Program (PReP) may need to collect non-routine samples such as in response to petroleum or chemical releases.

Sample Packing and Shipping

1. Place sample containers upright in a cooler up to the bottle neck with wet ice.
2. Ship all samples to the contracted lab as soon as possible.

4.7.1 Volatile Organic Compounds Including BTEX in Water

Note: Applies to CEDS group code VOCW. This can test for presence and quantity of gasoline.

1. A trip blank must accompany all volatile organic samples. Prepare the trip blank (including preservatives) in the same way as actual samples. Fill a 40 mL glass vial with Teflon lined septum (blank acidified if sample is acidified) with lab grade water at the office. Always keep the trip blank vial with the sampling vials.
2. Collect sample in a clean 500 mL stainless steel beaker. If suspected, test for chlorine.
3. If the sample contains or is suspected to contain residual chlorine, add 25 mg ascorbic acid preservative to the empty 40 mL sample vial just before going to the site or at the site. If residual chlorine is greater than 5 mg/L, add 25 mg ascorbic acid for every additional 5 mg/L.
4. Fill two 40 mL sample vials to a positive meniscus so that no air bubbles pass through the sample when filling the vial. Do not over fill the vial.
5. Add 4 drops of 6N HCl acid to the vial to preserve the sample.
6. Seal the vial so that no bubbles are inside. ***Do not*** remove the cap once it is secured. Invert to check for air bubbles. If air bubbles seen, discard old sample and container and fill a new vial. Place vials in provided Styrofoam packing to prevent breakage.
7. Immediately place Styrofoam containers in a cooler filled with wet ice.

4.7.2 Base Neutrals and Acid Extractable (Semivolatiles)

Note: Applies to CEDS group codes SVBW (Base Neutral only) and SVW (BN and acid)

1. If it is suspected that the sample contains residual chlorine, add 80mg sodium thiosulfate to each of two one-liter amber glass bottles and mix well.
2. Immediately place bottles in a cooler filled with wet ice. Keep away from light.

4.7.3 Petroleum Identification and Quantity in Water

Note: Applies to CEDS group code PIDW and used only to identify the type of petroleum product. No other analysis can be performed from the PIDW tagged container.

1. When collecting pure product from the water surface, fill a 40 mL glass vial with Teflon-lined cap. Avoid including water in the vial.
2. Add 25 mg ascorbic acid and acidify to pH <2 with hydrochloric acid. Vial can contain air. Tightly secure cap.
3. Immediately place vials in a cooler filled with wet ice and keep away from light. Samples must be tested within 14 days of collection.

4.7.4 Total Petroleum Hydrocarbon (TPH) in Water Samples

Note: TPH analysis is for kerosene, diesel, or heavier oils. TPH testing is more appropriate for follow-up monitoring or when the nature of petroleum is known (e.g., tank closure).

1. When possible, collect water samples directly in sample containers.
2. If residual chlorine is present, add 80 mg sodium thiosulfate to sample jar.
3. Collect sample in one 1/2-pint amber glass jar with Teflon lined cap.
4. Immediately place sample bottles in a cooler filled with wet ice. Keep away from light.
5. Refrigerate samples until analysis. Have samples tested within 7 days but analysis up to 14 days is allowable.

4.7.5 Sampling Unknown Petroleum Product

Note: Applies to CEDS group code PIDW and used only to identify the type of petroleum product. No other analysis can be performed from the PIDW tagged container.

1. When possible, collect samples directly in sample containers. If direct sampling is not possible, collect the sample using a clean 500 mL stainless steel beaker.
2. If the sample contains residual chlorine, add 80 mg sodium thiosulfate to 1/2-pint amber glass jar and 25 mg ascorbic acid to 40 mL vial prior to adding the sample.
3. Slowly fill the jar and vial with sample to prevent transferal of air bubbles to the sample. Acidify jar sample to pH $\leq$2 using 6 N HCl. Check pH using litmus paper. Fill vial to a positive meniscus. Tightly secure cap and invert to check for air bubbles. Do NOT unscrew vial cap. Discard and resample with a new vial if air bubbles are present.
4. Immediately place sample bottles in a cooler filled with wet ice. Keep away from light.
5. Refrigerate samples until analysis. Analyze sample within 14 days after collection.

4.7.6 Water Toxicity Sampling

Note: Consult with the contracted laboratory for specific sampling and shipment requirements.

1. Rinse containers three times with sample water. Discard rinses away from the sampling location.
2. Fill the containers. Do not add any preservatives and remove all air from the container. If residual chlorine is present, add sodium thiosulfate and note it on the chain of custody form along with the amount of thiosulfate added.
3. Immediately place the containers in a cooler filled with wet ice. Keep away from light.
4. Toxicity samples must be analyzed within 36 hours of collection. Hand-deliver or overnight ship the sample to the toxicity laboratory. If shipping samples, label coolers with the laboratory address and containing the statement: **Deliver Immediately to laboratory**.

4.7.7 Pesticides and Herbicides

Note: Consult with the contracted laboratory for specific sampling and shipment requirements.

1. Fill the sample container with water from a representative area. All sampling equipment that contacts the sample water must not contain plastic such as tubing and gaskets. Automatic composite samplers should use refrigerated glass sample containers.
2. Samples analyzed for herbicides/pesticides must have a pH between 5.00 and 9.00 SU. Field teams are not to adjust the sample pH. The lab can do so if noted on the sample tag in the Comment field. The lab may not need to adjust pH if tested within 72 hours.
3. For the analysis of Aldrin, add 3.2 mg sodium thiosulfate if residual chlorine is present.
4. Immediately place samples in a cooler filled with wet ice.

4.7.8 Metals in Soil Samples

Note: Applies to CEDS group code MET1S.

1. Using a clean stainless steel or Teflon lined scoop, fill a certified clean glass jar with material. Leave at least 1 inch of airspace in the container to prevent breakage if the sample freezes during storage.
2. Carefully pour off any remaining water in the sample to avoid losing fine sediment.
3. Cap and label the container and place in a cooler containing wet ice.

4.8 Collection of Trace Element Samples (Clean Metals)

Clean metals samples are designed to measure trace levels (parts per billion) of metals in water for specific programs like TMDL or PROBMON. To eliminate sampling contamination, a "clean hands/dirty hands" approach to sampling is required.

4.8.1 Scope and Applicability

This procedure outlined below is intended to be used to collect dissolved and/or total trace metals in freshwater, groundwater, saltwater, and wastewater for laboratory analysis with results typically in the 200 ppb or less range.

The below procedures are appropriate for any surface, ground, or waste effluent waters with a conductivity below 1000 µS/cm. Saltwater, brackish water, and highly turbid wastewater such as landfill leachates, use the same sampling procedure but require special laboratory preparation and analysis.

If metals concentrations are expected to be above 200 ppb, notify the lab in advance, as different analysis is required.

Method Detection Limits (MDL) for clean metals analysis are available in CEDS or by the contracted laboratory.

4.8.2 Summary

Ambient samples are collected midstream by submerging a precleared 4-liter plastic bottle referred as a Bridge Bottle (see **Figure 4-4**). Such containers are provided by DCLS. Using a piece of flexible tubing connected to the bridge bottle and in lined with a capsule filter, the sample is transferred by peristaltic pump from the bridge bottle into a plastic sample container**,** see **Figure 4-3** and **Figure 4-5**. A sample wand configuration may be used if sampling while wading or from the boat, see **Figure 4-7** for a diagram of the ambient sampling apparatus.

Effluent samples are collected directly into a sample container by submerging a Teflon tube at the sample site. Using a peristaltic pump, sample water is transferred though a piece of flexible tubing in-lined with Teflon tubing though a capsule filter and into the sample bottle. See **Figure 4-8**.

Note: It is recommended that two field technicians work with collecting trace metals.

4.8.3 Equipment Preparation and Ordering Sample Kits

4.8.3.1 Regional Field Equipment Preparation

Store all trace metals sampling equipment in a plastic container to prevent dust contamination. Ideally, use a clean plastic bag to store equipment needed to sample one station to allow ease of transport to the field and prevent contamination.

Prior to sampling, charge peristaltic pump batteries using the charger adaptor provided with the pump. Do not use other battery chargers to avoid damaging the pump. A charged battery will work continuously for about 7 hours.

Run through the checklist to ensure there are adequate supplies to collect the scheduled samples. Gloves are the main item needed in excess as many changes will be required. At least one additional site worth of clean metals sampling equipment should be included.

Figure 4-3. Loop and mercury sample bottles

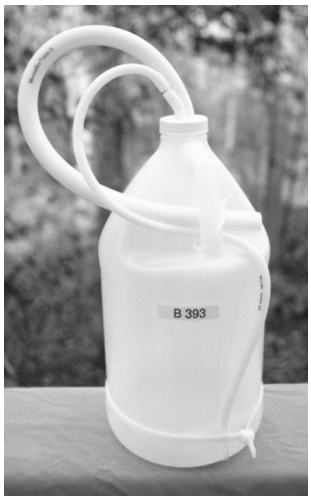


Figure 4-4. Bridge bottle

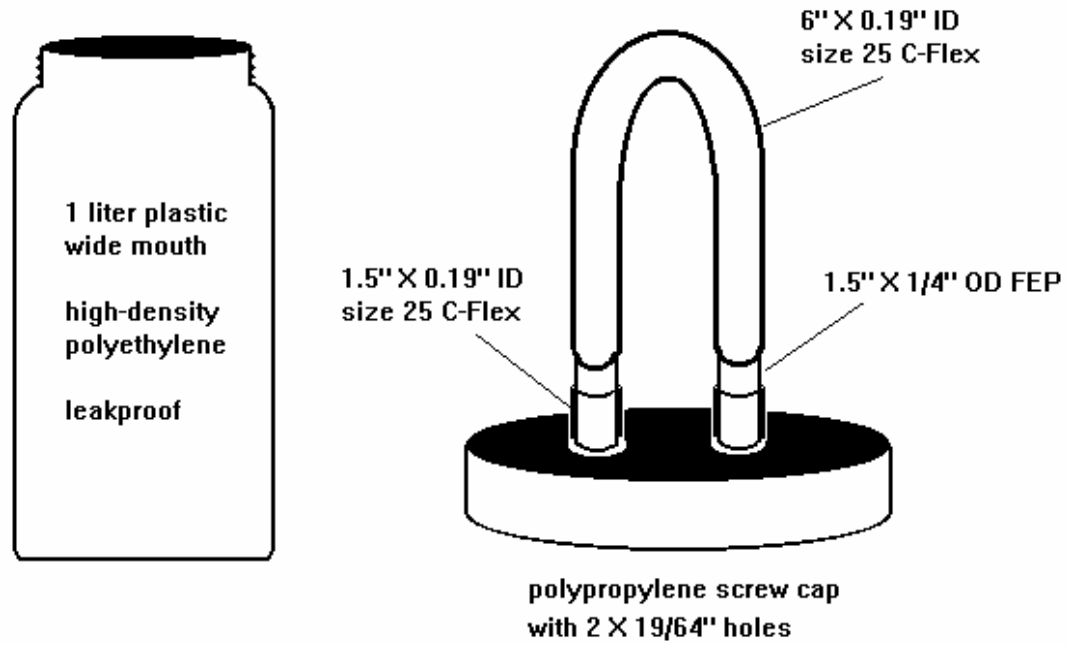


Figure 4-5. Clean metals sample container schematics

4.8.3.2 Ordering Kits

Regions can maintain a small supply of clean metals sampling kits and containers, but kits and bottles over six months old must be returned to the lab. Avoid ordering too many kits as they are expensive. Use a FIFO (First In, First Out) inventory system to ensure containers do not exceed this storage time.

Note: All quality control blanks are handled as separate samples and one blank should be ordered for each sample site and event.

Ambient sampling sites should be established in CEDS prior to sample collection and then processed using the CEDS system.

Prior to sample collection, the sample containers must be ordered directly from the laboratory and must be scheduled through CEDS.

To order sample kits:

Order sample containers from DCLS by e-mailing David Gulick (David.Gulick@dgs.virginia.gov) and Cindy Johnson (Cynthia.Johnson@deq.virginia.gov) with the number and type (by group codes) of samples you wish to collect, when they will be collected, and your region. **ALLOW 6 WEEKS FOR DELIVERY.**

Please refer to **Table 4-1** for the parameter codes to request for containers based on the sample matrix type.

Freshwater sample kit includes the following supplies:

1. One bridge bottle
2. One tubing kit
3. Two loop sample containers
4. Two 100 mL Mercury bottles

Saltwater and effluent sample kit includes the following supplies:

1. One tubing kit
2. Two loop sample containers
3. Two 100 mL Mercury bottles

4.8.3.3 Monthly Run Schedule

Most routine clean metals samples collected are for dissolved metals. Total metals are usually collected only for very specific special studies. Only when a special study requires it should regions collect total metals in addition to dissolved metals.

1. Schedule samples with DCLS through CEDS using the group codes found in **Table 4-1**.
2. Refer to **Figure 4-6**. Refer to the Run ID that corresponds to your type of sample whether it is an effluent (EFF), freshwater (FRESH), or saltwater (SALT). Field equipment blanks (EB) use group code CMETB. Be sure to note the Equipment Blank in the **Blank/Dup** field. One CMETB should be run at each sample site tested to confirm equipment is clean between sites.

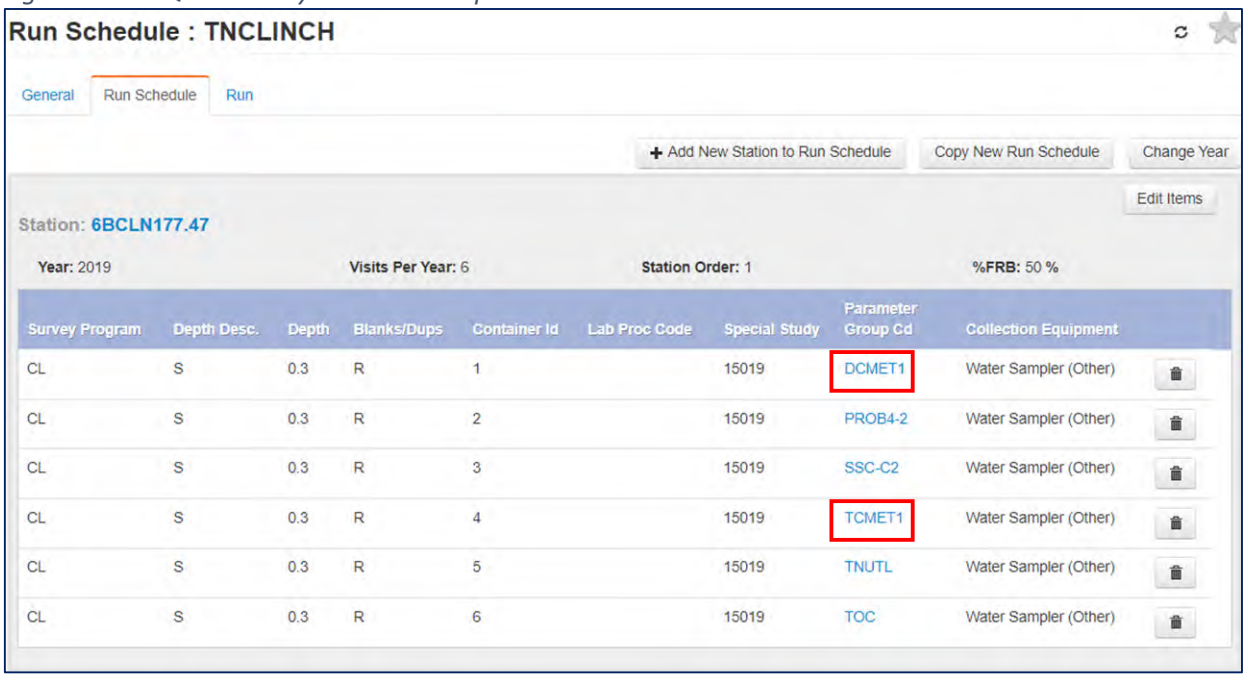
Note: Due to the time involved at each site, usually only four or five sites can be tested in a day.

Table 4-1. Trace metals parameter group codes.

SALTWATER	
DCMETS1	Dissolved clean metals in saltwater
TCMETS1	Total clean metals in saltwater
FRESHWATER	
DCMET1	Dissolved clean metals in freshwater
TCMET1	Total clean metals in freshwater
QUALITY ASSURANCE	
CMETB	Clean Metals Equipment Blanks

MERCURY ONLY	
DCHG	Dissolved mercury in freshwater
TCHG	Total mercury in freshwater
EFFLUENT	
CMETSB	Dissolved clean metals in effluents
DEQMET	Total clean metals in effluents

Figure 4-6. WQM monthly run schedule parameters.



4.8.4 Equipment and Supplies

4.8.4.1 Essential Items to Store in Equipment Box

Table 4-2 lists supplies required for sampling clean metals. Supplies for each site and sample run should be stored in a plastic bag and in a plastic container to prevent contamination.

Table 4-2. Essential clean metals equipment list.

Item	Supplier
Peristaltic pump unit	Scientific supply store
Quick release pump head	Scientific supply store
Cigarette lighter adapter cable	Scientific supply store
Portable battery pack	Scientific supply store
Powder free vinyl gloves	Scientific supply store
Clear polyethylene drop cloth (4-6 mil)	Hardware store
Preprinted laser jet waterproof labels (e.g., Avery)	Office supply store, Avery, etc.
Indelible markers (e.g., Sharpie)	Office supply store
Bridge bottle	DCLS
Bridge bottle tubing kit	DCLS
Teflon tubing kit	DCLS
Sample bottles	DCLS
One-gallon Ziploc bags	Grocery store
Two-gallon Ziploc bags	Grocery store
Bridge bottle weights	Sporting goods store
White polypropylene line	Hardware Store

4.8.4.2 Ancillary Items

Other items which may be needed include those listed in **Table 4-3**.

Batteries need to be charged overnight. Prior to each sampling run, check to make sure there are enough supplies, and the battery is charged and functioning. The leads and fuse system on the batteries are prone to breaks and shortages. Every six months, completely discharge batteries and recharge to extend battery life.

Table 4-3. Ancillary clean metals supplies.

Item	Supplier
Plastic bubble wrap	Consolidated Plastics
Rubber bands (large)	Office supply store
Ice	RO ice machine
Duct tape	Hardware store
Knife or cutters	Hardware store
Fuses for pump and battery	Hardware store

4.8.4.3 Sampling Apparatus, Bottles and Containers

DCLS will supply all the necessary sample containers, bridge bottles, and tubing kits based on the number and types of samples ordered.

- When placing orders for samples, try to group four to five sites that field teams can sample on the same day. DCLS will send out coolers with kits and bottles batched for the number of samples scheduled, but DCLS may request coolers for this process. The same cooler can be used to return the samples for analysis.
- Dispose or recycle tubing kits, filters, bridge bottles, and mercury bottles. Never use the same equipment at another site.

4.8.5 Bridge Bottle Protocol for Freshwater and Saltwater

4.8.5.1 Equipment Setup

1. Identify an area where sample processing will occur. The area must be on a flat, smooth surface protected from the wind that is free of falling debris and swirling dust. The tailgate of an enclosed truck bed or SUV is often a good location.
2. Place the equipment box and coolers containing the sample containers and kits as close as possible to the sample processing area.
3. Cover the work area with a large piece of plastic sheeting (>2 mil thickness). Set out the pump and connect the battery. Switch the pump on and dial the pump speed to 5. Turn off the pump until needed.
4. Remove a tubing kit and necessary sampling containers from the plastic bag in the cooler and place on the plastic near the pump.
5. Remove a pack of powder free gloves from the storage container, place on the plastic.
6. Remove the plastic sample caddy from the storage box and place it on the sample processing area near the pump. Secure the sample bottles in the caddy.

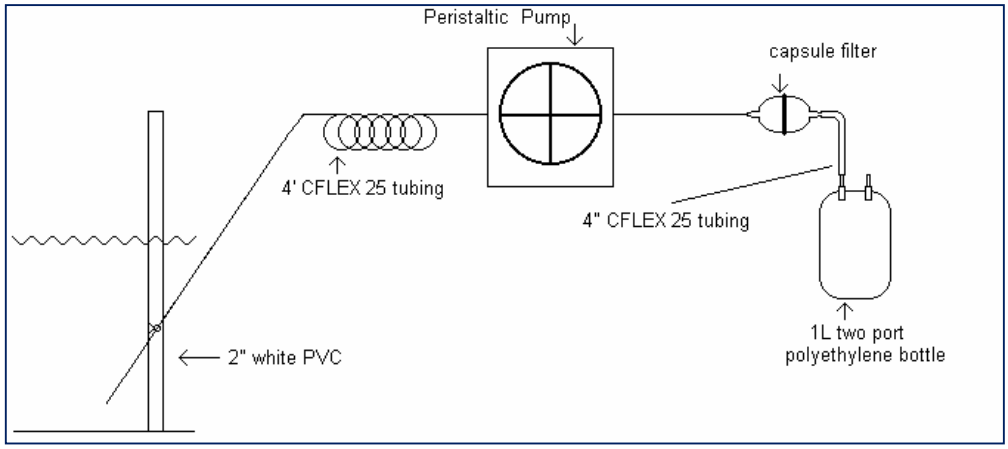


Figure 4-7. Ambient clean metals sampling apparatus

4.8.5.2 Bridge Bottle Filling

1. If sampling from a bridge or similar location, locate the sample weights to connect to the bridge bottle. Avoid using exposed metal weights. Rubber or plastic encased metal weights may be used. No weights are necessary if filling directly in a stream.

