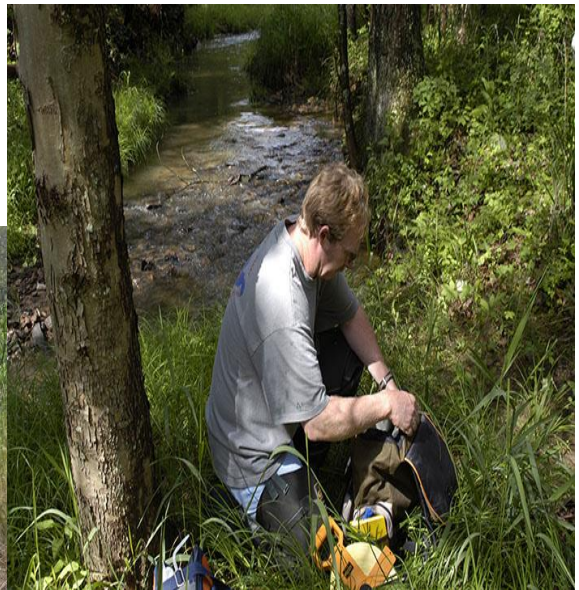


# WV Department of Environmental Protection Watershed Assessment Branch



## Modified Standard Operating Procedures for Volunteer Monitors



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To learn more go to: <http://www.dep.wv.gov/WWE/watershed/Pages/WBSOPs.aspx>

## **Water Quality Sample Collection and Preservation**

### **Materials and Reagents**

1. Analysis Request Form with Chain-of-Custody (COC) - for sample identification and tracking of samples from the field to lab and results from the lab back to us.
2. Water Quality Sample Labels-featuring the unique WQ Sample ID for each distinct water sample.
3. Waterproof pen or sharpie - for labeling sample bottles.
4. Sterile Fecal bottles with Sodium thiosulfate tablet - for collecting bacteria samples.
5. Plastic Containers (e.g., cubitainers with Lids) - for collecting other water quality samples, except phenols.
6. Cooler - for sample preservation.
7. Wet Ice - for sample preservation.
8. Fixatives (nitric acid, sulfuric acid, and sodium hydroxide) - for sample preservation.
9. Waterproof plastic bags or other suitable container - for holding bacteria sample bottles during transport.

### **Safety Precautions**

Rubber gloves and protective eyewear should be worn during sample collection to avoid bacterial contamination and for personal health protection as many streams may have sharp objects embedded in the substrate (e.g., glass, metal, wire, etc.). They should also be worn during sample preservation or at any time while handling the fixatives, which are concentrated acids. Bottles containing fixatives should be stably seated inside a lidded container to prevent breakage and leakage.

**WARNING: SOME FIXATIVES ARE CORROSIVE AND MAY EMIT TOXIC FUMES. BE SURE TO USE THE APPROPRIATE SAFETY GEAR AND PRESEVE SAMPLES IN A WELL VENTALIATED AREA. DO NOT FIX SAMPLES IN THE VEHICLE, AS ACCIDENTAL SPILLS CAN AND WILL OCCUR.**

Do not place liquid acid or base into sample bottles prior to sample collection. Always add fixatives to sample.

**WARNING: NEVER ADD SAMPLE WATER TO LIQUID ACIDS OR BASES, AS A STRONG CHEMICAL EXOTHERMIC REACTION CAN OCCUR.**

## Part 1. Procedures for Collecting Water Quality Samples

### Labeling Sample Containers

Label each sample container with a sharpie. The following information must be included: Association Name (FOH), County Name, Stream Name, {**AN-code: see this website for potential assistance; <https://apps.dep.wv.gov/dwwm/wqdata/>**}, Date/Time (Military) collected, Location Identifier (Upstream of intake, DS of country route 2, etc...) and type of fixative/preservation used. It is recommended that some additional identifying mark be put on the lids as the sides of the containers can be abraded/smudged pretty easy and lose their labels. This additional identifying mark can be something as simple as the time of collection.