Note: If collecting field data (pH, DO, etc.), place the sonde downstream or away from the sampling location to avoid contamination. In addition, other samples such as nutrients should be collected after the clean metals sample is collected.

2. Locate the polypropylene sampling rope spool, cut a sufficient length of rope to allow for deployment.
3. Don one or two pairs of vinyl gloves using clean procedures, specifically, by touching only the cuff or backside of the glove with a bare hand.
4. Tie one end of the sampling rope to the five-pound plastic coated weight leaving approximately one-foot of free rope at the end to connect to the bridge bottle.
5. Untie or tear open the top of the outer plastic bag containing the bridge bottle.
6. Reach into the outer bag and untie the inner bag near the handle connection. Check the configuration of the tubing to ensure that proper filling will occur. Inspect the smaller vent tubing and adjust if it appears crimped. While the bottle is still in the inner bag, it is acceptable to remove the cap fitting to check the inner sipper tube. Adjust all fittings appropriately.
7. When the fittings have been properly secured and adjusted, remove the bridge bottle from the inner bag and lay on the plastic film. Tie the weighted end of the rope onto the handle of the bottle leaving about six inches of line between the bottle and the weight.
8. Proceed to the sampling location with the bridge bottle apparatus. Carry several extra pairs of gloves to the site to ensure clean handling of the bridge bottle.

Note: Deploying bridge bottles in high flow waters can be difficult. Sampling bridges on the downstream side is acceptable to avoid losing the bottle assembly due to the current. When stream velocities are high, adding additional weight may help. If adding additional weight, extend the bridge bottle vent tube past the bottom of the bottle to avoid an air lock.

9. When deploying from bridges with moderate to low stream velocities collect the sample upstream of the bridge by lowering the assembly into the water. Ensure that the assembly does not touch any structures or other objects as it is lowered into the water.
    a. The weight will partially submerge the bridge bottle and begin to fill.
    b. Check to ensure the air vent is above the water level and not blocked. When the bottle is first submerged, it should push a small slug of water from the air vent tube. The bottle will fill within a few minutes if properly adjusted.
    c. The bridge bottle is allowed to sink completely below the surface if the inlet tube does not contact the bottom.

d. When full, carefully retrieve the bridge bottle, taking care to not contact any structures or other objects.

e. If the inlet tube becomes clogged during filling, it is often due to:

i. The vent tube contains a slug of water or other obstruction.

ii. The vent tube is below the surface of the water.

iii. The weight is not positioned close enough to the bottle.

iv. The vent tube or inlet tube has become disconnected from the bottle.

Note: Most blockages are cleared by flipping the bridge bottle right side up (bottle opening pointing up). If the blockage does not clear by this method, a new bridge bottle may be necessary to collect a representative sample.

10. When deploying a bridge bottle while wading or from a small boat, the bridge bottle can be submerged by hand without using weights.

11. For shallow water where the bridge bottle cannot be submerged, use the effluent sample configuration seen in **Figure 4-8** where the stream sample is pumped directly into the loop sample container. However, this will require bringing a pump to the sample site. This is best accomplished by attaching the pump assembly to a backpack.

12. When the bridge bottle is approximately 2/3 full retrieve the bottle to return to the sample processing area. Reconnect the inlet and vent tubing to keep the sample from spilling out or contaminants entering the bottle.

Note: If hiking back to the processing area, place the bridge bottle back in the plastic bags it arrived in to help protect the sample.

13. Once back at the processing area, set it next to the pump and remove the weight if it is attached. With the inlet and vent tubing closed together, the bridge bottle is protected from atmospheric contamination.

4.8.5.3 Dissolved Grab Sample Blank Procedure

Refer to **Figure 4-7** for the schematic of the field sampling equipment used to process blanks and samples.

Determine which field specialist will be clean hands and which will be dirty hands.

1. **Dirty hands** and **clean hands:** don one or two pairs of Nitrile or vinyl gloves. Only touch the areas of gloves with bare hands which will not contact sampling equipment.
2. **Dirty hands:** ensure the plastic sheeting is fixed on the work area and pump is ready to run and the outer bags for the two (or three) loop and mercury bottles are opened.
   Clean hands: open the inner bag for the loop and mercury bottles and place the bottles on the plastic sheet.
3. **Dirty hands:** open the outer bag containing the bridge bottle.
   Clean hands: open the inner plastic bag containing the bridge bottle.
4. **Dirty hands:** open the tubing kit outer plastic bag.
   Clean hands: open the inner plastic bag and remove the tubing assembly.
5. **Clean hands:** disconnect one side of the sample loop on the first sample container and connect the end of the tubing kit opposite the filter to the opened sample container. The sample container is full of clean water from the lab.
6. **Dirty hands:** connect the peristaltic tubing at approximately the mid-point of the length to the field pump.
   Clean hands: invert the sample container and point the outflow nozzle of the sample filter cartage upwards (flow arrow points up). This will ensure proper wetting of the filter and remove air bubbles.
   Dirty hands: switch on the pump.
7. Process the entire contents, 1000 mL, of the sample container through the tubing and filter apparatus at a flow rate of 500 mL/min (pump setting of 5).
   Dirty hands: switch off the pump when the last continuous stream of water enters the filter. The filter must not be allowed to go dry or excessive back pressure will blow the tubing off the filter.
8. **Clean hands:** disconnect the pump tubing from the now empty loop bottle and reconnect this same end to the second loop bottle containing ultrapure water provided by the lab for the sample blank and inverts the container.
   Dirty hands: switch on the pump. Process the blank water from the loop bottle until approximately 125 mL have flowed from the filter. **Dirty hands:** switch off the pump.
9. **Clean hands:** open the first mercury container and discard the water. Then hold the outlet of the capsule filter just above the open mouth of the mercury bottle.
   Dirty hands: turn on the pump.
10. **Clean hands:** fill the mercury bottle to overflowing.
    Dirty hands: shut off the pump.

11. **Clean hands:** lay the nozzle down on the plastic sheeting or inside the clean bag holding the sample loop bottles so the tip does not contact any surface and caps the mercury bottle tightly shut. The mercury bottle should have no air bubbles larger than a pea.
12. **Clean hands:** connect the capsule filter outlet to the empty loop container via the sample loop tubing and process the remaining contents (≈875 mL) of the remaining ultrapure water through the tubing and filter apparatus into the first sample container. **Dirty hands:** switch off the pump before the filter is completely dry.
13. **Clean hands:** disconnect the outlet tubing from the blank sample container and immediately reconnect the loop tubing on the top of the blank bottle.
14. **Dirty hands:** fill out the sample tag for the blank bottle and partially stick the label on the mercury and metals equipment blank (EB) bottle without touching the bottles. **Clean hands:** secure the label and place the blank container in the inner Ziploc bag with similar processed samples from the site. Remove excess air from the bag and seal.
15. **Dirty hands:** hold the outer bag open for c**lean hands** to place the bagged sample into. **Dirty hands:** seal the outer bag, remove as much air as possible, and place the bagged sample in a cooler separate from other samples to prevent contamination from the wire tags.

The field blanks collected in this manner are comprehensive blanks because they are collected in the same equipment as the sample and processed like the sample through all steps of the protocol. This is the most important check of contamination in the protocol.

4.8.5.4 Dissolved Grab Sample Procedure

1. **Clean hands:** immediately (immediately means less than one minute) disconnect the vent tubing from the bridge bottle containing sample water and then connect the inlet side of the pump tubing in place of the vent tubing.
2. **Dirty hands:** switch on the pump and process the sample water from the bridge bottle until approximately 125 mL has flowed from the filter. **Dirty hands:** switch off the pump.
3. **Clean hands:** open the first mercury container and discard the water. Then hold the outlet of the capsule filter just above the open mouth of the mercury bottle.
   Dirty hands: turn on the pump.
4. **Clean hands:** fill the mercury bottle to overflowing.
   Dirty hands: shut off the pump.
5. **Clean hands:** lay the nozzle down on the plastic sheeting so the tip does not contact any surface and cap the mercury bottle tightly shut. The mercury bottle should have no air bubbles larger than a pea.
6. **Clean hands:** unscrew the cap of the second loop sample container and discard the small amount of water remaining in the container.
   Clean hands: return the top to the container and then connect the capsule filter outlet to the second empty loop container via the sample loop tubing. If total recoverable metals are to be processed from the bridge bottle, **dirty hands** rocks the bridge bottle using the handle to agitate the water while filtering the sample to prevent settling. It is acceptable to fill the sample container to overflowing, however avoid filtering more than 1000 mL through the filter.
7. **Dirty hands:** switch off the pump**.**
   Clean hands: disconnect the outlet tubing from the sample container and immediately reconnect the loop tubing back in place to seal the sample bottle.
8. **Dirty hands:** fill out the sample tag for the blank bottle and partially stick the label on the mercury and metals equipment blank bottle without touching the bottles.
   Clean hands: secure the label, place the blank container in the inner Ziploc bag, and seal closed, removing as much air as possible.
9. **Dirty hands:** hold the outer Ziploc bag open for **clean hands** to insert the bagged sample.
10. **Dirty hands:** seal the outer Ziploc bag, remove as much air as possible, and place the bagged sample in the cooler separate from other samples to prevent contamination from any wire tags used on routine samples.
11. Rinse the rope and weights with water to remove any visible dirt and place inside a plastic bag and storage container. Rope may be reused several times if rinsed frequently.

4.8.5.5 Total Recoverable Grab Sample Procedure

If collecting total recoverable metals along with dissolved samples, the bridge bottle must be shaken regularly during sample processing to ensure proper mixing of suspended solids. Additionally, the bridge bottle must be shaken regularly during total recoverable metals processing.

Note: Process total recoverable after dissolved samples to avoid having to change the tubing.

1. **Clean hands:** remove the capsule filter from the tubing and open the third mercury container and the third total recoverable loop bottle and discard the water. Replace the loop bottle cap immediately after discarding the water.
2. **Dirty hands:** switch on the pump.
   Clean hands: hold the outlet of the capsule filter just above the open mouth of the mercury bottle. Fill the mercury bottle to overflowing and loosely cap followed by tightly capping while slightly tilting and squeezing the bottle. Make sure any air bubbles are smaller than a pea.
3. **Clean hands:** connect the tubing to the total recoverable loop container and fill the container until full. **Clean hands:** immediately reconnect the loop tubing to seal the container.
4. **Clean hands:** hold the total recoverable loop container to allow **dirty hands** to place a filled out WQM label directly on the midsection of the bottle. The mercury container also has a WQM label placed on the midsection in the same manner as above.
5. **Clean hands:** place the mercury total recoverable container into the inner bag with the total recoverable loop container and seals the inner bag.
   Dirty hands: proceed to seal the outer bag.
6. Immediately place blanks and samples on ice in a separate dedicated sample cooler containing only clean metal containers. This prevents contamination from other samples or wire tags.

4.8.6 Effluent Sample Collection Protocol

4.8.6.1 Equipment Setup

1. Locate an area near the effluent sampling location where sample processing will occur. The area must be on a flat, smooth surface protected from the wind that is free of falling debris and swirling dust. The tailgate of an enclosed truck bed or SUV is often a good location.
2. Locate the equipment box and coolers containing the sample containers as close as possible to the sample processing area.
3. Cover the work area with plastic sheeting (>2 mil thickness). Set out the pump and connect the battery. Switch the pump on and dial the speed to 5. Turn off pump.
4. Remove a tubing kit and sample containers from the cooler and place on the plastic near the pump.
5. Remove a pack of powder free vinyl gloves from the storage container and place on the plastic. Remove the plastic sample caddy from the storage box and place it on the sample processing area near the pump.
6. Locate the sample wand used for positioning the Teflon sample tubing in the effluent.
7. Refer to **Figure 4-8**, for the final layout for effluent sampling.

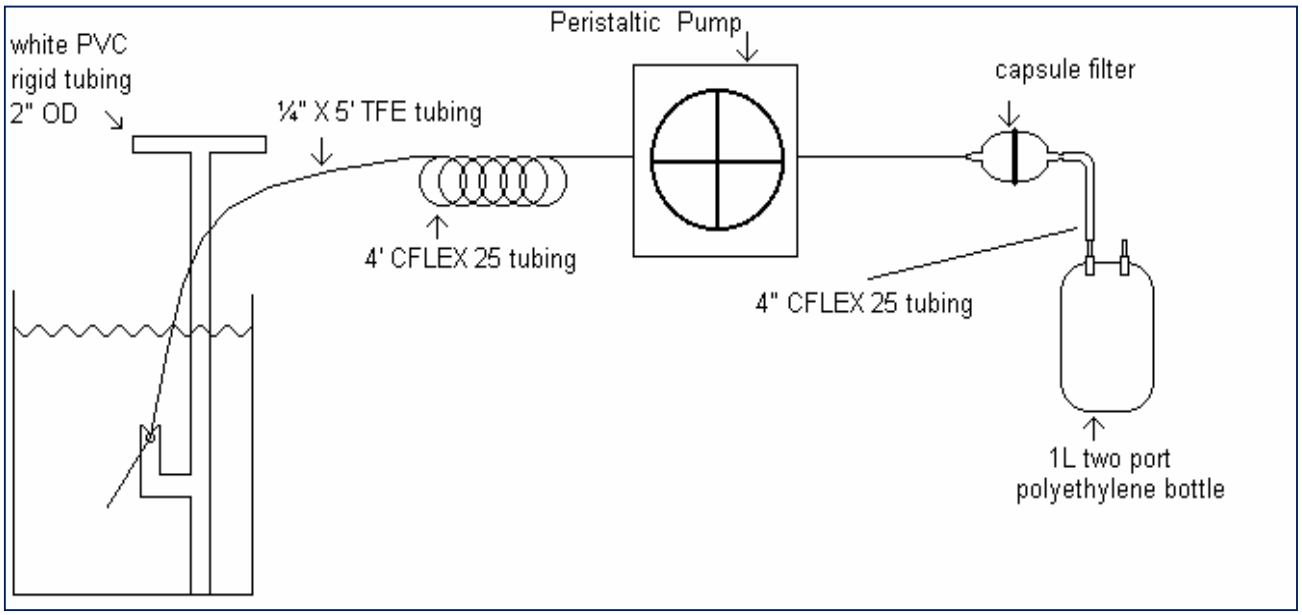


Figure 4-8. Clean metals effluent sampling apparatus

4.8.6.2 Dissolved and/or Total Recoverable Grab Blanks and Samples

1. Refer to **Figure 4-8** for the schematic of the field sampling equipment used to process blanks and samples.
2. The effluent grab blanks and samples are collected in the same manner as the ambient grab blanks and samples.
3. Instead of collecting from a bridge bottle, use a PVC sample wand equipped with a special notch to hold the Teflon tubing.
4. **Clean hands:** present a section of the Teflon tubing just past the inlet to **dirty hands,** who then attaches the tubing to the sample wand.
5. The entire assembly: sample caddy containing the empty sample container, sample tubing, pump/battery, and sample wand are transported to the effluent sampling location.
6. **Dirty hands:** place the sample wand into the collection zone and avoiding touching the sample tube tip on any structures, sediment, or debris.
7. At this point, refer to **sections 4.8.5.3** and **4.8.5.4** on how to process blanks and samples respectively.

4.8.7 Clean Metals Labeling

After scheduling a run, print the labels from CEDS. Use labels with good quality glue (i.e., Avery). Use a laser printer to print labels to avoid smudging. Unless specified otherwise, fill out labels with date and time and attach to the bottles before getting them wet. Never place a label on the outside of the plastic bag, as this will result in an unlabeled sample bottle.

4.8.8 Shipping Clean Metals Samples

4.8.8.1 Shipping Supplies and Materials

1. An insulated shipping cooler such as a 28-quart cooler is usually sufficient to hold sample bottles, wet ice packs, and protective material.
2. Liner Bags which are 30-gallon plastic trash bags with a dimension of 30”x36”x1 mil.
3. Non-DCLS laboratories may request wrapping the 1 L sample bottles with plastic bubble wrap. If so, ideal packing material is bubble wrap with 1/2” bubbles in 12”x16” sheets. A 1’ wide roll of the bubble wrap is suitable for the loop containers.
4. Size 33 or similar rubber bands are large enough to secure the bubble wrap around 1-liter containers packed in two Ziploc bags.
5. Wet ice cubes. Unless directed otherwise, do not use blue ice packs. The gel does not ensure proper transport temperature.
6. Strapping tape, 1” filament type.

7. Duct tape, 2" utility type.
8. 3" clear acrylic adhesive tape to seal ice bags and labels to bottles and coolers.
9. Packing list envelopes, clear plastic self-adhesive type.
10. Address Labels, specific to the carrier.

4.8.8.2 Sample Packing

1. Immediately following sample collection, place sample bottles in storage cooler with wet ice for transport back to the regional office for packing into shipping coolers.
2. Insert two trash bags into the cooler to provide a double lining.
3. Fill the cooler with ice to the shoulder of the sample bottles.
4. Place the chilled sample containers upright into the lined cooler and surround with ice. The sample containers and ice should be tightly packed. When the cooler is properly packed there will be no extra space left in the cooler.
5. Seal each liner bag by twisting the top of the bag and tying in a knot.
6. If appropriate, attach a 1-gallon Ziploc bag that will hold the packing list envelope to the underside of the shipping cooler lid. Insert the appropriate sample documentation (e.g., chain of custody form, field data sheets, or special lab instructions) and seal the envelope. Place the sealed envelope in the Ziploc bag and seal bag for protection.
7. Close the lid, seal horizontal joints with duct tape, and secure with strapping tape.
8. Attach address label to side of cooler and protect with clear sealing tape.
9. Check with specific lab to verify proper shipping procedures.

4.8.8.3 Sample Transportation

For samples shipped via standard DCLS courier service, no special precautions beyond normal shipping procedures are required. Sample packaging and transportation items listed below are provided for those samples that are to be shipped long distances (generally interstate) and are intended for worst case shipping conditions.

1. Samples shipped by common carrier must comply with applicable Department of Transportation Hazardous Materials Regulations, 40 CFR Part 172. The person offering such material for transportation is responsible for ensuring such compliance. See 40 CFR Part 136 Table II for guidance on applicability of preserved environmental samples.
2. Ship samples on the day of collection and use a reliable courier service for priority or next day delivery.
3. A large amount of effort is required to prepare and sample four to five sites on a typical run. Four samples represent over $1000.00 in equipment and laboratory costs so coordinate sample shipment closely with DCLS until delivery is confirmed and condition of samples upon receipt is verified.

4.8.9 Clean Metals Quality Control

1. The protocols in this SOP are designed to include all the necessary Quality Control steps needed to produce reliable, accurate data.
2. **Table 4-4** lists the critical control points of the sampling protocol. These control points are the minimum steps required for the collection of samples. When field contamination is detected, additional blanks and other quality control samples are necessary to identify and correct the problem.
3. Field equipment blanks (identified with group code CMETB and container ID EB with a depth of 0.0) should be collected with every sample including the mercury blank. If total recoverable samples are also collected, the dissolved equipment blank will be representative of the total recoverable sample. If only total recoverable samples are collected, then collecting a field equipment blank is required.
4. For effluent sites, blank samples must be collected prior to each sample and all trace metal samples.
5. If ambient site conditions indicate potential problems, then it would be wise to collect additional samples. Some site conditions which would warrant blanks prior to sample collection are:
    - **a.** Road construction producing visible dust.
    - **b.** Any operation causing visible dust emissions.
    - **c.** High total suspended solids conditions instream.
    - **d.** Recent deicing of bridges.
    - **e.** High traffic volume on bridge.
    - **f.** Heavy rain events during sampling.

Table 4-4. Quality control recommendations for trace metals sample collection.

Sampling Requirements	Criteria	Frequency
Type of Method	Performance based by demonstration of no detectable contamination of target analytes or interferences in samples or blanks. Method 1669 and the sampling apparatus and techniques used by the DEQ are recommended for sample collection.	Demonstration of contamination free samples and blanks every time a variation is made to the method.
Media Type	Freshwater and treated final effluent wastewater for dissolved and total recoverable metals	N/A
Training	Sample collection by only thoroughly trained personnel. Personnel must demonstrate proficiency in collecting contaminant free blanks and samples	Train a minimum of one time prior to any sample collection. Stop and provide additional training if field QC demonstrates problems until the criteria is achieved.
Filtration	0.45 µm capsule filter with nominal surface area of 60.0 cm^2. Maximum sample volume 1000 mL through single use filter	Onsite at time of collection or within one hour for composite samples after the sample sequence is complete.
Sample Containers	No detectable target analytes above MDL	Minimum of 1% of containers checked by the laboratory per batch after initial demonstration of acceptable blank QC.
Sampling Equipment	No detectable target analytes above MDL	Minimum of 1% of equipment checked by the laboratory per batch after initial demonstration of acceptable blank QC.
Comprehensive Grab Field Blank	Blanks must be <10% sample concentration or if sample is < MDL, field blank contamination is OK.	Process one with every sample collected. When duplicate samples are collected, only one blank is necessary.
Comprehensive Composite Field Blank	Blanks must be <10% sample concentration or if sample is <MDL, field blank contamination is OK	Process one per site for every ten samples. When 10% frequency rule is applied, blanks are to be collected with the first sample. Process field blanks every time equipment is field cleaned to be reused between sites or sample events.
Field Duplicate	Statistically equivalent to the RPD of the matrix spike and matrix spike duplicates for quantifiable concentrations	Process one per site for every ten samples.
Preservation	Samples must be iced in the field. Composite samples must be iced during collection. Adjust pH <2 SU within 72 hours of collection and samples must remain in original containers for a minimum of 18 hours prior to digestion or analysis.	All samples must be acid preserved in the field or by the laboratory using ultra-pure HNO_3 to pH <2 SU. Samples should be iced in field immediately after collecting.
Documentation	Sampling activities must be documented on paper or by computerized sample tracking.	Documentation must be done per sample, per site.

4.8.10 Clean Metals Quick Reference Guide

Ambient Sample Collection Quick Reference

1. Tie the 5-pound weight to the bridge bottle.
2. Collect the sample using the bridge bottle.
3. Untie the 5-pound weight.
4. Connect the tube to the first loop container.
5. Rinse the filter with the contents of the container.
6. Remove the tube from the empty bottle and place on the second loop container.
7. Pump 125 mL of water to waste through the filter to purge previous sample.
8. Fill the mercury blank and seal.
9. Connect the filter to the empty first loop container.
10. Pump out of the second loop container into the first without letting the filter go dry.
11. Seal the blank loop container.
12. Remove the tube from the now empty second loop container and reconnect the tube to the bridge bottle vent tube.
13. Pump 125 mL of water to waste through the filter to purge previous sample.
14. Collect the mercury sample.
15. Unscrew the lid of the second loop container and discard the water and replace the lid.
16. Connect the filter to the second loop container and fill.
17. Seal the sample containers.
18. Remove the filter and collect the total recoverable sample.
19. Collect field parameters.
20. Pack in ice and transport.

Effluent Sample Collection Quick Reference

1. Connect the tube to the first loop container.
2. Rinse the filter with the contents of the container.
3. Remove the tube from the empty bottle and place on the second loop container.
4. Pump 125 mL of water to waste through the filter to purge previous sample.
5. Fill the mercury blank and seal.
6. Connect the filter to the empty first loop container.
7. Pump out of the second loop container into the first without letting the filter go dry.
8. Seal the blank loop container.
9. Remove the tube from the now empty second loop container and connect the tube to the sample wand.
10. Pump 125 mL of water to waste through the filter to purge previous sample.
11. Collect the mercury sample.
12. Unscrew the lid of the second loop container and discard the water and replace the lid.
13. Connect the filter to the second loop container and fill.
14. Seal the sample containers.
15. Remove the filter and collect the total recoverable sample.
16. Collect field parameters.
17. Pack in ice and transport.

Ambient Sample Collection without the Bridge Bottle Quick Reference

1. Connect the tube to the first loop container.
2. Rinse the filter with the contents of the container.
3. Remove the tube from the empty bottle and place on the second loop container.
4. Pump 125 mL of water to waste through the filter to purge previous sample.
5. Fill the mercury blank and seal.
6. Connect the filter to the empty first loop container.
7. Pump out of the second loop container into the first without letting the filter go dry.
8. Seal the blank loop container.
9. Remove the tube from the now empty second loop container and connect the tube to the sample wand.
10. Pump 125 mL of water to waste through the filter to purge previous sample.
11. Collect the mercury sample.
12. Unscrew the lid of the second loop container and discard the water and replace the lid.
13. Connect the filter to the second loop container and fill.
14. Seal the sample containers.
15. Remove the filter and collect the total recoverable sample.
16. Collect field parameters.
17. Pack in ice and transport.

4.8.11 Clean Metals References

Benolt G. 1994. Clean technique measurement of Pb, Ag, and Cd in freshwater: A redefinition of metal pollution. Environ. Sci. Technol. 28: 1987-1991.

Horowitz AJ, Demas CR, Fitzgerald KK, Miller TL, Rickert DA. 1994. US Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water. US Geological Survey, Open-File Report 94-539.

Horowitz AJ, Elrick, KA, Colberg MR. 1992. The effect of membrane filtration artifacts on dissolved trace element concentrations, Wat. Res. 26: 753-763.

Horowitz AJ, Lum KR, Garbarino JR, Hall GEM, Lemieux C, Demas CR. 1996. Problems associated with using filtration to define trace element concentrations in natural water samples. Environ. Sci. Technol. 30: 954-963.

Martin GR, Smoot JL, White KD. 1992. A comparison of surface-grab and cross sectionally integrated stream-water-quality sampling methods. Water Environment Research 64: 866-876.

US Environmental Protection Agency. 1996. Method 1669: Sampling ambient water for trace metals at EPA water quality criteria levels. EPA 821-R-95-034.

4.9 COLLECTION OF AQUEOUS PCB SAMPLES

Polychlorinated biphenyls (PCBs) samples involve measurement of ultra-trace levels (parts per trillion or quadrillion) of PCB in water or sediment for specific special studies. To eliminate sampling contamination, use of clean sampling protocols is required.

4.9.1 Scope and Applicability

This procedure outlined below is intended to be used to collect PCB samples in freshwater, saltwater, wastewater, and sediment, with results typically in the 10 ppt or less range per congener.

PCB analysis is typically performed by a contracted Virginia Environmental Laboratory Accreditation Program (VELAP) certified laboratory. Method Detection Limits (MDL) for each of the 209 PCB congeners is provided by the contracted laboratory.

Note: The below listed equipment and procedures apply with collecting PCB samples in a water matrix. Sediment collection protocols are covered in **Section 4.6**.

4.9.2 Summary of Method

The samples are collected by submerging the certified pre-cleaned 2.5-liter sampling container at a specified depth. Ideally, the sample will be taken from mid-channel. Samples will be analyzed for PCB congeners, suspended sediment concentration (SSC), total organic carbon (TOC), and dissolved organic carbon (DOC). DOC will be filtered in the laboratory. The SSC, TOC, and DOC samples are collected by a separate clean container rinsed in site water or decanted from the PCB sample bottle.

4.9.3 Equipment Checklist

The following equipment is typically used to collect aqueous samples.

1. Certified pre-cleaned 2.5 L amber glass bottle with a Teflon cap
2. Disposable nitrile gloves transported in a fresh Ziploc bag
3. Large coolers with ice
4. Field equipment cleaning kit (Liquinox detergent, pesticide grade ethanol or methanol solvent, lab grade water, rinsate receptacle)
5. Field data sheets and waterproof notebook
6. Aluminum foil
7. Black indelible ink pens
8. Chain of Custody forms
9. Weighted bottle sampler and neoprene cap (optional based on project)
10. DOC, TOC, SSC sample containers and preservatives (optional based on project)

4.9.4 PCB Equipment Cleaning Instructions

PCB sampling equipment requires cleaning prior to each sampling event.

Laboratory cleaning: For cleaning equipment in the laboratory, refer to **Section 2.2.2**.

Field cleaning: For cleaning equipment in the field (between sites), refer to **Section 2.2.3.**

4.9.5 Water Sampling Preparation

1. Accessing the sample site is left to the discretion of the field staff.
2. Wear nitrile gloves and associated protective gear. Wear new gloves for each sample.
3. Make a note on the field sheet if samples are not collected while facing upstream or in the main channel.
4. If wading or using a boat to access the sample site, take care to not disturb sediment when collecting water samples.
5. If sampling by wading or bridge using a sample devise is unsafe, sample from the streambank in a manner that will most closely represent the entire stream.
6. Always collect water samples prior to sediment samples at each site.
7. Collect any other water quality samples and readings either downstream from, or after collecting the water PCB sample.

4.9.6 Water Sampling Procedure

1. Remove the Teflon lined cap from the bottle, and place cap on a fresh piece of aluminum foil to minimize PCB contamination.
2. Place the bottle at the appropriate depth and fill the bottle. If collecting samples below one meter, place the bottle in a weighted sampler and insert a solvent rinsed neoprene bottle stopper. At the appropriate depth, pull out the stopper to fill the bottle.
3. Retrieve the sample bottle while being careful to avoid dislodging materials into the bottle opening.
4. If collecting DOC and TOC samples at the site, fill the DOC and TOC samples (including duplicates) from a separate bottle or the PCB sample bottle. If decanting from the PCB sample bottle, be sure the bottle does not touch the DOC/TOC bottles.
    a. Preserve DOC and TOC samples. The lab will filter DOC samples.
    b. Collect SSC samples by submerging the cubitainer below the water surface. Immediately cap, label, and place on ice. If a sample from a greater depth is necessary, use the sampling vessel to decant into the cubitainer.
5. Cap, label, and place all samples in the cooler.

4.9.7 PCB Trip/Bottle Blank

Due to the ultralow detection limits used to measure PCB congeners and how easily equipment can become contaminated due to aerosol deposition or poor cleaning practices, a trip/bottle blank is occasionally performed.

1. Before collecting the regular sample, remove the cap of the provided bottle of blank water and empty sample bottle. Place lids on a fresh sheet of aluminum foil.
2. Pour the blank water bottle contents into the empty trip/blank sample bottle.
3. After collecting the regular sample in a separate bottle, cap the now filled trip/ blank bottle.

4.10 Filamentous Algae Sampling

This monitoring method was developed to collect data for determining the areal density of algae across a lateral transect. The algae sample is analyzed for Chlorophyll-*a* as a means of estimating algal biomass in swift moving, rocky bottom, wadeable rivers in the mainstem and tributaries of Virginia's Shenandoah River. The Chlorophyll-*a* results are expressed in mass per unit area (mg/m^2). This process requires a minimum of two staff: one sampler and one observer as described below. **FILBEN** is the parameter group code for filamentous algae samples.

Virginia's monitoring process is based on the established methods for evaluating nuisance algal conditions in wadeable rivers and streams (Boulton, et al., 1985; Montana DEQ, 2011; Morgan, et al., 2006; Schaller, et al., 2004; West Virginia DEP, 2018).

4.10.1 Nuisance Algae Sampling Checklist

1. Data sheet(s) printed on waterproof paper
2. CEDS labels for each site visited and wire tags for labels
3. Clipboard (a loop of rope through the paper clamp enables the Observer to carry around neck)
4. Fine-tip waterproof marker (e.g., Sharpie) and pencil
5. Cooler with ice
6. Water Quality sonde
7. Waterproof box to carry small sampling gear
8. Range finder (check battery before leaving office)
9. GPS (check battery before leaving office)
10. Wading staff calibrated in cm
11. Surber sampler w/ 500µm mesh net
12. Waterproof camera (with polarizing filter if available, if not shoot through polarized glasses lens)
13. 1- 1gal, and 1-L wide mouth plastic bottle per site (use 1L bottle for smaller samples
14. 5-gal bucket with screw top or snap on lid
15. Aquascope, dive mask and snorkel, or goggles (optional)
16. Stainless steel scissors
17. Hand brush (toothbrush, etc.)
18. Dipnet with 500µm mesh netting
19. Sieve bucket
20. Rinse bucket (about 2-1/2 gal)
21. Chest waders and shoulder length gloves (if water is > 20°C, wet wading is more convenient)
22. Scale with precision to 0.00g
23. Portable spin dryer (Example of acceptable spinner: https://www.amazon.com/Panda-Portable-Dryer-22lbs-Stainless/dp/B01IRMBG7I)

4.10.2 Filamentous Algae Site Evaluation

1. For established monitoring stations, schedule visits monthly at roughly 30 day intervals.
2. For new citizen complaints, attempt to visit site within three days of receipt of the complaint, conditions permitting.
3. At the site, estimate the percent coverage of benthic algae visually by wading or viewing from a bridge.
4. Photo-document the site using polarizing filter when necessary.
5. If estimated benthic coverage exceeds 10%, take a FILBEN sample.

4.10.3 FILBEN Sample Collection

1. Prior to visit, create or obtain a Station ID from CEDS. Enter the run schedule using a "VALGAEn" format, where 'n' is the station number for established algal monitoring stations. If the site is being visited in response to a complaint, use "VALGAEd" where 'd' is the sampling date in mmddyy format. For complaint stations, obtain coordinates (latitude/longitude) in the field with a GPS unit. Use FILBEN as the selected parameter.
2. Print labels from CEDS, and an Algal Collection datasheet (**Figure 4-9**) on waterproof paper.
3. Calibrate sonde as per **Section 3** and record calibration data in sonde logbook.
4. Assemble sampling gear as indicated in Nuisance Algal Sampling Checklist (**Section 4.10.1**).
5. Notify DCLS personnel as soon as possible that FILBEN sample(s) may arrive next day at lab.
6. File the run plan with the manager and receptionist and depart for sample station(s).
7. **Designate one monitor as the Observer, and the other as the Sampler at the site.** Their respective responsibilities are described in the following steps.
8. Upon arrival at the station, select a transect that meets the following criteria:
    a. Best available algae habitat suitable for Surber collection at the station location.
    b. Average depth less than about 0.75 m (≈30 inches) to ensure wadeable condition.

    The attempt is made to use a transect in a 90' angle from the bank, but the angle may be altered slightly to ensure wadeable conditions or in-stream obstructions. The transect may be at any angle to the bank up to 45 degrees to ensure appropriate conditions.
9. **Observer**: Upon arrival at station, estimate the algal percent coverage at the selected transect (4.3.10.8). Visual observations are made either from bridge or bank. Do not include coverage by submerged aquatic vegetation (SAV) but do include blue green algae coverage if present.

10. **Sampler**: While Observer performs the cover estimate, deploy the sonde, and collect and record water quality data (Temp °C, pH, DO mg/L, and specific conductance µS/cm).
11. **Sampler**: Observe and record narrative account of turbidity ("clear," "slight," "moderate," "heavy"). If water is substantially turbid, visibility may make sampling impossible. In this case, the sample is rescheduled one week if conditions and resources allow.
12. Record time, weather, flow conditions, and estimated percent algal coverage from Observer in 4.3.10.9.
13. If estimated % cover is <10%, document with photos and return to office. If estimated cover >10%, then continue to the next step for algal sample collection.
14. Use a rangefinder to measure the length of the transect identified in 4.3.10.8, that is, the wetted width of the water body at the point of measurement.
15. Divide the transect length by 11 (the number of subsamples that will be collected along the transect) to obtain the subsample interval. Eleven subsamples will comprise a total area of 1.02 m^2.
16. Divide the subsample interval by two and collect the first subsample at that distance from the starting bank. The final (11^{th}) subsample should end up ½ the sample interval from the far bank.
    a. **For example**, if the length of the transect is 78 meters, round down to 77 (for an even multiple of 11) for a subsample interval of seven meters. The first subsample is collected at 7÷2, or 3.5 m from the starting bank.

Note: The sampling crew should remain downstream of the transect to avoid disturbing algae at the subsample locations

17. **Observer**: When moving to each subsample location along the transect, guide the **Sampler** along the transect line using either rangefinder or wading staff until the Sampler is in the correct subsample position. This will reduce the chance of sample bias.
18. **Sampler**: When the **Observer** indicates that the Sampler is at the correct subsample location, without looking down, place the Surber frame on the bottom of the stream as flat as possible. In moderate current, the Sampler can hold the Surber in place; under heavier flow, it may be necessary to move to the downstream side of the Surber to avoid creating eddies in front of the collection net, which could result in loss of algae from that subsample point. If the substrate is too uneven for the Surber to rest relatively flat on the bottom or too deep for the Sampler, it is permissible to move up or downstream to the nearest suitable habitat within 5 meters.
    a. If the team encounters a location along the transect which is unsuitable for sampling and there is no workable subsample location within a few meters either upstream or downstream, it is permissible to omit that subsample. When entering data, reduce the 'total area of composite sample' field accordingly (resulting in <1.02 m^2).

19. **Sampler**: With the Surber in place, estimate the following parameters within the frame of the Surber and report them to the **Observer** for recording:
    a. Dominant substrate type (gravel, cobble, etc.). See **Table 4-5** for reference.
    b. % filamentous green algae (FGA), excluding filaments < 5cm in length.
    c. Average length (cm) of the filamentous algae (**length not limited to frame; may be several meters or more**)
    d. Estimated height in centimeters the FGA extends into the water column.
    e. % submerged aquatic vegetation (SAV) coverage.
    f. % blue green algae (BGA) coverage.
    g. % other periphyton coverage (includes filamentous algae <5cm in length).

Note: Total percent coverage may add to >100% since some groups may overlap.

20. **Sampler**: use scissors, brush, or fingers to remove all filamentous strands encompassed by the Surber frame and place them into the Surber net. Include all filaments in the water column directly over the frame and any floating clumps that drift directly over the frame during collection at that subsample location.
    a. If backflow increases due to a high volume of algae and risks loss of collected algae from the net, remove the algae from the Surber net and place into the five-gallon bucket with a few liters of river water, to keep the algae wet during collection.
21. After algae has been completely removed at the current subsample location, retrieve the Surber; making sure to retain all algae in the net. Proceed to next subsample location and repeat steps 17-20. As the team moves along the transect, they may choose to take pictures representative of overall conditions.
22. At the last subsample location, the sampling team should be half the subsample interval distance from the far bank.

4.10.4 Replicate Sample Collection Procedures

Collect replicate samples by placing the Surber frame immediately adjacent to the location of each subsample along the same transect and repeating steps 19-22 in section 4.10.3, taking care to keep replicate samples separated. See section 4.10.8 for frequency of replicate samples.

4.10.5 FILBEN Sample Processing

1. Return to shore to process the sample. Abundant water will be required for processing, so locate a convenient spot at the edge of the stream; fine gravel bars or other flat areas work well.

2. Using either a sieve bucket or 500 µm D-net, gently wash entrained sediment from the algae. Place the algae in the net or bucket and suspend it in the water column, gently swirling or stirring the algae to remove as much sediment as possible.
3. Place rinsed algae in the sieve bucket and leave it in water at the edge of the stream to keep the algae wet.
4. After the algae has been washed, there will still be non-target material (NTM) in the sample. This could include Corbicula shells, snails, other macroinvertebrates, SAV, leaves, twigs, etc. This will require hand-picking for removal.
5. Using a small handful at a time, pick through the algae and remove NTM. This may take half an hour or longer, depending on the volume of the algae and the amount of entrained foreign material. For samples with large amounts of NTM, it may be necessary to pick through the sample twice to sufficiently clean the sample.
6. Once the sample is sufficiently clean, place it in an appropriately sized wide-mouth plastic bottle and put it in the cooler on ice.

Note: If weather or other conditions preclude completing cleaning in the field, cleaning may be completed back at the office/lab using water obtained in step 8.

7. Use a fine tip water-proof marker to fill out CEDS sample tag; collection time should be the time the crew began sampling.
8. Fill the 5-gallon bucket with about 3 gallons of clean stream water and close the lid. This water will be used for final processing at the lab prior to obtaining spun weight.

4.10.6 FILBEN Spun Weight Collection

1. Remove the sample from the 1-gallon wide-mouth bottle into a deep, large tray.
2. Use a portion of the river water in the 5-gallon bucket to further clean the sample, if it was not sufficiently cleaned on-site.
3. Place equal amounts of sample algae on either side of the spinner chamber, to ensure algal mass is as balanced in the spinner as possible.
4. Close the spinner lid, and begin spinning; spin for about 90 seconds, or until water stops flowing from the bottom of the spinner discharge chute.
5. Remove spun algae, re-wet it with river water, and repeat spinning 2 more times. After the third spin cycle, the water discharged from the spinner should be relatively clear.
6. On a balance or scale with at least 1 g precision, tare the sample bottle.
7. Remove the spun algae from the spinner and place it in the tared sample bottle.
8. Weigh the spun algae and record on the field data sheet.
9. Add enough stream water back to the algae to fill bottle so that it doesn't lyse; tighten lid.

10. Label bottle with collection data. Place in cooler for shipment to DCLS.

4.10.7 Filamentous Algae CEDS Data Entry

1. Enter field data into CEDS as normal.
2. To record visual observations, enter the estimated % coverage in the Comments field. If less that 10%, use the following language: "<10% FGA". If the river is too high or turbid to make an estimate with confidence, the following should be entered: "High Flow. Very turbid. FGA % coverage: no estimate. River too high and turbid to see the bottom."
3. To record data after FILBEN sample collection, in the comment field, record the bank estimate %FGA, Surber estimate %FGA, and %BGA , and wet wrung weight in that order. The following is an example: "Bank Estimate %FGA = 50%; Surber %FGA = 51.8%; Surber %BGA = 0%; Wet Wrung Weight = 100g"
4. In the Samples section in CEDS, add the total area sampled in meters in the "volume sampled" field and in the Comment field, add the total area of composite sample (usually 1.02m^2). This number could be different than 1.02 m^2 if less than 11 subsamples were collected due to substrate conditions or lack of wadeability.
5. If the station was not established, enter station information including lat/long into CEDS.

4.10.8 Filamentous Algae QC Samples

Replicate samples are collected at approximately 10% of field visits. In the event that fewer than 10 samples are collected, one replicate sample will be collected along with the last sample of the season. Duplicate data are used to determine the overall precision of field and laboratory procedures.

4.10.9 Filamentous Algae References

Boulton AJ. 1985. A sampling device that quantitatively collects benthos in flowing or standing waters. Hydrobiologia 127: 31–39.

Montana Department of Environmental Quality. 2021. Sample collection and laboratory analysis of chlorophyll-*a* standard operating procedure.

Morgan AM, Royer TJ, David MB, Gentry L. 2006. Relationships among nutrients, chlorophyll-*a*, and dissolved oxygen in agricultural streams in Illinois. Journal of Environmental Quality 35: 1110–1117.

Schaller JL, Royer TV, David MB. 2004. Denitrification associated with plants and sediments in an agricultural stream. Journal of the North American Benthological Society 23: 667-676.

West Virginia Department of Environmental Protection. 2018 (revised). Watershed Assessment Branch Standard Operating Procedure, Periphyton/Algae Collection Procedures.

DEQ Stage 2 Algae Monitoring: Surber

Stream Name_____ Location_____

Station ID_____ Latitude_____ Longitude_____

Crew_____ Date____/____/____ Start Time_____ End Time_____

CEDS Run ID_____ Flow (S/F)_____

Wx_____ Turbidity (Clear, Slight, Moderate, Heavy) _____

Weather Codes (Wx): 1=Cloudy; 2= Rain; 3=Clear; 4=Fog/Mist

Sonde Data

Instrument ID_____

Temp (°C) pH Dissolve Oxygen (mg/l) Sp. Cond (µS/cm)

Bank % Cover Est_____

Transect Wetted Width (m)_____

Interval (Wetted Width/11)_____

Obs.	Dist. (m)	Depth (cm)	Substrate	%FGA	Column Height (cm)	Median Length (cm)	%BGA	%SAV	%Periphyton
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									

Wrung Wet Weight of collected algae (g)_____ Surber calc. % cover: _____

Figure 4-9. Filamentous algae sampling form.

Substrate Class		Size		score	Embedded
Bedrock Smooth		>4000 mm	Bigger than a Small Car	RS	0
Bedrock Rough		>4000 mm	Bigger than a Small Car	RR	0
Concrete or Asphalt				RC	
Hardpan			Firm Consolidate Sediments	HP	0
Large Boulder		1000-4000 mm	Meter stick to Small Car	XB	
Small Boulder		250-1000 mm	Basketball to Meter Stick	SB	
Cobble		64-250 mm	Tennisball to basketball	CB	
Coarse Gravel		16-64 mm	Marble to tennisball	GC	
Fine Gravel		2-16 mm	Ladybug to marble	GF	
Sand	100% embed	0.06-2 mm	Gritty between fingers to Ladybug	SA	100%
Fines	100% embed	<0.06 mm	Smooth, not gritty	FN	100%
Wood				WD	
Other write comment				OT	

Table 4-5. Substrate classification reference table.

4.11 Chain of Custody Record and Procedures

The Chain of Custody Record (COCR) documents everyone who has custody of the samples. The COCR starts with the sample collector. The COCR travels with the listed samples. The COCR must contain the written signature of everyone that has custody of the samples.

4.11.1 Transferring COC of samples from person to person

When sample custody changes from one person to another, the COCR must document the transfer of samples from one person to another in the presence of each other. The custody of the samples and the responsibility of maintaining sample integrity are transferred during this process. The transfer process is documented at the bottom of the COCR form.

4.11.2 Transferring COC of Samples via Courier

This transfer is the same as above, except that the transfer is not face to face. Both the collector and laboratory receiver document the integrity of the shipping container and the samples therein. The actual sample transfer is via authorized courier in a tamper-proof shipping container.

4.11.3 Priority Codes

Code 7 – Routine Turn Around Time (TAT), listed price

Code 6 – First In, First Out, COCR, listed price (no sooner than routine TAT)

Code 5 – ½ standard TAT, 1.5X listed price

Code 4 – 7-day (if method allows) TAT, 2X listed price

Code 2 – Potential for legal action 1.2 X listed price (chain of custody required)

Code 1 – Emergency: Price will be determined after completion

Note: Only use **Code 6 or 7** for parameters with 48 hour or less holding times (e.g., BOD5, fecal bacteria, etc.) as they cannot be run faster by the lab. **Code 6** may be used for COCR documented samples, but the samples do not need to be retained (e.g., TMDL studies). **Code 2** is used if samples that need to be retained for legal purposes (e.g., PReP, enforcement). **Code 1** requires regional or agency director approval as lab staff must work around the clock to finish analysis.

4.11.4 Preparing the COCR form

The COCR form may be prepared manually or through CEDS. Using CEDS is preferred as it automatically fills in many of the COCR fields. Manual COCR forms may use the template found in **Figure 4-10**. The COCR does not take the place of a field sheet or CEDS data shipment. **A separate COCR form must be completed for each sample cooler shipped.** The COCR must exactly match shipped sample tag information.

4.11.5 COCR Fields

Note: The COCR form must be filled out by the person who takes initial custody of a sample.

Shipping Seal Number: The unique numbered seal used to seal individual COC coolers. Unless delivered in person to the laboratory, all COC samples shipped in coolers must have a numbered shipping seal in place with the same unique number recorded on the COCR. Upon receipt, the lab will compare an unbroken seal number of each cooler to the number recorded on the COCR.

Samplers: The person who collects (or is present at sampling) and takes initial sample custody.

RUN ID: Used to record the CEDS run identification number or other program specific value for the sampling event. Follow program protocols when entering this number.

Agency, Address: The region the sample was delivered from.

24-Hour Contact Information: **Note:** Only use if a Priority Code 1 sample is collected. Provide 24-hour contact information so the laboratory can confer about sample analysis and results. Examples include home, work, and cellphone numbers, and e-mail addresses.

Station ID: A DEQ station ID as outlined on **Section 4.11.7** of this document. If an ID is not available, a brief description so the sampler can identify where it was collected. Station ID information must exactly match what is listed on associated sample tags and field log.

Date & Time: The date and time at which the samples were collected. The date is in the form MMDDYYYY and record time of sample using military time HHMM.

Depth Desc: Note if the sample is from the surface (S), bottom (B), or integrated (I).

Depth: The sample depth in meters. Surface samples are 0.3. Blank samples are 0.0. Other depth samples should record the value on the log sheet (e.g., 5 m depth sample is recorded as 5.0)

%FRB: The approximate location of the sample point in reference to the right bank when facing upstream. Mid channel samples are recorded as 50. Samples closer to the left bank will be greater than 50 while right bank samples will be below 50.

Parameter Group Code: The analysis code used by the laboratory for analysis (e.g., TPLL)

Type: Notes if the sample is a routine sample (R), split (S1, S2, etc.), or equipment blank (EB).

Observations: Optional field to enter observations or field tests. These should be entered in the field log and on the lab sheets as well.

Relinquished By, Date/Time, Received By: Used to record sample custody transfers. Unless shipping by courier in a sealed cooler, transfer of COC samples must be in the presence of both the person relinquishing and receiving sample custody. The custodian signs the "relinquished by" and "Date/Time" fields of the COCR form. The new custodian signs the "received by" field. The process is repeated until the sample arrives to the authorized laboratory receiving custodian.

Shipping Seal Received Intact, No. of, Lab Remarks: Field used by the laboratory to note if the seal was intact and to record the seal number when accessing the contents of the cooler. They will also note any other remarks such as the condition of the samples, ice present, etc.

Group Code and Preservative Description: Code used for analysis along with sample preservation. **Section 4.11.11** has DEQ and DCLS contacts to obtain group code information.

4.11.6 Using CEDS for COCR Forms

CEDS can be used for shipping sample information to lab and for printing the COCR from. Since the COCR is printed from CEDS after returning from the field, this method may not be used when sample custody is transferred from person to person in the field. Having copies of the blank COCR Form in **Figure 4-10** can be useful in such circumstances.

When using CEDS to ship COC sample information to the lab, stations must be established in the station screen and all the pertinent information must be entered in the field data screen using established protocols. It is critical to record the **Shipping Seal Number** that will be using on the cooler and the **Shipped Date**.

After entering the Shipping Seal Number, Shipped Date, and field data, and while still on the "**Enter Field Data**" screen, click the "**Chain of Custody Report**" button to generate the form. Review the on-screen information with the sample tags and field log sheet before printing the COCR form. The COCR form may be changed in CEDS and reprinted if errors are made up to when CEDS ships data to DCLS (9 am and 10 pm).

Print two copies of the COCR form.

Sign one copy as "Relinquished by:" and complete the date/time at which the samples are relinquished or sealed in the cooler. This signed COCR is the official COCR. Place it inside the cooler in a Ziploc type waterproof container. The collector retains one copy with the field log.

Shipping Seal No: _____ Virginia Department of Environmental Quality Page of
1111 East Main Street, Richmond, VA 23219
Shipped Date: _____ Chain of Custody Record Sample Date: _____
Samplers: _____
Office: _____ Office Address: _____ RUN ID: _____
If this is an Emergency (Priority1) sample, please print 24-hour contact name and number: _____

Station Id	Date & Time	Depth Desc	Depth	%FRB	Observations

Relinquished By: (Signature)	Date/Time	Received by: (Signature)	Relinquished By: (Signature)	Date/Time	Received by:(Signature)
Relinquished By: (Signature)	Date/Time	Received by: (Signature)	Relinquished By:(Signature)	Date/Time	Received by:(Signature)
Relinquished By: (Signature)	Date/Time	Received in Laboratory by: (Signature)		Date/Time	Shipping Seal received intact?
				No. Of	Lab Remarks

	Group Code	Preservative Description
1		
2		
3		
4		
5		
6		
7		

Figure 4-10. Blank COCR form

4.11.6.1 Blank COCR Forms

If for some reason a COCR form must be filled out before returning to the office (e.g., sample team handing off a COC sample to a second team returning to the office), use the blank COCR form found in **Figure 4-10** and record the necessary information on two copies.

All information on the COCR form must exactly match information on the sample tags, field log, and lab sheets. Field teams may correct minor mistakes on the form by a single line cross out and initialing the crossed-out portion. Major mistakes will require completing a new form and destroying the form with the mistake.

Sign the bottom portion of the COCR as "Relinquished by:" and complete the date/time at which the samples are relinquished or locked in the cooler. The original signed copy is sent inside the cooler in a Ziploc type waterproof container. The collector retains one copy.

4.11.7 Sample Tag Fields

Use a #2 lead pencil or indelible ink to fill out the sample tag. The information on sample tag must exactly match the information found on the lab sheet or entered into CEDS.

Station ID: Station IDs generally follow the following format: **9ABCD000.00**

Where: **9:** The major watershed's prefix ranging from 1 to 9.
ABCD: The unique three (following a hyphen) or four-letter waterbody code.
000.00: Location based on the mileage upstream from the waterbody confluence.

Station IDs at **NPDES permit outfall** use the following format: **VA1234567-000**

Where: **VA:** The state the NPDES permit is issued. This is always VA.
1234567: The seven-digit permit number for the facility.
000: The outfall number being sampled.

Note: The station ID is derived from the run ID which is a CEDS identifier for the site.

Date collected: Fill in the day, month, and year (DDMMYYYY) that the sample was collected.

PRIOR: The priority code for the sample as outlined in **Section 4.11.3** of this document.

Time collected: Time that the sample was collected using 24-hour military time (HHMM). The printed time on the sample tag must exactly match the time entered in CEDS and/or COCR form.

Depth: Sampling depth to nearest tenth of a meter. 0.3 m indicates surface samples.

Unit Code: Budget code for analysis. CEDS prints this value automatically.

Lab Proc: Field for the laboratory, leave blank.

Group Code: Parameter group code for the sample. CEDS prints this value automatically.

Container #: Identifies each specific container with the lab sheet. Do not use the same number more than once per sampling event. The number on the sample tag or label and the number in this block must match with what is entered in CEDS and/or COCR form. It is recommended to use 1-9 for regular samples, 11-19 for duplicate samples, and 21-29 for equipment blanks.

Blanks/Dups: Notes if the sample is routine (R), split sample (S1, S2, etc.), or blank (EB, FB, etc.). CEDS enters these values if the run is set up with the necessary information (**Appendix D**).

Preservatives: Notes sample preservative (e.g., sulfuric acid), milliliters filtered, and similar information. CEDS will enter default values on each tag based on the group code. However, staff must verify and correct these values if different. For example, for filtered chlorophyll *a* samples, record the actual amount of water filtered if printed differently on the tag and note it in CEDS.

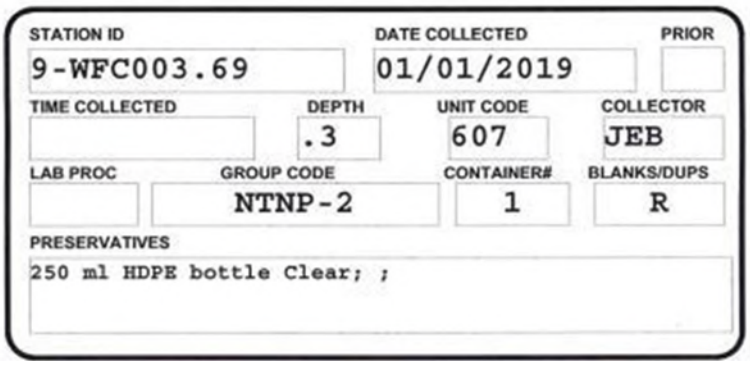


Figure 4-11. Example sample tag with CEDS-entered fields.

4.11.8 Preparing Samples for Shipment

Before shipping samples, ensure the sample tag information exactly matches what was entered in the COCR, the field log, and lab sheets or the CEDS field data entry screen.

1. Securely attach labels or wire tags to sample containers.
2. Fill the cooler with enough ice to reach the necks of the sample containers. The maximum weight of the cooler is 70 lbs.
3. If shipping a COC cooler, record the wire shipping container seal number on the COCR and sign the form. Place the COCR and any lab sheets in a Ziploc type bag and tape to the inside lid of the cooler. Each individual cooler must contain only the documentation for the samples it contains.
4. If shipping a COC cooler, close and seal the cooler and secure it using the numbered seal tag. Put the seal through both the bail and the eyelet of the hasp to prevent opening the cooler without breaking the tag. Before sealing, ensure the seal serial number matches the number on the COCR form.
5. Place coolers in the designated area for courier pickup. The pickup location should be secure from unauthorized access.

4.11.9 Possible COCR Problems and Solutions

Problem 1: The sample tags do not match CEDS information lab sheets or the COCR form.

Solution: The collector can correct these errors only if their field log contains information that will rectify the error. A correction of this type must be meticulously documented in the field log. Only the collector can make changes of this type. If the samples have been shipped, the collector will have to contact the lab to make the corrections.

Problem 2: Cooler sealed before adding all samples or wrong number entered on COCR form.

Solution: Break the seal to inspect the cooler contents and to add or remove samples as needed. Use a new seal and fill out a new COCR form. In CEDS, go to the field data screen (prior to automated data shipment @ 0900 and 2200, check for the lab send date in the CEDS field data screen), change the seal number and print a new COCR. Replace all three of the original COCR forms. Staff can simply line through the original seal number on the COCRs and write the new number by it and initial the change then make the correction in CEDS. If using the multiple-copy COCR form, clearly correct the seal number on the COCR and initial the correction.

Problem 3: There are no COC numbered seals.

Solution: Packing tape may be used as an emergency COC seal. Using a COCR template, print and enter the required information. Place this form in a Ziploc bag and tape to the cooler so that the opening of the bag is sealed with tape. Place sufficient tape around the cooler lid to secure the lid shut and two straps of tape to bind the lid to the cooler to prevent unauthorized access.

Another option is for the sampler or someone else who assumes custody of the samples to accompany the samples to DCLS. Samples delivered directly to the lab by custodian do not require custody. Container seals are suggested, however.

4.11.10 The Personal Field Log

The personal field log is a legal document used to record information concerning all aspects of an investigation. The log must be bound and have numbered pages. The log should be kept in a secure place. Only the owner of log should make notations in the personal field log.

At a minimum, the field log should record information which links that section of the field log with the information found on the COCR. The following information should be page headers:

1. Investigation identification information such as PC, or permit number
2. Date of investigation

The field log should support (but not duplicate) COCR information. At a minimum, the log should include:

1. Names, addresses, phone numbers of complainant, permit holder, operators, etc.
2. Detailed descriptions of the sampling sites
3. Variations, if any, from the WQM SOP manual
4. Type of samples collected (grab, straight timed composite including time frame, volume weighted composite, cross-section composite, vertically integrated composite)
5. Pre and post meter calibration information
6. Number and type of QA/QC samples collected
7. Detailed site observations including physical lay of the land such as upstream, up-gradient, east/west, etc.
8. Information to be included as CEDS or lab sheet comments such as “expect high BOD”
9. Documentation of changes to the COCR
10. Shipping seal number

4.11.11 Call List for Sample Related Issues

The agency maintains a list of key DEQ and DCLS staff to contact regarding ordering sampling kits, address issues in CEDS and courier services. This list is continually updated and posted in the following folder: https://covgov.sharepoint.com/:f:/r/sites/deqnet/Shared%20Documents/Water%20Division/Water%20Planning/Office%20of%20Ecology/WMA/Monitoring/DCLS?csf=1&web=1&e=tqMLR7. Regions are encouraged to regularly check and print and post the call list in the field preparation area for staff to refer to in the event DEQnet is offline.

4.11.12 Directions to DCLS

DCLS is located at: **600 North 5th Street Richmond, VA 23219**

To drop off samples to DCLS sample receiving, temporary parking is available at 600 North 4th Street. The DCLS main lobby is on the other side of the building at 600 North 5th Street.

Note: Sample receiving is the large garage door in the middle of the block on the right.

From West of Richmond:

1. Start out going East on I-64 E toward RICHMOND.
2. Take Exit 75WILLIAMSBURG/NORFOLK. 0.17 miles
3. Take the 3RD STREET ramp toward COLISEUM/DOWNTOWN. 0.09 miles
4. Stay straight to go onto N 3RD ST. 0.13 miles
5. Turn LEFT onto E LEIGH ST. 0.06 miles
6. Turn LEFT onto N 4TH ST. 0.04 miles

From South of Richmond:

1. Start out going North on I-95 N toward RICHMOND.
2. Take Exit 76ACHAMBERLAYNE AVE 0.16 miles
3. Turn LEFT onto CHAMBERLAYNE AVE/CHAMBERLAYNE PKWY. 0.20 miles
4. Turn SLIGHT LEFT onto W LEIGH ST. 0.30 miles
5. Turn LEFT onto N 4TH ST. 0.04 miles

From East of Richmond:

1. Start out going West on I-64 W toward RICHMOND.
2. Take Exit 190 I-95 S/5TH STREET/DOWNTOWN/COLISEUM. 0.29 miles
3. Stay straight to go onto N 5TH ST. 0.12 miles
4. Turn RIGHT onto E JACKSON ST. 0.05 miles
5. Turn LEFT onto N 4th ST. 0.04 miles

From North of Richmond:

1. Start out going South on I-95 S toward RICHMOND.
2. Take Exit 75 WILLIAMSBURG/NORFOLK. 0.17 miles
3. Take the 3RD STREET ramp toward COLISEUM/DOWNTOWN. 0.09 miles
4. Stay straight to go onto N 3RD ST. 0.13 miles
5. Turn LEFT onto E LEIGH ST. 0.06 miles
6. Turn LEFT onto N 4TH ST. 0.04 miles

5 QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance (QA) and quality control (QC) procedures and samples serve to ensure that monitoring activities produce data that meet defined standards at an established level of confidence. Two types of QC samples regularly collected by field staff serve to assess elements of field monitoring QA.

Appendix D contains instructions to enter QA/QC samples into the CEDS WQM module.

- **Field Blank** – An analyte-free sample (e.g., deionized water) processed at a sample site and exposed to sampling conditions, which is analyzed in a lab for sample run parameters. Field blanks serve to evaluate potential contamination introduced to samples from handling, processing, and analysis.
    - **Equipment Blanks** – A blank sample collected using sample-collection equipment to be analyzed at a laboratory to test for and measure contamination. Equipment blanks additionally check for carryover contamination between sample sites and effectiveness of cleaning procedures.

- **Field Replicate Samples** – Two or more samples collected in the field in an identical manner that represent the same population (i.e., water samples collected at the same place and time). Replicates are collected to evaluate variability in samples that may stem from environmental variation as well as sample collection and analysis processes. Two primary types of replicate samples may be collected:
    - **Duplicate samples** – A specific type of replicate sample in which two replicate samples are collected (i.e., two direct grab samples).
    - **Split samples** – A specific type of replicate sample where replicates are collected from a homogenized sample. Replicates from bucket samples are split samples because they are poured from a single homogenized sample.

Note: For the purposes of this SOP, the term **split sample** will refer only to replicates from a homogenized sample and **duplicate** will refer to replicates that are not homogenized. The term **replicate** will refer generally to split and duplicate samples.

Note: **Lab grade water** contains analytes of interest below method detection limits. For the purposes of this document, “lab grade water” is typically deionized (DI) water, which can be obtained from DI water systems at each regional office. Some programs may specify a particular type of lab grade water (or “reagent water”), which may be supplied by a laboratory. Always follow program-specific SOPs and QAPPs where applicable.

Note: **Labeling *QC Samples*** - For instructions on labelling QC samples, see **Section 2.4.1**.

QC Samples: General Guidelines

- Use only lab grade water for blank samples, blank sample rinses, and final in-house cleaning rinses of equipment.
- Transport sufficient lab grade water to the field in clean containers of suitable construction, such as cubitainers or large plastic jars.
- When possible, collect equipment blanks and field replicates on the same sample run.

5.1 QA OF FIELD PARAMETERS

Field probes should be calibrated and checked as outlined in **Section 3** of this manual. **Table 3-2** lists the acceptable calibration and end of day check ranges. If a unit fails a quality assurance check:

1. Do not upload affected parameters collected by the unit on that day into CEDS.
2. Perform any necessary maintenance/repair.

5.2 QC SAMPLES FOR GENERAL WATER QUALITY SAMPLING

Procedures listed below apply to general WQM based sampling procedures. Specific frequencies for QA/QC samples are program specific. Refer to applicable SOP documents for specific requirements.

Note: Always defer to program specific QA/QC requirements for specific instructions on collecting QC samples when a program has its own dedicated section in this document or in a separate SOP and/or QAPP.

5.2.1 Equipment Blanks for General Water Quality Parameters

When collecting an equipment blank, always run the lab grade water through all equipment used to collect the sample such as sample buckets or tubing.

Collect equipment blanks before collecting a sample at a sample site. Whenever possible, collect an equipment blank at the site designated for a field split sample.

For general ambient water quality sampling, an equipment blank shall be collected at a minimum of once for each 25 sites sampled (4%) unless other specific program requirements specify otherwise. The only exemption to this is for bacteria samples, as the bottles are certified sterile. Each regular field specialist should meet this 4% equipment blank check.

1. Flush or rinse the sampling device with lab grade water at least once prior to collecting the equipment blank. Rinsing must follow the same procedure (number of rinses, equivalent volume, and manner of rinsing) as when performing routine rinsing with sample water. Discard the rinse water.
    a. For the pump and hose method, first rinse the outside of the pump and hose intake assembly with lab grade water then rinse the pump and hose using the

same procedure when rinsing with sample water. This will typically require at least 5 gallons of lab grade water.

2. **Attach labels with the code "EB" on sample bottles to avoid confusing them with regular samples collected at the site.**
3. Rinse sample bottles with lab grade water three times. Discard rinse water.
4. Run lab grade water through or pour into the sampling equipment (e.g., pump and hose, bucket, etc.) and then pour or transfer the water into the respective sampling containers.
    a. Rinse non-sterile sample containers three times with lab grade water from the sampling equipment.
    b. Then fill each container with lab grade water from the sampling equipment and preserve according to normal procedures for filling bottles and preserving samples.
5. When entering data into CEDS, be sure to enter the EB sample designation for any equipment blank samples.

5.2.2 Field Replicates for General Water Quality Parameters

For general ambient water quality sampling, a field replicate or split sample of each routinely sampled analyte shall be collected once for each 25 sites sampled (4%). Each regular field specialist should meet this 4% field split check.

Stations designated for replicate and/or split samples will be chosen randomly. Split samples must follow the same collection, preservation, and handling in accordance with the procedures in this manual unless a different procedure is described in an associated program or study specific QAPP or SOP.

Note: Sites monitored under the Chesapeake Bay Program must follow the protocols listed in the SOPs located here: https://www.deq.virginia.gov/our-programs/water/water-quality/monitoring/chesapeake-bay-monitoring

5.2.2.1 Replicate Samples: Bucket Sampling

1. Follow instructions in **Section 4.3** to rinse and fill a bucket with sample water.
2. Fill containers in sets by parameter group/container type (i.e., fill TNUTL S1, then TNUTL S2, then do the same for each subsequent sample/container type). See example below.
    a. Ensure that the water in the bucket remains homogenized by stirring with a clean, stainless-steel spoon or by swirling the bucket between pours.
3. For bacteria duplicates, lower both bottles at the same time into the water using two bacteria samplers or a sample bucket with bacteria bottle holders.

Example: A station typically requires three bottles for two parameter groups: FCMFECQENT, IONTR, and TNUTL. A split sample requires an extra bottle for each parameter group. Each parameter group will then have two bottles, labelled with S1 and S2 in the "Blanks/Dups" field on container labels.

1. Fill both bacteria bottles concurrently using two bacteria samplers or a sample bucket with bacteria bottle holders.
2. Collect a bucket of water according to the protocol in **Section 4.3**.
3. Rinse and fill bottles in this order (while ensuring sample remains homogenized):
    a. TNUTL S1
    b. TNUTL S2
    c. IONTR S1
    d. IONTR S2

5.2.2.2 Replicate Samples: Wading and Streambank Sampling

When conducting instream samples according to **Section 4.3.3**, use the following protocol to collect duplicate samples.

Note: If working in pairs and conditions allow, both samplers shall collect duplicate samples concurrently and side-by-side.

1. Follow the steps from **Section 4.3.3** to reach the instream sampling location with sample containers.
2. Once at the sampling location, fill containers in sets by parameter group/container type either sequentially (if working alone) or concurrently and side-by-side (if working in pairs) following these procedures:
    a. **Sequentially** (one sampler) - Rinse and fill containers in sets by parameter group/container type (i.e., fill TNUTL S1, then TNUTL S2, then do the same for each subsequent sample/container type).
    b. **Concurrently** (two samplers) - While standing side-by-side, each sampler takes a bottle from the same parameter group (i.e., sampler one takes TNUTL S1, sampler 2 takes TNUTL S2), and both samplers perform rinses and fill the containers in synchronized fashion.

5.2.2.3 Replicate Samples: Pump and Hose Sampling

If collecting duplicate pump and hose samples, use one of the following two methods to fill containers.

1. Place the identical split sample containers side by side (e.g., TNUTL S1 and TNUTL S2).
2. Rinse bottles according to normal pump and hose sampling procedures.

3. Rapidly and at a steady pace move the hose discharge back and forth across the tops of the containers until both containers are filled. Repeat the process for each required sample container set.

OR

1. Use a T or Y-fitting at the end of the discharge hose.
2. Rinse bottles according to normal pump and hose sampling procedures.
3. Fill both sample containers simultaneously. When filling, keep the attachment as level as possible to avoid filling one container before another.

Note: Collect bacterial duplicate samples side by side directly from the source.

5.3 QC Samples for Sediment Sampling

As with water sampling QC samples, sediment equipment blanks and replicates follow similar procedures as regular sediment samples and test for carryover contamination between sample sites and cleaning procedures, and variability introduced by collection and analysis.

5.3.1 Equipment Blanks for Sediment Samples

A minimum of one sediment equipment blank per day is required. If cleaning of field equipment occurs between sites sampled on the same day, one additional equipment blank is required to account for between-site carryover contamination.

To reduce the risk of carryover contamination and field cleaning, field staff are encouraged to carry enough equipment (e.g., pans, dredges) for each site on the sample run along with a spare set. Staff would then only need to collect an equipment blank at the first station prior to Flush or rinse sampling device with DI water following the same procedure (number of rinses, equivalent volume, and manner of rinsing) as when performing routine sediment sampling.

1. Place sample bottle labels with the **Blank/Dups code EB on the equipment blank sample** bottle to avoid confusing the bottle with regular samples collected at the site.
2. Run lab grade water through all the sampling equipment that contacts with sediment samples and collect the rinsate in a cleaned stainless-steel tray used to prepare sediment samples.
3. Transfer the rinsate from the tray to the labeled sediment container.
4. Upon returning from the field, enter the information into CEDS and be sure to **use the EB designation in the sample code field**.

5.3.2 Replicate Samples: Sediment Sampling

As with water samples, sediment samples must be collected at a rate of at least one split sample per 25 samples collected (4%).

1. Collect a sediment sample according to routine sediment sampling instructions (see **Section 4.6**), collecting enough volume of sediment to divide into two separate samples.
2. Homogenize the sample using a clean stainless-steel spoon or spatula.
3. Split the homogenized sample into two labeled sample jars.

5.4 QC Sample Acceptance Criteria

Blank Samples

If an equipment blank result is three times higher than the method detection limit, data collected by the sampler for that date and parameter are considered suspect and will be flagged in the database by the QA Coordinator. If on more than three occasions per year/per analyte equipment blanks come back unacceptable, the QA Coordinator will investigate and apply corrective actions as necessary.

Replicates

If replicate results vary by a difference greater than the acceptable ranges (listed in **Table 5-1** below), the data collected on the sample run for that particular date and analyte are considered suspect and will be flagged in the database by the QA Coordinator.

Parameter	Acceptable difference between replicates
Bacteria	≥ 0.6 log-transformed values
Turbidity	10%
Chlorophyll a	30%
TSS	30%
All other routine parameters	20%
Non-routine parameters	See WQM QAPP or project specific QAPP

Table 5-1. Acceptance criteria for field replicates by parameter.

6 CORRECTIVE ACTION PLAN

The Corrective Action Plan is a plan set in place to identify and respond to problems in sample collection, preservation, handling, and analysis.

For the Corrective Action Plan to work, all associated program personnel must report any suspected deficiencies in procedures or equipment. This is especially important for DEQ field and DCLS lab personnel.

The Corrective Action Request (CAR) form (**Appendix C**) is used to document the problem and steps taken for correction. CAR forms may originate in regions, central office, or DCLS. On the CAR form, the CAR originator shall:

- Identify the problem.
- List possible causes (if known).
- Note the date the problem was identified.
- Identify samples or field data that may be invalid as a result of the problem.
- Recommend corrective action if warranted.

CAR forms that originate in the region or central office are forwarded to the appropriate QA officer for review and recommendations. The QA officer forwards the form to the appropriate supervisor for review, recommendations, and a final decision on appropriate corrective action.

After resolution of the problem, the supervisor (e.g., project coordinator, team leader, or technical reviewer) provides copies of the completed CAR form to appropriate staff and the CO QA Officer. The supervisor is responsible for implementing the corrective action. The CO QA Officer may provide additional comments or recommendations.

DCLS contacts the DCLS Liaison with any known issues that may require corrective action. DCLS then forwards that information to the relevant QA officer to determine the final decision and implementation per section 3.1.4 of the WQM QAPP.

It is the responsibility of the originator to notify management and the CO QA Officer if the corrective action system is not operating effective. In this situation, the originator may elect to call or send a CAR form directly to the appropriate QA coordinator.

7 SAFETY

This section provides safety information specific to activities related to sampling of water and associated media. For general safety information, https://covgov.sharepoint.com/sites/DEQ-Health contains other useful safety resources.

- Boating Operations and Water Safety (BOWS) Policy
  - https://covgov.sharepoint.com/sites/DEQ-Health/SitePages/Boating-Safety.aspx
- Chemical Hygiene Plan
  - https://covgov.sharepoint.com/sites/DEQ-Health/SitePages/Resources.aspx
- Emergency Action Plan
  - https://covgov.sharepoint.com/sites/DEQ-Health/SitePages/Resources.aspx
- Safety Manual
  - https://covgov.sharepoint.com/sites/DEQ-Health/SitePages/Resources.aspx
- Traffic Control Plan
  - https://covgov.sharepoint.com/sites/DEQ-Health/SitePages/Resources.aspx

Note: Staff should review and be familiar with the above documents as the material presented below was designed to reinforce these policies.

7.1 BASIC SAFETY PREPARATION

Basic preparations should be routine before every sampling run. Per the agency Emergency Action Plan, each employee is responsible for maintaining and sharing their work calendars with their immediate supervisor. At a minimum, complete a trip plan for each field trip, and leave it at a designated location in the office. The plan may be in the form of a shared calendar, a whiteboard list/table, a logbook, or similar system. The trip plan should include the following information:

Trip plan

- List participants, including guests and observers, with emergency contact information.
- Itinerary including where and when sampling will occur, expected return date and time.
- For overnight trips, hotel information and contact phone numbers.
- Cell-phone numbers or radio frequencies.

General safety preparation guidelines

- Perform a pre-trip safety inspection of vehicles and gear.
- Be certified in Basic First Aid and CPR to provide emergency medical services.
- Whenever possible, crews shall consist of at least two staff, and work on-site shall be conducted in pairs.

- Have a cell phone, radio, or other emergency communication available when in the field.
- Carry basic safety equipment: first-aid kit, flashlight, boots, rain gear, and hand cleaner.
- Check the weather forecast before traveling to the site. While in the field, be aware of changing weather conditions and the potential for flash floods and severe weather.
- Be aware of potential hazards at a monitoring site. Examples include unsafe entry or exit locations, presence of unusual materials near the site or in the water, and similar hazards.
- Carry a packet of general safety information in each vehicle or boat.
    - Safety Data Sheets (SDS) for chemicals used at the site.
    - Basic first-aid manual.
    - Emergency phone numbers and radio frequencies.
    - Addresses and phone numbers of local emergency facilities (hospitals, police, and fire departments, etc.).

Table 7-1. General safety equipment checklist.

Yes	No	Safety Items
General Items		
		First-aid kit
		Flashlight and spare batteries
		Cell phone and/or marine radio
		Rain gear
		Hat, sunscreen, and sunglasses
		Drinking water or sports drinks
		Safety cones, ANSI Class 2 or 3 garments (for working on bridges, ROW)
		Toolbox with basic tools (for vehicles)
		Antibacterial soap or hand cleaner
		Acid spill kits (if carrying >100 ml of preservatives)
		SDS for preservatives
		Hand-held eyewash unit (with unexpired wash solution)
		Protective goggles appropriate for specific task
		Secondary container to carry preservatives, clearly labelled
		List of emergency phone numbers and office contacts
		Fire extinguisher (for vehicles, including boats)
Boating or Wading		
		Waders, hip boots, rubber knee boots (if electrofishing or wading)
		Personal flotation device (PFD) per team member

7.2 General Laboratory and Warehouse Safety

When working in the field preparation room or warehouse, keep the following in mind.

- Turn on and use the fume hood and wear appropriate personal protection equipment (goggles, apron, gloves, etc.) when pouring reagent grade chemicals into beakers or when preparing standards. **Section 7.3** contains additional information on handing reagents.
- When not in use, store hazardous materials in the appropriate chemical storage cabinet as listed in **Table 2-1** in **Section 2.6.1**. Never place incompatible materials in the same storage cabinet. (e.g., oxidizers with acids, safety flares with flammable liquids, etc.)
- Maintain sufficient clearance around storage cabinets, electrical panels, and exits to ensure safe access. Typically, this is at least three feet.
- Ensure emergency equipment such as fire extinguishers, eye wash and shower stations, and related items are charged or otherwise in good working order.
- When disposing of significant quantities of hazardous materials, use a certified hazardous waste contractor. To determine what constitutes a significant quantity for a particular hazardous material, consult the chemical hygiene plan and/or contact the regional chemical hygiene officer (see link below).

Note: Contact the regional or agency Chemical Hygiene Officer if there are questions about procedures. A contact list is available at https://covgov.sharepoint.com/sites/DEQ-Health/SitePages/Committee-Members.aspx.

Note: The chemical hygiene officer conducts a monthly inspection of regional office labs.

Yes	No	Safety Items
General Items		
		First-aid kit
		Spill kit
		Fire extinguisher
		Fire blanket
		Chemical storage cabinets, labeled, stored, and sorted properly
		Chemical storage inventory (SDS available)
		Eyewash station
		Shower station
		Fume hood
		Fume hood indicating powder or lab smoke test materials
Personal Protective Equipment (PPE)		
		Safety glasses/goggles
		Gloves
		Lab coats
		Apron

Table 7-2. Lab safety equipment checklist.

7.3 Reagent Chemical and Hazardous Material Safety

Ensure that Safety Data Sheets (SDS) are available for all chemicals in all locations where chemicals are used. These documents describe signs and symptoms of exposure, list first-aid procedures, and spill cleanups. An online inventory of SDS forms is available at https://covgov.sharepoint.com/:f:/r/sites/deqnet/Shared%20Documents/Health%20%26%20Saftey. Contact the regional Chemical Hygiene Officer if there are questions about chemical safety and handling. Below are some general guidelines for safe chemical handling:

- Secure all chemicals transported to and from the field using a secondary container, such as a cooler, that will resist and contain the material in the event of an accident or spill.
- If transporting large quantities (>100 ml) of chemicals to the field, carry a spill kit containing neutralizing or absorbing agents such as Amphomag™. Each region is equipped with sufficient spill cleanup materials for field use. Acids are the most common and dangerous chemicals carried into the field. A container of baking soda is an effective acid neutralizing agent.
- Label all chemical containers clearly. Include a handheld eyewash bottle (with unexpired wash solution) in a chemical-safety kit whenever chemicals are used in the field.
- If possible, use small dropper bottles or sample bottles prefilled with sufficient volume of preservative instead of transporting large containers of preservatives. Handling smaller volumes of chemicals lowers the risk of injury or damage if a spill occurs.
- Do not pipette or siphon by mouth. Always use mechanical pipettes or pipette bulbs, or siphon starters.

When transporting fuel, follow these guidelines:

- Ensure fuel is transported and stored in approved containers.
- Remove portable fuel tanks from the vehicle or boat before filling them with fuel. Touch the fuel container or gas tank with the spout to prevent sparks from static buildup.
- Do not fill portable fuel containers completely, leave headspace to allow for fuel expansion.
- Cap fuel containers and tanks tightly to prevent vapors from escaping. Inspect cap O-rings and gaskets at each filling and replace promptly if worn or damaged.
- Clean up fuel spills immediately and air out used rags before storing them. Store containers in a well-ventilated area away from the engine and passenger compartments.

7.3.1 General Safety Procedures for Handling Acids

Follow these guidelines while handling and working with acids:

- All acid fumes are harmful. When using any concentrated acids in a laboratory setting, use a laboratory fume hood and set the fume hood to exhaust the gas. Be sure the hood is set so the fumes are carried away from the technician. If possible, do not raise the fume hood sash above its optimal operational position.
- Concentrated acids will quickly react with organic and metal surfaces. Nitrile and acid grade gloves are better than latex at slowing absorption to the skin. Wearing a lab coat and chemical apron gives the person time to remove the garment before soaking onto the skin. Always wear chemical splash goggles when handling acids. A face shield along with goggles is ideal when handling large containers (1 gallon or greater) of chemicals.
- Know where the safety shower and eyewash stations are located. The regional Chemical Hygiene Officer can provide training on using the stations. If acid or any other chemical comes into contact with your eyes or your body, wash the affected area for at least 15 minutes. Pull back eyelids to allow water to wash away any foreign material splashed in the eye. Report all incidents to the regional Safety Officer and seek immediate medical attention.
- All acids react with water. When mixing acid with water, heat is created. Never rapidly mix acid with water or add water to concentrated acid as it could boil and splatter causing burns, break glassware, and chemical exposure.
- Do not discard high strength acids down the drain, as it will damage the pipes. Small quantities (<100 ml) of used acid can be neutralized by slowly pouring into a solution of water with sodium hydroxide or baking soda. If neutralizing acids, do so in the fume hood and check the pH of the solution. When the solution reaches a pH of ≥ 4 (using litmus paper to check) and bubbles stop forming from adding sodium hydroxide or baking soda, it can be flushed down the drain with tap water.
    - For disposing of large quantities (>100 ml) of concentrated acid, contact the regional Chemical Hygiene Officer to coordinate disposal.

7.4 Wading Safety

Follow these guidelines while wading:

- Do not attempt to wade in a stream where the depth multiplied by the velocity is greater than or equal to 10 ft^2/s. For example, a stream 2 ft. deep with a velocity of 5 fps or more can be dangerous (Lane and Fay 1997). In streams with slick surfaces like algae coated rocks, stream flow as low as 5 ft2/s can make wading hazardous.

- When wading in deep or fast flowing water, wear a Coast Guard–approved personal flotation device (PFD). Use of a PFD is encouraged when doing any type of wading as a stream may have depressions, holes, or loose footing, which may cause a fall.
- Wear hip boots or chest waders. Boots and waders protect against cold, contaminants, and underwater objects.
- Avoid hip boots with tight ankles and waders with tight-fitting tops. They are difficult to remove in an emergency. When using chest waders, it is best to wear a PFD as waders can pull someone underwater should they fill with water.
- Be aware of surrounding conditions. Watch for floating debris, areas of quicksand/muck, and deep pools. Watch the stream stage, especially if there is a chance it could raise rapidly.

7.5 Bridge Safety

Staff often collect samples from bridges and along roadways. Staff should take precautions such as using agency approved reflective vests, four-way flashers or amber lights on vehicles, and other traffic warning devices as necessary. Staff must wear a PFD at sites that necessitate climbing over a bridge railing to collect a sample.

The agency has developed a traffic control plan to help staff in taking proper precautions when working along roadways including when to use traffic control signs. This traffic control plan is available at https://covgov.sharepoint.com/sites/DEQ-Health/SitePages/Resources.aspx.

7.5.1 Selecting Bridges for Sampling

When selecting possible bridge sample sites, consider the following:

- Does the bridge have a shoulder/sidewalk to sample from? If not, is there sufficient room to perform sampling while not obstructing traffic?
- Will traffic volume/speed allow for safe access?
- Are there sharp curves at one or both ends of the sampling area? If there is a sharp curve, will drivers have enough time to respond and slow down?
- Can an agency vehicle park and not obstruct traffic? If sampling is likely to take more than 15 minutes, is there enough space to park the vehicle so it can act as a buffer to protect the sampler from a crash or place caution signs?
- If a bridge has a posted sign stating no fishing, consider a new site as it may be too hazardous to sample due to traffic and bridge width.

7.5.2 Vehicle Parking Procedures

- Park in a location away from sharp curves to allow time for drivers to slow down.
- Pull completely off the roadway and onto the shoulder. Leave sufficient room to exit and enter the vehicle without interfering with traffic flow.
- If parked on the shoulder of a road, turn on the vehicle hazard signal or amber lights.
- If an agency vehicle or staff will be on the road shoulder for more than 15 minutes, use the traffic control plan at https://covgov.sharepoint.com/sites/DEQ-Health/SitePages/Resources.aspx.
- Set up sampling away from the vehicle to allow observing of traffic from both directions.

7.6 Boat Safety

Staff must provide their immediate supervisor a complete float plan, including a cell phone number or STARS radio frequency. The complete information can be conveyed via email or by using the example in **Figure 7-1**.

Note: It is recommended to use a checklist to inspect boats, trailers, and towing vehicles. **Table 7-4** has an example checklist.

Follow these guidelines when operating or working from a boat:

- Staff shall work in pairs when conducting operations from any watercraft.
- While functioning in an official capacity, staff (and DEQ-sponsored guests) shall wear approved PFD while aboard boats on any body of water.
- Boat operators must have valid certification through a DWR approved boat safety course (https://dwr.virginia.gov/boating/education/requirement/steps-to-requirement/). All staff assigned to perform work on a boat must successfully complete a course in basic boat operations and safety.
- Know the capacity of the boat. Look for a capacity plate near the operator's position or on the transom. This plate indicates the maximum weight capacity (persons and gear) or the maximum number of persons the boat can safely carry.
- On outboard powerboats, check the capacity plate for the maximum horsepower rating; do not use motors that exceed the rating.
- While a boat is underway, remain seated in designated areas. When moving to another part of the boat, use secure handholds to prevent falling.
- Use caution when refueling a boat. Check the entire fuel system for leaks and tighten connections frequently. Turn off the engine and all electrical equipment before adding fuel to the tanks. If the boat is equipped with a power ventilation system, turn it on for

at least four minutes before starting the engine to clear gasoline vapors from the bilge. Never smoke or strike a match while fueling or near a fueling dock.

- Ensure the boat is in good operating condition and full of gas before taking it out on the water. The checklist in **Table 7-4** may be used to ensure the boat is ready for use.
- Check weather conditions before departure. If a storm develops while on the water, head for shore. Always carry a marine radio or cell phone.
- Unless electrofishing is being performed, do not wear waders and hip boots in a boat, as they are a safety hazard if the boat should tip, or a person is thrown overboard.
- Report any collision, accident, or other incident that results in death or injury to any person or property damage involving a state vehicle, to the state police and the **Virginia Management Control Center (VMCC) at 1-866-857-6866**. **If emergency services are needed, call 911 or the state police before contacting VMCC**. Accident reporting materials are found in the glove box of all fleet automobiles. If an incident involving injury, death, or property damage greater than $500 while operating a boat, contact Department of Wildlife Resources (DWR).
- The driver involved in an accident MUST contact the VMCC. A State Police officer must investigate all accidents involving a state vehicle, regardless of the amount of damage. The employee involved in an accident must complete all accident forms and notify their supervisor, HRO, DEQ's Office of General Service, and the Commonwealth's insurance company.

Table 7-3. State Police Division Headquarters contact information.

Location	Toll Free Telephone	Local Telephone
Division 1- Richmond	1-800-552-9965	804-553-3444
Division 2- Culpeper	1-800-572-2260	540-829-7401
Division 3- Appomattox	1-800-552-0962	434-352-7128
Division 4- Wytheville	1-800-542-8716	276-228-3131
Division 5- Chesapeake	1-800-582-8350	757-727-7288
Division 6- Salem	1-800-542-5959	540-375-9500
Division 7- Fairfax	1-800-572-4510	703-803-2660

Figure 7-1. Boat Safety Float Plan form.

Virginia Department of Environmental Quality Boat Safety Float Plan

1. Region: _____ Date: _____ Purpose of Trip: _____
2. Name of Boat _____
3. Description of Boat: _____
   Type: _____ Color: _____ Trim: _____
   Registration Number: _____ Length: _____
   Name: _____ Make: _____ Other: _____
4. Engine Type: _____ Horsepower: _____
   Number of Engines: _____ Fuel Capacity: _____
5. Safety Equipment: ☐ PFDs ☐ Paddles ☐ Anchor
   ☐ Smoke Signals ☐ Drinking Water ☐ Food
   ☐ ANSI Safety Garments ☐ Other: _____
6. Radio: ☐ Yes / ☐ No Type: _____ Frequency: _____
   Cell Phone: ( ) -
7. Tow Vehicle License _____ State _____ ☐ Yes / ☐ No
   Make and Model of _____ Color: _____
   Trailer License: _____ Where _____
8. Persons on Board:

Name:	Age:	Address & Telephone Number:

9. Trip Leaving at: _____ ☐ AM/ ☐ PM Leaving From: _____
   Returning at: _____ ☐ AM/ ☐ PM If not returned _____ ☐ AM/ ☐ PM
   Call USCG: ( ) - Police: ( ) -

Table 7-4. Boating safety checklist.

TRAILER	YES	NO	COMMENTS:
Sizes of coupler and ball hitch match			
Tire pressures are at the maximum noted on the rim			
Tire treads are at least $^{3}/_{32}$"			
Tires are in good condition: Show no bulging, cracking, or tread separation			
Brake lights and turn signals function			
Safety chains are attached in an *X* under the coupling			
All boat straps are tight			
License plate is present and firmly attached			
Trailer stand is secure			
BOAT	**YES**	**NO**	**COMMENTS:**
Boat plugs are present			
Battery is charged			
Gas tank is full			
Anchor and rope are aboard			
Navigation lights operational: Lights are appropriate for boat size; no other lights that may be mistaken for navigation lights are exhibited			
Emergency paddles are aboard			
First-aid kit is available			
First extinguisher is charged and accessible			
Flashlight with working batteries is available			
An air horn or whistle is aboard			
Rain gear is aboard			
Personal flotation devices are available for every person on board			
The emergency kill switch for the boat motor is functioning			
Radio or cell phone is available and functioning			

7.6.1 Personal Floatation Devices

Approximately 90 percent of all boating fatalities are from drowning. Virtually all drowning victims are not wearing or used inadequate personal flotation devices (PFDs). All boats must be equipped with life jackets or PFDs approved by the U. S. Coast Guard (**Table 7-5**). The quantity and type depend on the length of the boat and the number of persons aboard.

Follow these guidelines:

- PFDs must be in good condition. Regularly test for buoyancy, weakened material, or insecure snaps or zippers. Dispose and replace damaged units.
- For inflatable PFDs, replace spent inflation cartridges and tag spent inflation cartridges to indicate they are out of service.
- Read the PFD label to ensure that it is the right size for a person's weight and chest size.
- Keep all PFDs readily accessible.
- All personnel wear PFDs when in boats and while wading in deep or fast flowing water.
- For boats 16 feet long or longer, keep an extra Type IV PFD, in addition to those required for passengers, immediately available.
- Select PFDs that are appropriate for the area being sampled.

Table 7-5. Types of Personal Flotation Devices

Type	Conditions of Use	Positives	Negatives
I	Offshore work or remote areas where rescue may take a while.	Excellent for flotation and will turn most unconscious persons face up in the water.	None
II	Near-shore vests.	Good for calm waters and fast rescues.	Lacks the capacity to turn wearers face up.
III*	Vests or flotation aids.	Good for calm waters and fast rescues.	Will not turn an unconscious person face up and should not be used in rough waters.
IV	Throwable devices, cushions, or buoy rings.	Designed to be thrown to someone in trouble.	Not good for long hours in the water, rough water, non-swimmers, or the unconscious.
V*	Type V, or special-use devices, are designed for specific activities. They are only appropriate for use in accordance with the specific instructions on the label of the device.		

*Some Type III and Type V PFDs are designed to inflate when the wearer enters the water. This type must be worn when under way to be acceptable.

7.7 Fish Collection Safety

7.7.1 Electrofishing

Electrofishing is hazardous work as electrocution of staff can occur. Use extreme caution and never electrofish alone. Staff must be made aware of the hazards and safety requirements.

Below is a list of general safety practices. More details are available in section 4.2 of the QA/QC Project Plan for the Fish Tissue and Sediment Monitoring Program at: https://www.deq.virginia.gov/home/showpublisheddocument/6996/637520993335570000

- Be familiar with and inspect all equipment before each use. Correct any equipment problems immediately. Tag any equipment waiting for repair as “Out of Service”.
- Evaluate the equipment annually during a preventive maintenance inspection.
- Ensure no wiring splices are in the equipment. If connections are necessary, ensure the connector is rated the same or greater than that of the wire. All junction boxes must be weatherproof or rain tight. Junction boxes with switches must be weatherproof.
- Only use gel type batteries for backpack electrofishing units.
- Ensure hip and shoulder straps are of the quick-release type, not damaged, and are long enough for the person who will use them.
- Ensure that the backpack unit has a functional trip switch that breaks the circuit if the user falls. The switch must require a manual reset before reestablishing the circuit.
- Have at least three people when electrofishing so one person can administer CPR while the other seeks medical assistance. At least two members of the crew must have valid certifications in CPR and first aid.
- Wear waders and rubber gloves rated at or above the maximum voltage that the generating unit can produce. Breathable waders are typically not appropriate for electrofishing.
- When electrofishing by boat, all personnel must wear a Coast Guard–approved PFD. Hip or chest waders are required when electrofishing by boat.
- Inspect all nets and poles to ensure they are made of nonconductive material and are long enough to keep the user's hands out of the water.

7.7.2 Handling Fish

When electrofishing, do not pull fish out of the water with bare hands while the generator is on. Use nonconductive nets or turn off the generator before reaching into the water. Take care when working with fish that have barbs like catfish. Barbs are usually located on the pectoral or dorsal fins.

7.8 CONTAMINATED WATER

Always assume waterways are contaminated with pathogens or hazardous chemicals. Pathogens can be found in pristine looking waterways due to untreated sewage, storm water runoff, and direct deposit. Never drink untreated water. Wearing nitrile or similar gloves is recommended. If suspected sewer overflows or unusual water colors or odors are observed, note it on the sample tags to alert the laboratory. Wash hands with soap and water or use hand cleaner after sampling to reduce infection risk.

7.9 WEATHER

Always check weather forecasts for the sampling area before going out into the field. While in the field, stay alert to changing conditions like developing clouds, wind shifts, and graying skies.

If on a boat when weather conditions are deteriorating, immediately head for shore. When encountering rough water, head the bow into the waves at a 45° angle and reduce speed. Seat passengers in the bottom of the boat, as close to the center line as possible.

Leave creeks and rivers to avoid flash floods. Avoid using low-water crossings due to uncertain road integrity. Floating debris may damage the vehicle or even push it from the roadway.

7.9.1 Lightning Safety

When lightning or thunder is observed, seek shelter in an enclosed vehicle or a substantial building. If on a boat, head to the nearest dock and take shelter. Avoid high ground, bodies of water, trees, or open spaces. Unsafe shelters include canopies, small picnic or rain shelters. Do not exit the vehicle or shelter until 30 minutes after the last observed lightning or thunder.

7.9.2 Cold Emergencies (Hypothermia)

Hypothermia is a lowered body temperature due to cold exposure. It is intensified by wet clothes, wind, hunger, and exhaustion and can occur even when air temperatures are above 16°C (60°F).

7.9.2.1 Hypothermia Warning Signs

Symptoms of hypothermia include uncontrollable fits of shivering, incoherence, listlessness, fumbling hands, frequent stumbling, drowsiness, and the inability to get up after resting.

7.9.2.2 Hypothermia Treatment

Place the victim in a dry, warm place. Take the following temporary measures until medical help is available: Replace wet clothes with dry ones. Warm the body slowly. Give warm, nonalcoholic drinks if the victim is conscious. Seek medical attention immediately.

7.9.2.3 Hypothermia Prevention

The best way to prevent hypothermia is to stay warm and dry.

- Put on rain gear before it rains.
- Dress in layers and add more before getting cold.
- Find shelter before conditions become severe.
- During colder weather, carry a complete change of dry clothes.

7.9.3 Heat Emergencies (Heat Stress, Hyperthermia)

Hyperthermia is an increased body temperature due to heat exposure. It is intensified by physical exertion, clothing (e.g., waders), humidity, no breeze, high air temperature, and dehydration.

7.9.3.1 Hyperthermia Warning Signs

Symptoms of hyperthermia include, headache, unsteadiness, dizziness, nausea, cool pale skin (heat exhaustion), hot and red skin (heat stroke), rapid pulse, muscle pain, and spasms.

7.9.3.2 Hyperthermia Treatment

Treatment consists of providing plenty of fluids and cooling down the victim. **Do not give salt tablets**. Heat stroke is life threatening. Quickly cool down heat stroke victims and watch for signs of shock. Call 911 or, if in an isolated area, transport the victim to a hospital immediately.

7.9.3.3 Hyperthermia Prevention

The best way to prevent heat emergencies is to keep cool and hydrated.

1. Hydrate before working; every 15 minutes, find shade to take frequent hydrating breaks.
2. Do not drink sodas or caffeinated drinks as they will increase dehydration.
3. Wear lightweight, light-colored clothing, wide-brimmed hat; cooling towels can help.
4. Schedule the most strenuous activities for the early morning or late afternoon.

7.10 Hazardous Plants and Animals

The following tables summarize specific hazardous Virginia organisms and how to minimize exposure.

Table 7-6. Harmful plants.

Plant	Characteristics, Habitat, Treatment and Prevention
Poison ivy  **Poison oak**  **Poison sumac** 	**Characteristics:** ***Poison ivy*** has pointed leaves in clusters of three. Climbing vines with fuzzy looking aerial roots or shrub like plant. Color varies from green in spring and summer to red and yellow in the fall. ***Poison oak*** is very similar to ivy in having three leaves, seasonal colors. Poison oak is typically shrub-like but can be vine-like. The leaves have a vague oak leaf appearance. ***Poison sumac*** is either a small shrub or tree. Leaves consist of 7-13 leaflets in pairs with a single leaflet at the end. Leaf colors change seasonally (green in summer, orange or red in spring and fall). Stems of the plants can also cause skin reactions and the urushiol sap can remain on unwashed clothing and equipment for an extended time. **Habitat**: Poison Ivy and Oak are found statewide and frequently in forested areas. Poison Sumac found in swampy or boggy waterbodies. **Treatment**: Rinse the skin area with plenty of cold water as soon as possible. A little water will only spread the poison. Use anti-itch cream. Some Urushiol cleansers can be used up to 8 hours after exposure. Persons sensitive to urushiol may require medical attention. **Do not** use hot water or soap as it will increase the effects of poison ivy. **Prevention:** Pre-exposure lotion provides a barrier against the urushiol oil. Wear gloves and long sleeve clothing and avoid direct contact.

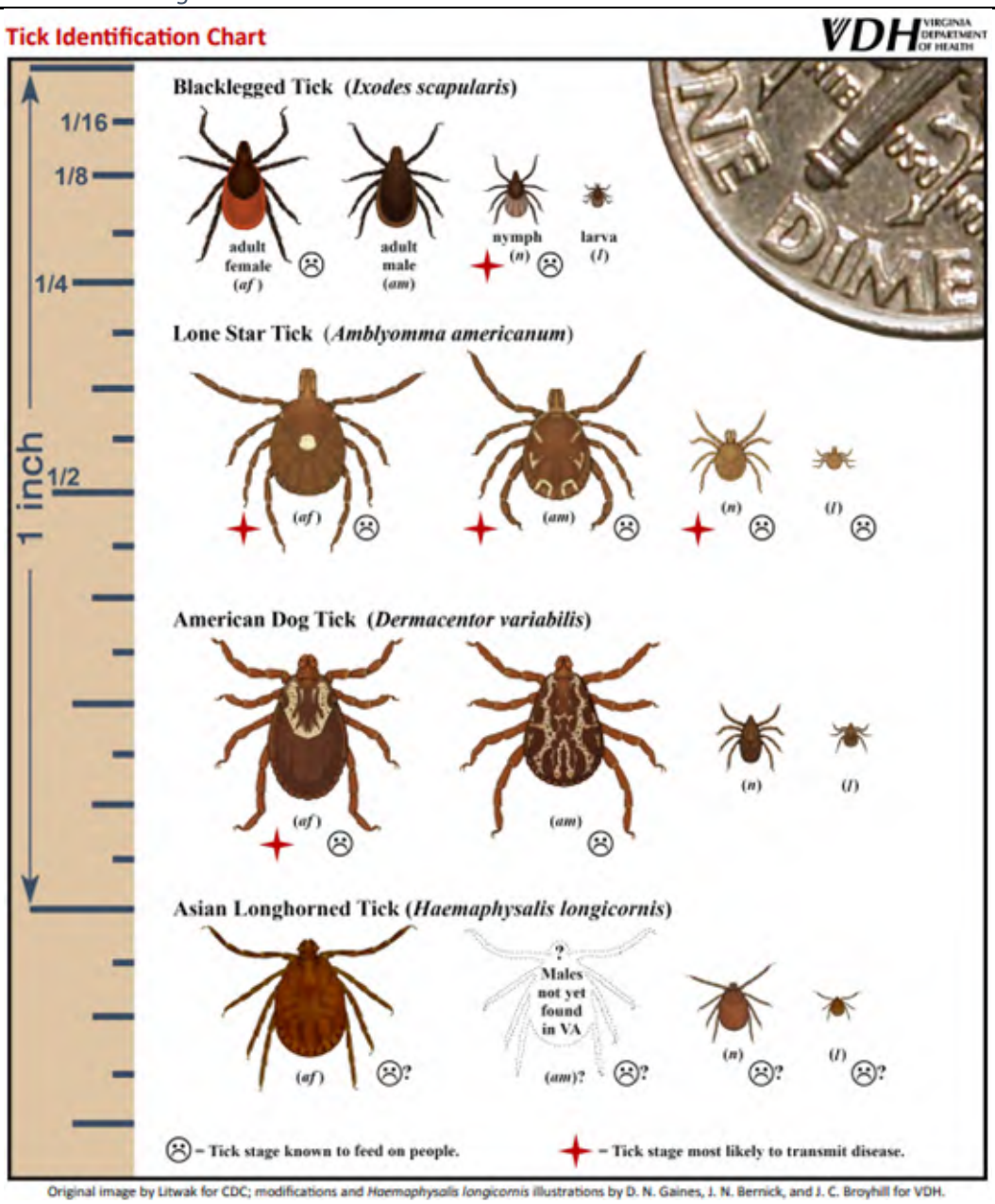
Table 7-7. Stinging insects.

Animal	Characteristics, Habitat, Treatment and Prevention
Bees and wasps  	**Characteristics: Bees** vary in size from 2 mm to 4 cm long. **Wasps** vary from minute to 5 cm long. Adults have a narrow waist between the first and second abdominal segments. **Habitat:** Vary from ground nests to trees and human-built structures. **Treatment:** Scrape off the stinger with a knife or flat object (e.g., a credit card). Wash area with soap and water. Apply cold pack, sting ointment, or mixture of water and baking soda to relieve the sting and swelling. Field team members that are allergic to insect bites or stings should inform the team and carry an emergency sting kit. Symptoms of an allergic reaction include excessive pain, swelling of the throat, severe redness, or discoloration in the area of the sting, itching, hives, decreased consciousness, or difficult or noisy breathing. **Prevention:** Avoid beehives and wasp nests. Limit use of scented personal care products and fruits. Avoid swatting or killing bees or wasps as this may encourage a swam attack

Table 7-8. Venomous spiders.

Animal	Characteristics, Habitat, Treatment and Prevention
Black widow spider 	**Characteristics:** Female (only one that bites) is black with almost spherical abdomen, with a red hourglass or two transverse red mark on the underside of abdomen **Habitat:** Statewide- Inhabits fallen branches and under objects. **Treatment:** If bitten, seek medical attention immediately. **Prevention:** Take care when reaching into small, dark spaces.
Brown recluse spider 	**Characteristics:** Orange-yellow thorax with dark violin pattern. Bases of legs orange-yellow, rest of legs grayish to dark brown. Abdomen grayish to dark brown. Very rare in Virginia. **Habitat:** Prefers dark spaces. Found outdoors in sheltered corners, among loose debris, indoors on the floor and behind furniture. **Treatment:** If bitten, seek medical attention immediately. **Prevention:** Take care when reaching into small dark spaces.

Table 7-9. Illness-causing ticks.



Characteristics: Small round to teardrop shaped body, usually less than 3 mm (< $^{1}/_{8}$ in) long. Clamp to hosts using a dart-like anchor just below the mouth.

Habitat: Found in wooded areas and tall grass.

Treatment: Remove with tweezers. Wash and disinfect bite area. Report all tick bites to regional Safety Officer.

Prevention: Wear long pants and tuck into socks and use DEET insect repellent Look for ticks during and after field work.

Table 7-10. Venomous snakes of Virginia.

Animal	Characteristics, Habitat, Treatment and Prevention
Northern Cottonmouth (Water moccasin) 	**Characteristics:** A dark, heavy-bodied water snake. Broad-based head noticeably wider than neck. Olive, brown, or black. Top of head is flat, eyes not visible from directly above as in other harmless water snakes. Unlike other water snakes, it swims with head well out of water. When disturbed, tends to stand its ground, or moves to attack, exposing the light cottony lining of its mouth. **Bite can be fatal.** **Habitat:** Rarely found far from water. Most active at night. Present in southeast Virginia in lowland swamps, lakes, rivers, bayheads, irrigation ditches, and canals.
Eastern Copperhead 	**Characteristics:** Stout body, copper, orange, or pink tinged with bold chestnut or reddish-brown cross bands narrowing in the middle of the back. Top of head unmarked. **Bite is painful but rarely fatal**. **Habitat:** Found statewide in wooded hillsides with rock outcrops above streams or ponds, edges of swamps and periodically flooded coastal plains. Seen basking during fall and winter months, but more nocturnal during warm weather. Favorite warm weather habitats include stone walls, piles of debris, rotting logs, and large flat stones near streams.
Timber Rattlesnake 	**Characteristics:** Heavy-bodied with head distinctly wider than the neck. Most have blotches or cross band patterns on the back. Rattlesnakes have a distinctive rattle on the tail but may not sound rattle prior to striking. **Bite can be fatal.** **Habitat:** Found mostly in the mountains of Virginia and sparsely vegetated rocky foothills. Can deliver fatal bites. When disturbed, normally stands its ground, lifting its head well above the coils and may sound a buzzing or rattle warning.
Treatment and Prevention for all snake encounters: **Treatment:** If bitten, reassure and try to calm the victim. Treat for shock. Keep victim lying down; elevate feet 10 to 12 inches. Seek medical attention as soon as possible. **Do not:** Cut or suck the bite area, apply ice or a tourniquet, or leave victim unattended. **Prevention**: Do not disturb. Best defense is to avoid snakes whenever possible. Most snakes will go the other way unless unusually agitated or disturbed. Take care when electrofishing and seining near logjams, fallen trees, and undercut banks. If the snake is not retreating, slowly back away from the snake.	

APPENDIX A

MULTIPROBE MAINTENANCE AND CALIBRATION LOG SHEETS

Multiprobe Maintenance Log		**Sonde Model:**				**S/N:**		
Year:		Date/Initial						
DO (Optical)	**Clean membrane** As needed when dirty							
	Replacing Membrane Yearly or when needed							
pH	**Clean pH sensor** As needed due to slow readings or dirty bulb							
	Refill reference junction/ replace Teflon cap (In-Situ and Hydrolab only) Erratic pH readings, calibration fails, or Teflon cap is dark in color							
	Change pH Sensor Yearly or sooner (**YSI**). Erratic pH or calibration fails, buffer mV readings outside range							
Other Sensors	**Clean conductivity Sensor** As needed when dirty							
	Clean depth sensor As needed when dirty							
	Clean temperature sensor As needed when dirty							
	Sensor Wipers As needed when dirty/damaged							
	Other (list below)							
	Other (list below)							
Storage	**Long term storage** (Longer than one month storage)							

Comments:

Multiprobe Cal Log Sheet **Sonde Make/Model:** **Sonde S/N:** **Region:**

					DO			Specific Conductivity		pH		
Cal Type	**Date/Time**	**Initial and Run ID**	**Temp C**	**BP (mmHg)**	**Chart DO**	**Meter DO**	**Cal DO**	**Cond Std. (µS/cm)**	**Cond Init/Cal**	**pH 7 Init/Cal**	**pH 4 or 10 Init/Cal**	**3rd pH check Init/Cal**
Pre												
Post												
Comments:					**DO QA:**			**Cond QA:**		**pH QA:**		
Pre												
Post												
Comments:					**DO QA:**			**Cond QA**		**pH QA:**		
Pre												
Post												
Comments:					**DO QA:**			**Cond QA:**		**pH QA:**		
Pre												
Post												
Comments:					**DO QA:**			**Cond QA:**		**pH QA:**		
Pre												
Post												
Comments:					**DO QA:**			**Cond QA:**		**pH QA:**		

DO QA: YSI ODO Gain 0.75 to 1.25, **Cond QA: YSI Cell Constant** 4.55 to 5.45 **pH QA:** pH 7: -50 to 50 mV, pH 4: 130 to 230 mV, pH10: -230 to -130 mV

APPENDIX B

THEORETICAL DISSOLVED OXYGEN CHART

How to Calculate Dissolved Oxygen Saturation Values

Proper calibration of Dissolved Oxygen (DO) probes is important to collect accurate data. Because oxygen solubility in water decreases with temperature and increases with barometric pressure, an easy way to see if a probe is calibrated correctly is to compare the probe's reading in water-saturated air against the DO saturation value for your temperature and pressure. This is the maximum possible concentration of DO in equilibrium with air at a given temperature and barometric pressure.

Note: Salinity also affects DO potential, by reducing the solubility of oxygen, so this guide is applicable only for freshwater measurements.

DO Saturation Concentration Based on Temperature at 1 Atmosphere Pressure

The top table on the attached chart allows users to find the DO saturation concentration based on temperature at a pressure of 1 atmosphere (atm; 760 mmHg). The row and column headings of the table corresponds to the temperature that the probe is reporting (Row headings = temperature whole numbers, column headings = temperature tenths). The intersection of the two axes displays the DO saturation concentration at 1 atm for that temperature. Write this number down to start calculating the DO saturation level for your temperature and pressure.

Correction Factor for Barometric Pressure

Barometric pressure measures how much atmosphere is pressing down on a surface. Weather systems and elevation above (or below) sea level can change this value. The bottom table of the attached chart will compensate for these changes in pressure. Dissolved oxygen probes normally show pressure in millimeters of mercury (**mmHg**) or millibars (**mbar**).

Having a barometer on hand is a good way to get pressure data. A weather station can also provide this information. Websites such as www.wunderground.com are useful to find nearby stations. Please note that most barometers and weather stations report pressure in inches of mercury (**inHg**).

Using Weather Station Barometric Pressure Readings

Weather stations standardize barometric pressure readings to make it appear as if the station were at sea level. To calculate the actual atmospheric pressure at the station, reduce the station-reported barometric pressure by 1.07 inHg per 1,000 feet in elevation of the weather station. This final value is known as **absolute barometric pressure (ABP)**.

Which can also be computed as:

$$ABP\ inHg = Reported\ Pressure\ inHg - \left(\frac{1.07\ inHg}{1000\ ft\ elev.} \times Station\ Elev.ft\right)$$

Example: Find the absolute barometric pressure of a station located 222 feet above sea level that reported 30.12 inHg.

$$ABP\ inHg = 30.12\ inHg - \left(\frac{1.07\ inHg}{1000\ ft\ elev.\Big/_{222\ ft\ elev.}}\right) = 30.12 - \left(\frac{1.07}{4.50}\right) = 30.12 - 0.24$$

$$= \mathbf{29.88\ inHg\ ABP}$$

After finding the ABP for your location, use the bottom table to find the proper correction factor to use. The chart includes mmHg and mbar to determine the pressure correction factor using different types of barometer readouts. To convert inHg to mmHg, multiply inHg by 25.4. Thus 1 atm = 29.92 inHg x 25.4 mm/in = 760 mmHg.

Example: For a barometric pressure of 730 mmHg you would use a correction factor of 0.96 (second column, fourth row down).

DO Saturation Calculation

To find the DO saturation concentration, use the following formula.

$$\boldsymbol{DO\ saturation}\ (\boldsymbol{mg/L})$$
$$= (DO\ level\ based\ on\ temperature)\ x\ (barometric\ pressure\ correction\ factor)$$

Example: If a probe had a temperature of 18.4 C and the barometric pressure was 730 mmHg, the theoretical DO value would be 9.00 mg/L (9.37 mg/L x 0.96 correction factor).

Dissolved Oxygen Calibration Sheet

Directions: Find the dissolved O2 concentration for your water temperature (top chart), then multiply by the pressure correction factor for your local pressure (bottom chart) to obtain the DO saturation concentration in water in equilibrium with air.

Temp in °C	O_2 concentrations in mg/l									
	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
0	**14.59**	**14.55**	**14.51**	**14.46**	**14.42**	**14.38**	**14.34**	**14.30**	**14.26**	**14.22**
1	**14.18**	**14.15**	**14.11**	**14.07**	**14.03**	**13.99**	**13.95**	**13.91**	**13.88**	**13.84**
2	**13.80**	**13.76**	**13.72**	**13.69**	**13.65**	**13.61**	**13.58**	**13.54**	**13.50**	**13.47**
3	**13.43**	**13.40**	**13.36**	**13.32**	**13.29**	**13.25**	**13.22**	**13.18**	**13.15**	**13.12**
4	**13.08**	**13.05**	**13.01**	**12.98**	**12.94**	**12.91**	**12.88**	**12.84**	**12.81**	**12.78**
5	**12.75**	**12.71**	**12.68**	**12.65**	**12.61**	**12.58**	**12.55**	**12.52**	**12.48**	**12.45**
6	**12.42**	**12.39**	**12.36**	**12.32**	**12.29**	**12.26**	**12.23**	**12.20**	**12.17**	**12.14**
7	**12.11**	**12.08**	**12.05**	**12.02**	**11.99**	**11.96**	**11.93**	**11.90**	**11.87**	**11.84**
8	**11.81**	**11.78**	**11.76**	**11.72**	**11.69**	**11.67**	**11.64**	**11.61**	**11.58**	**11.55**
9	**11.53**	**11.50**	**11.47**	**11.44**	**11.42**	**11.39**	**11.36**	**11.33**	**11.31**	**11.28**
10	**11.25**	**11.23**	**11.20**	**11.18**	**11.15**	**11.12**	**11.10**	**11.07**	**11.05**	**11.02**
11	**10.99**	**10.97**	**10.94**	**10.92**	**10.89**	**10.87**	**10.84**	**10.82**	**10.79**	**10.77**
12	**10.75**	**10.72**	**10.70**	**10.67**	**10.65**	**10.63**	**10.60**	**10.58**	**10.55**	**10.53**
13	**10.51**	**10.48**	**10.46**	**10.44**	**10.41**	**10.39**	**10.37**	**10.35**	**10.32**	**10.30**
14	**10.28**	**10.26**	**10.23**	**10.21**	**10.19**	**10.17**	**10.15**	**10.12**	**10.10**	**10.08**
15	**10.06**	**10.04**	**10.02**	**9.99**	**9.97**	**9.95**	**9.93**	**9.91**	**9.89**	**9.87**
16	**9.85**	**9.83**	**9.81**	**9.79**	**9.76**	**9.74**	**9.72**	**9.70**	**9.68**	**9.66**
17	**9.64**	**9.62**	**9.60**	**9.58**	**9.56**	**9.54**	**9.53**	**9.51**	**9.49**	**9.47**
18	**9.45**	**9.43**	**9.41**	**9.39**	**9.37**	**9.35**	**9.33**	**9.31**	**9.30**	**9.28**
19	**9.26**	**9.24**	**9.22**	**9.20**	**9.19**	**9.17**	**9.15**	**9.13**	**9.11**	**9.09**
20	**9.08**	**9.06**	**9.04**	**9.02**	**9.01**	**8.99**	**8.97**	**8.95**	**8.94**	**8.92**
21	**8.90**	**8.88**	**8.87**	**8.85**	**8.83**	**8.82**	**8.80**	**8.78**	**8.76**	**8.75**
22	**8.73**	**8.71**	**8.70**	**8.68**	**8.66**	**8.65**	**8.63**	**8.62**	**8.60**	**8.58**
23	**8.57**	**8.55**	**8.53**	**8.52**	**8.50**	**8.49**	**8.47**	**8.46**	**8.44**	**8.42**
24	**8.41**	**8.39**	**8.38**	**8.36**	**8.35**	**8.33**	**8.32**	**8.30**	**8.28**	**8.27**
25	**8.25**	**8.24**	**8.22**	**8.21**	**8.19**	**8.18**	**8.16**	**8.15**	**8.14**	**8.12**
26	**8.11**	**8.09**	**8.08**	**8.06**	**8.05**	**8.03**	**8.02**	**8.00**	**7.99**	**7.98**
27	**7.96**	**7.95**	**7.93**	**7.92**	**7.90**	**7.89**	**7.88**	**7.86**	**7.85**	**7.83**
28	**7.82**	**7.81**	**7.79**	**7.78**	**7.77**	**7.75**	**7.74**	**7.73**	**7.71**	**7.70**
29	**7.69**	**7.67**	**7.66**	**7.65**	**7.63**	**7.62**	**7.61**	**7.59**	**7.58**	**7.57**
30	**7.55**	**7.54**	**7.53**	**7.51**	**7.50**	**7.49**	**7.48**	**7.46**	**7.45**	**7.44**

Barometric Pressure Correction Factor:

Units	Pressure	Correction	Pressure	Correction	Pressure	Correction	Pressure	Correction
mmHg mbar	775 – 771 1033 – 1028	**1.020**	745 – 741 994 – 988	**0.980**	715 – 711 954 – 948	**0.940**	685 – 681 914 – 908	**0.900**
mmHg mbar	770 – 766 1027 – 1021	**1.014**	740 – 736 987 – 981	**0.973**	710 – 706 947 – 941	**0.934**	680 – 676 907 – 901	**0.893**
mmHg mbar	765 – 761 1020 – 1015	**1.007**	735 – 731 980 – 975	**0.967**	705 – 701 940 – 935	**0.927**	675 – 671 900 – 895	**0.887**
mmHg mbar	760 – 756 1014 – 1008	**1.000**	730 – 726 974 – 968	**0.960**	700 – 696 934 – 928	**0.920**	670 – 666 894 – 888	**0.880**
mmHg mbar	755 – 751 1007 – 1001	**0.993**	725 – 721 967 – 961	**0.953**	695 – 691 927 – 921	**0.914**	665 – 661 887 – 881	**0.874**
mmHg mbar	750 – 746 1000 – 995	**0.987**	720 – 716 960 – 955	**0.947**	690 – 686 920 – 915	**0.907**	660 – 656 880 – 875	**0.867**

APPENDIX C

CORRECTIVE ACTION REQUEST FORM

Corrective Action Request Form

Section I: *To be completed by originator.*

Submitted by: _____ Date: _____

A. Nature of Problem:

B. Possible Cause:

C. Date of Problem Identified: _____

D. Samples That May Be Invalid:

E. Recommended Corrective Action (Optional):

Continued on next page

Corrective Action Request Form- *continued*

Section II: *To be completed by program manager.*

Name: _____ Date: _____

A. Recommended Corrective Action:

B. Follow Up Action Required:

C. Implementation Will Begin On:

Section III: *To be completed by QA Officer.*

Name: _____ Date: _____

A. Recommended Corrective Action:

B. Follow Up Action Required:

C. Implementation Will Begin On:

APPENDIX D

ENTERING QA/QC INTO CEDS

Setting up an Ambient Watershed QA/QC Station into CEDS

A QA/QC run can be developed that can be merged with a desired station in the run screen. A QA/QC run needs to have the correct parameter group codes for the station you are merging it with; separate QA/QC runs can be set up for the typical parameter group codes that are collected for each program (e.g. an AW QA run, TR QA run, etc.)

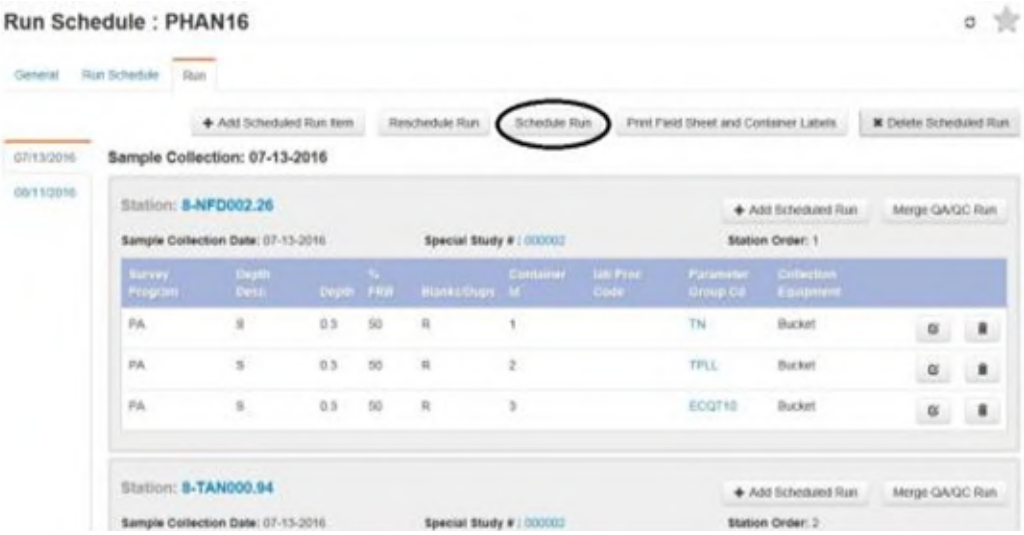
1. **Begin by selecting Run Schedules using the search button from the Home screen.**

2. **Select "Create Run Schedule".**

3. **Populate the QA/QC run schedule based on parameters for the survey program.**

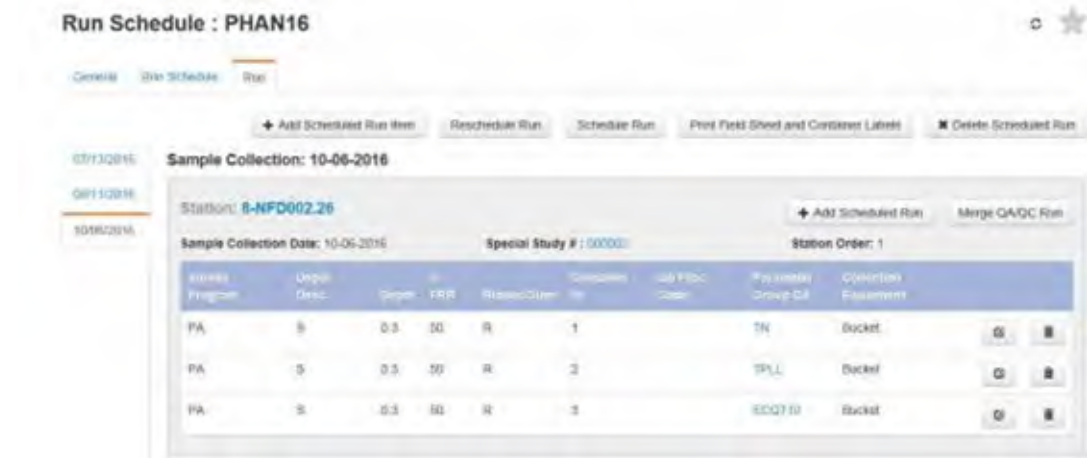
4. After creating the QA/QC run, search for the run that you wish to collect QA/QC samples in. Click "Run" within that run screen.

5. Select "Schedule Run".



6. Select "Create New Run" to schedule the run for the appropriate date.

7. Select "Merge QA/QC Run" on the station that you plan to collect QA/QC samples.



8. Select appropriate QA/QC run ID to merge with station and select "Merge Run".

9. QA/QC have now been added to desired station. Note that "R" Blanks/Dups were automatically changed to "S1". Run is now set up for QA/QC samples.

APPENDIX E

DISSOLVED OXYGEN AND pH PROBE VERIFICATION METHODS

Winkler DO Method

Summary of method

This test is the most precise and reliable titrimetric procedure for Dissolved Oxygen (DO) analysis by adding divalent manganese sulfate, followed by alkaline iodide azide, to the sample bottle. The DO oxidizes the manganese sulfate, and after acidification, releases iodine at a 1:1 ratio. The released iodine is then titrated with a standardized solution of sodium thiosulfate or phenylarsine oxide (PAO).

Interference

Iron salts, organic matter, excessive suspended matter, sulfide, sulfur dioxide, residual chlorine, chromium, cyanide, and certain oxidizing and reducing agents.

Apparatus and materials

Equipment

1. Digital titrator
2. 300 ml glass stopper BOD bottle
3. 250 ml wide-mouthed Erlenmeyer flasks
4. 200 ml volumetric flask
5. Stir bar and stir bar retriever (optional)
6. Magnetic stir plate (optional)

Chemicals

1. Hach Iodate-Iodide standard solution 0.00125 N (Catalog #40149)
2. Hach Manganese Sulfate powder pillow (Catalog #107166)
3. Hach Alkali-Iodide-Azide powder pillow (Catalog #107266)
4. Hach Sulfamic acid powder pillow (Catalog #107399)
5. Starch indicator solution (Catalog #34932)
6. Sodium Thiosulfate standard solution 0.025N (Catalog #2409353)

Sample bottle and equipment cleaning

- Use lab grade detergent and brush, wash and rinse glassware thoroughly with tap water followed by lab grade water. Allow the bottle to dry in an upside-down position.
- After completing the Winkler titration, clean all equipment to prevent accumulation of residues in the containers, which will affect future samples.

Instrument or method calibration

Calibrate digital titrator by following the manufacturer's instructions.

Sample Collection

Note: Winkler DO is usually taken to verify DO probe accuracy and performance.

1. Collect the Winkler sample from the same water being measured by the DO probe.
2. Rinse the BOD bottle twice with sample water, discarding rinses.
3. Fill the bottle by tilting the bottle and submerging it under the water surface at an angle. Avoid introducing air bubbles into the sample by slowly turning the bottle up until it is filled and in an upright position.

Handling and Preservation

1. Immediately add 1 pillow of Manganese sulfate, followed by 1 pillow of alkali-iodide-azide powder. Allow most of the powder to settle below the neck of the bottle.
2. Carefully stopper the bottle to avoid air bubbles. Twist the stopper to ensure a snug fit.
3. Mix by inverting the bottle until a uniform color. Resample if air bubbles appear. Set the bottle down to allow for settling.
4. When the flock precipitate settles to the shoulder of the bottle, mix the sample again by inverting the bottle several times.
5. Once the precipitate has settled to the bottle shoulder a second time, add a pillow of Sulfamic Acid powder. Again, place the stopper on the bottle and invert to mix until a uniform color. This may take several minutes.

Sample Analysis

Verify Titrant Strength

Before titration, verify the titrant strength (sodium thiosulfate or PAO). Failure to perform this verification prior to titration may result in inaccurate results invalidating the test.

1. Add 200.0 ml of Iodate-Iodide Standard Solution, 0.00125 N, to an Erlenmeyer flask.
2. Add one Sulfamic Acid Powder Pillow and swirl to mix.
3. Prime the digital titrator before titrating to ensure no air bubbles are present. Draw up approximately 20 ml of titrant into the digital titrator and then dispense into a chemical waste container.
4. Pull approximately 20 ml of fresh titrant into the pipette for the analysis and zero titrator.
5. Titrate the sample until the solution is a pale straw yellow color. Use a stir plate or gently swirl by hand to mix the solution during titrant addition.

6. Add about 2 ml of starch indicator to turn the solution blue. Mix to a uniform color.
7. While mixing, slowly titrate until the color disappears. The displayed value is reported as mg/L DO.

Titration of Sample

1. Prime the digital titrator before titrating to ensure no air bubbles are present. Draw up approximately 20 ml of 0.025N titrant into the digital titrator and then dispense into a chemical waste container. Zero the digital titrator.
2. Pour 200 ml of the sample from the BOD bottle into a 200 ml volumetric flask and transfer to an Erlenmeyer flask containing a magnetic stir bar. Place the flask on the magnetic plate and turn the stirrer on.
3. Titrate the sample until the solution is a pale straw yellow color. Use a stir plate or gently swirl by hand to mix the solution during titrant addition.
4. Add about 2 ml of starch indicator to turn the solution blue. Mix to a uniform color.
5. While mixing, slowly titrate until the color disappears. The displayed value is reported as mg/L DO

Quality Control criteria

In the field, the difference between probe DO and Winkler DO should be within 0.6 mg/L. For laboratory checks, the difference between probe DO and Winkler DO should be within 0.2 mg/L.

Corrective Action

If the difference is between the titration and DO probe is greater than 0.6 mg/L, most likely the DO sensor needs a new DO cap. Record the date of the cap change on the log sheet. Collect a Winkler sample on the next sampling run using that probe. If the difference between Winkler and the probe is less than 0.6mg/l, the problem has been resolved.

APPENDIX F

PROBE AND SCALE VERIFICATION FORMS

Regional Office

Verified Date:

Verified By:

Multiprobe Parameter Comparison

		Dissolved Oxygen			pH			Temperature		
Instrument Model	Serial #	Reading mg/L	Average DO	Difference mg/L	Reading SU	Average SU	Difference SU	Warm Bath (30-35 C)	Average C	Difference C

Comments:

Regional Office:

Multiprobe Thermistor Check

Verified Date:

Verified By:

		Ice Bath (0-4 C)			Room Temperature (18-22 C)			Warm Bath (31-35 C)		
Instrument Model	Serial or Tag #	DEQ Master NIST	Thermistor	Difference	DEQ Master NIST	Thermistor	Difference	DEQ Master NIST	Thermistor	Difference

Comments:

Virginia Department of Environmental Quality Analytical Balance and Weight Verification

Verification Date: ________________ Verified By: ________________ Regional Office: ________________

DEQ Master Weight Calibration date: ________________ Certificate Number: ________________

Scale Accuracy Check		Certified Weight 1			Certified Weight 2			Certified Weight 3		
Scale Make/Model	Scale S/N	DEQ Master Weight	Reported Weight	Error	DEQ Master Weight	Reported Weight	Error	DEQ Master Weight	Reported Weight	Error

Daily weight verification check: Only performed using a scale that passed (< +/-0.0005 gram error) of the verification check above.

Scale S/N used:

Analytical Weight S/N:		
	Scale Reading	Error
100.0000 gram		
50.0000 gram		
10.0000 gram		
5.0000 gram		
1.0000 gram		
_________ gram		

Analytical Weight S/N:		
	Scale Reading	Error
100.0000 gram		
50.0000 gram		
10.0000 gram		
5.0000 gram		
1.0000 gram		
_________ gram		

Analytical Weight S/N:		
	Scale Reading	Error
100.0000 gram		
50.0000 gram		
10.0000 gram		
5.0000 gram		
1.0000 gram		
_________ gram		

APPENDIX G

SUPERSEDED FIELD PROBE CALIBRATION AND MAINTENANCE

Midday Clark Cell DO Calibration Confirmation

When sampling using a Clark Cell DO sensor at multiple sites during the day, a midday accuracy check is needed. This check confirms the DO sensor is still accurate and reduces the need to flag an entire sample run worth of readings. To perform the midday check:

1. Place the DO sensor in a 100% air/water saturated environment. Either wrap in a wet towel or in the storage cap with small amount water and away from direct sunlight. Follow manufacturer's instructions on water depth in the storage cup. Do not allow probe membrane to get wet.
2. Allow the readings to stabilize (<0.05 unit change in 10 seconds).
3. Record the DO reading in mg/L or % saturation (see below note), temperature, and barometric pressure on the field data sheet and enter it to the comment field of CEDS.
4. The reading should be within 0.49 mg/L of the Appendix B theoretical DO value.

Note: 95 to 105% saturation is an acceptable shortcut check up to 1,000 feet elevation. Over 1,000 feet, this shortcut may not work due to lower barometric pressure. Field packets should contain Appendix B in the event recalibration is needed or to check theoretical DO values.

If the midday probe check fails, recalibrate the probe in the field and flag the morning data. **Do not enter the run dissolved oxygen data collected prior to a failed mid-day check in CEDS.**

Handheld pH Meter

Applies to various models of handheld meters.

General procedures

1. Rinse electrode thoroughly with water after each sample or standard. Blot sensor dry. Make sure the pH buffer is not expired or appears contaminated before calibrating.
2. Calibrate with at least two pH buffers that most closely bracket the expected sample water pH. The buffers used for calibration are 7.0, 4.0 and/or 10.0.
    a. If sample pH was outside calibrated buffers used, check the accuracy by using the buffer that brackets the observed reading to see if recalibration is necessary.
3. If the probe is off more than ±0.20 SU of the buffer value, recalibrate and resample if possible. If not, exclude the data.
4. Between readings, rinse pH probe with water and blot dry.
5. The pH probe generally has a one-year service and shelf life.

Instrument setup

1. Connect sensor cable(s) to the appropriate meter jack(s) using any required adaptors.
2. Cover any unused meter AC power or ATC jacks, to maintain a waterproof state.
3. Turn the meter on by pressing the power button. When the unit finishes the startup checks, press the **pH**, **SETUP**, or **MODE** button to display pH values.

Calibration

1. Press the **CAL**, **SETUP**, or **MODE** button to enter into calibration mode. The display will usually indicate calibrate mode by a flashing number or the word CAL.
2. Remove the electrode protective cap and rinse with water. Shake or blot the sensor dry.
3. Immerse the electrode in the first buffer solution (usually 7.0) and slowly stir the electrode to ensure the sensor is properly reading the solution.
4. The display should recognize the pH buffer by displaying a steady value and/or beep when stabilized and locked. Some units require pressing the **CAL** button to lock readings. Record calibrated pH value on the log sheet.
5. Repeat steps 2-4 with a second or third buffers. The unit should then exit the calibration mode. If the meter failed to calibrate or has an error message, do not use until the sensor is serviced or replaced. Refer to manufacturer manual if a pH slope value is needed.
6. Place the protective cap over the probe when not in use. Be sure the cap has some fresh pH 4.00 buffer or electrode storage solution and placed in the bottom of the cap.

Field measurement procedures

1. Turn the unit on when ready to sample and make sure it is in pH measurement mode.
2. Remove the cap and immerse probe in the sample solution and stir at a moderate pace.
3. When the meter senses that the reading is stable, STABLE may appear under the measurement reading. Record this value on the field sheet. Enter pH data into CEDS to the hundredth place.
4. If AUTO is not displayed on the screen, the auto read function is not active, and the meter will continuously monitor the pH value of the sample.
5. If AUTO is displayed on the screen, the meter will fix the stabilized pH value on the screen. AUTO will flash on the display until a stable reading is obtained.
6. Rinse the probe with water and place the protective cap on which contains a moist tissue of pH 4.0 or pH storage solution.

Maintenance

Table G.1. Maintenance: Accumet, Beckman, Oakton, Orion, and similar series pH/ISE meter

Sensor Type	Item	Procedure
pH sensor	**Slow pH response or reconditioning sensor returned from long term storage.**	**Note:** If using a liquid filled sensor, make sure to fill the fluid chamber with the proper electrolyte and to the proper level. 1. Soak sensor in warm water with mild detergent for 10-30 minutes. 2. If ineffective, clean the glass sensor with mild soap/water soaked swab. 3. If ineffective or the sensor shows slow response, soak a few minutes with 10% HCl or several hours with pH 4 buffer (pH sensor only). 4. After cleaning, rinse with tap water and blot dry 5. Place storage solution for at least two hours before calibrating.
	Short term storage of pH/ISE electrode (<1 month)	1. Place electrode tip in container provided or other watertight container containing electrode storage solution or pH 4.0 buffer. 2. If using a liquid filled pH sensor, leave vent open while measuring. Close vent while in storage. Refill probe solution if below recommended levels.
	Long term storage of pH/ISE electrode (>1 month)	1. Disconnect sensor from meter. 2. Rinse sensor tip and blot dry. a. For liquid filled probes. Drain all liquid and rinse with lab grade water using the vent hole. Drain water and allow to air dry. 3. Remove batteries to avoid damage to the unit while in storage. 4. Place electrode in a protective container. Store in a cool and dry location.
General Maintenance	**Replacing batteries and/or using AC power supply**	1. Remove the battery cover from the back of the meter and old battery. 2. Install the new battery of the same type and voltage. Make certain any battery wires do not to interfere closing of the battery cover. 3. If using an AC adaptor, connect the adapter to the AC jack and power source. The meter is not waterproof when the AC adapter is connected

Handheld Dissolved Oxygen Meter

Applies to YSI 55, 85, 95, and PRO series handheld meters.

Note: YSI 58 users, refer to the manufacturer manual for calibration and operation of the unit.

Calibration

1. Ensure that the calibration cup sponge is wet. Insert the probe into the calibration cup.
2. Turn the instrument on and wait for stable dissolved oxygen and temperature readings which may take 10 minutes to an hour. Optical units stabilize in less than 5 minutes.
3. Enter the calibration menu. Depending on the model used, this either involves pressing the **UP ARROW** and **DOWN ARROW** buttons at the same time (YSI 55, 85, 95), or press the CAL button (YSI Pro)
4. The display may either prompt the user to enter the local altitude in hundreds of feet or barometric pressure of the calibration site. Use the **arrow keys** to increase or decrease the displayed value to match current conditions. When the proper reading is displayed, press the press the **ENTER** button once.
5. The instrument should now read CAL in the display. The calibration value may be displayed with the % saturation reading. Make sure readings remain stable.
6. Press the **ENTER** button to lock the saved reading and exit the calibration menu. The display should no longer say CAL and return to the normal readout display.
7. Record the calibrated DO and temperature readings on the log sheet.
8. If the probe can test for other parameters such as the YSI 85 sensor to check conductivity, calibrate the unit following above steps and calibration and end of day check steps outlined in section 3.4 of this document.

Taking Measurements

When arriving to the field, turn on the unit. It should display the current temperature and DO reading after a few seconds. An error message will display if an internal problem is detected.

If the probe has a Clark Cell sensor (clear plastic over the sensor tip), make sure the probe moves through the sample water at the rate of at least 1 foot per second to provide adequate stirring and representative results. Optical DO sensors (black plastic over the sensor tip) do not need moving water to get an accurate reading.

Record field parameter data and enter into CEDS based on the hundredth unit of the display.

Maintenance

Table G.2. YSI 55, 58, 85, 95, Pro Series General Maintenance

Sensor Type	Item	Procedure
Clark Cell DO Sensor	**Changing DO membrane.** **Every 2-4 weeks or if membrane is torn, wrinkled, has air bubbles, or sensor readings are erratic or slow.**	1. Discard old membrane or cap. Rinse electrode with lab grade water. Blot dry. 2. Fill electrode well or cap with KCl solution provided in the membrane kit. **a. If using a membrane cap** i. Fill cap ¾ full with KCl solution and remove any bubbles by tapping the side. ii. Lower the electrode into the membrane cap and tighten to finger tightness. iii. If bubbles or wrinkles are seen on the membrane, try again. **b. Using membrane film** i. With the electrode facing up, fill with enough KCl to form a positive meniscus. ii. Remove air bubbles by tapping the side of the sensor with a pencil. iii. Lay a sheet of membrane film so the KCl solution grabs the sheet. If bubbles are trapped under the sheet, remove and add more KCL solution. iv. Replace O-ring if older than 3 months or is damaged. Do not grease the O-ring. v. Secure the membrane with the O-ring by pushing down with both thumbs. vi. Note any air bubbles or wrinkles. If so, discard the membrane and try again. vii. If the membrane is satisfactory, trim excess film using scissors or a razor blade. 3. Allow the sensor to equalize (4 to 24 hours) before calibrating and using in the field**.**
	Cleaning silver anode. **Check for majority of anode is dark dull gray to black when changing DO membrane.**	1. Immerse the electrode in household strength ammonia solution (≈3% ammonia hydroxide) for up to 8 hours or use 14% ammonia solution and soak 2-3 minutes. **Note:** 14% ammonia solution will destroy the sensor if left in too long. 2. If still tarnished, gently buff with moist 400 or finer grit sandpaper. 3. Triple rinse sensor with lab grade water and blot dry. 4. Add a new membrane using steps listed above.
	Cleaning gold cathode. **Check for tarnished or dull gold color when changing membrane**	1. Wipe the cathode with a clean lent-free cloth, pencil eraser or hard paper. The proper color should be gold with a matte finish. 2. If still tarnished, gently buff with moist 400 or finer grit sandpaper. 3. Triple rinse sensor with lab grade water and blot dry. 4. Add a new membrane using steps listed above.
Optical DO Sensor	**Cleaning sensor** **Whenever dirt, algae, or mold on the sensor housing or membrane.**	1. Flush the entire sensor with clean, fresh water. 2. Use a lint free tissue and gently wipe away any foreign material on the sensor cap. 3. If the above fails, use a 15 minute white vinegar soak. Rinse with lab grade water. **DO NOT clean with alcohol or organic solvents, as it will destroy the membrane.** **DO NOT remove the membrane cap unless replacing with a new cap.**
	Replacing membrane **Damaged membrane, LED light seen through scratches (≥1mm), calibration failure**	1. Unscrew and discard the old membrane cap, old O-ring, and cap seal. 2. Place the new O-ring and cap seal at the appropriate locations of the optical sensor. **DO NOT add grease to the O-ring or cap seal**. 3. Attach new membrane cap to the sensor. Tighten to finger tightness. 4. Do not touch the outer or inner surface of membrane tip with ungloved fingers 5. Add the new calibration constants as outlined in the replacement sensor package.
	Rehydrate membrane **If sensor dried out after 2 hours not in a 100% humid environment**	1. If possible, remove the optical sensor from the probe housing. 2. Place 400 mL of room temperature water in a 600 mL beaker. 3. Place the sensor with the membrane in the room temperature water for 24 hours. 4. Store the sensor in either water or water-saturated air at room temperature prior to calibration and deployment.

Conductivity Sensor (YSI 85, PRO series only)	**Cleaning conductivity sensor.** **As needed**	1. Using a paper towel or cotton swab, clean the sensor of hardened foreign material using warm water and mild detergent. 2. Rinse sensor with lab grade water and blot dry. 3. If needed, repeat using a soft brush. Hard scouring will damage the sensor.
General care	**Short term storage (<1 month)**	Place DO sensor in calibration cup or bottle with a clean, moist sponge. Check to see the sponge is still moist every week when the unit is not in use.
	Long term storage (>1 month)	1. **Clark sensor units only**- remove membrane or cap and rinse electrode with lab grade water and blot dry. Attach a dry membrane or cap. Store in a cool, dry place. 2. **Optical DO units**- Add ≈10 ml lab grade water to keep probe hydrated. 3. Remove batteries.