The screenshot shows the 'Water Quality Data Report' interface. At the top is the WV DEP logo. Below it, the title 'Water Quality Data Report' is displayed. The form consists of several fields: 'County' (a dropdown menu with 'Ritchie' selected), 'Watershed' (an empty dropdown menu), and 'Parameter/Units' (a large dropdown menu with a scroll bar). The 'Parameter/Units' menu is open, showing a list of parameters such as Sulfate, Sulfide, TDS, TKN, TOC, TSS, Temperature (in °C and °F), Total Coliform, Turbidity, and various nitrogen and zinc measurements. A 'Display Report' button is located to the right of the parameter list. At the bottom of the form, there is a red text warning: 'Recent data should be considered provisional and subject to revision'. The footer contains the text: 'DepExEp1 - wwwprod1 | Privacy, Security and Accessibility | WV.gov | USA.gov | © 2009 State of West Virginia'.

### Direct Dip/Grab Method

1. At the selected water quality sampling location, (X-site for random sites), attempt to locate a good sampling location with adequate depth and flow near mid-stream. If mid-stream is not available due to high flows or deep water, you may take the sample from the bank if you are sure that there is no plumes from pollution sources or tributaries that may be flowing along either bank. Be sure to document where you sampled on the habitat form. **Be sure to not disturb the substrate above this point until all water sampling is completed.**



Figure 1. DEP Example of Sample Containers Labeled with sample information.

**NOTE:** The definitive order of sample container filling is as follows:

1. Fecal Coliform Sample
2. Unfixed Cubitainer
3. Nutrient ( $\text{H}_2\text{SO}_4$ ) Cubitainer
4. Total Metals ( $\text{HNO}_3$ ) Cubitainer
5. X-Bottle/Dissolved Metals (to be Filtered/ $\text{HNO}_3$ ) Cubitainer

2. Prior to any contact with stream water, look over the stream collection area. Decide where you will be collecting water quality samples, then be sure to have downstream location to take values with water quality meter (Temperature, pH, etc...) This will ensure that water collected will not be disturbed in any way (by meter installation, or by fellow samplers).
3. Collect the water samples upstream of the sonde/water quality meter as follows:

A. Fecal Coliform Sample:

- Use pre-sterilized bottle with Sodium thiosulfate tablet. Keep the bottle closed until you are ready to collect the sample.
- Open bottle and handle carefully to avoid contamination. Do not touch the inside of the lid or bottle.
- Using a quick dipping motion, submerge below the surface of the water (6 inches if possible) and fill the bottle to the 100 mL mark. Do not rinse or refill the bottle.
- If the bottle is too full, slowly pour a



Figure-1. Example of a Fecal Sample being taken from a stream.

little out. *The head-space is necessary in a fecal sample to provide oxygen to the bacteria until the sample can be analyzed.*

- Place cap tightly on bottle and secure cap lock.
- B. Other Water Samples (e.g., Unfixed, Total Metals, Dissolved Metals, Nutrient cubitainer samples):
- All remaining water quality samples are collected in containers (e.g., cubitainers) provided by the analytical lab (per the state analytical contract).

***IMPORTANT: If using cubitainers or other collapsible container, do not blow into the containers to open. The sample can become contaminated by your breath (e.g., Phosphoric acid effervescing from your mouth after drinking a cola and contaminate the Phosphorus readings).***

***NOTE: If water depth is limiting the ability to submerge the container lip without stirring up sediment and organic debris:***

- 1. Cut the top off of open a fresh, unused cubitainer.**
- 2. Thoroughly rinse with stream water as normal (three times).**
- 3. Use the cut cubitainer to carefully collect water and pour into an intact cubitainer.**
- 4. Discard the cut cubitainer after filling up all cubitainers for the site.**

- Rinse the sample container **three times** at least **one-half full** with sample water. During the rinse, secure the lid on the containers, shake for 5 seconds, and then empty (**see Error! Reference source not found. above**).
- Submerge below the surface of the water (6 inches if possible) and completely fill the containers with sample water (1000 mL).
- Expunge as much of the headspace as possible without losing sample water.
- Make sure to limit pieces of organic matter in the sample container as much as possible as these can cause contamination.
- When sealing the container, remove as much air as possible should be expunged from the sample container to avoid contamination (*i.e.*, no head-space).

## **Sample Preservation (Filtration, Fixation, & Holding)**

Samples should be preserved in the following order:

- 1) Unfixed or Iced (Wet Ice) Samples (e.g., Fecal Coliform, Unfixed container)
- 2) Filtered Samples (e.g., Dissolved Metals or Nutrients)
- 3) Fixed Samples (e.g., Total Metals or Nutrients).

The fecal coliform sample should be double bagged before being put on wet ice to prevent accidental contamination of other samples should the sample container become compromised. Do not submerge the fecal sample in ice water! The samples that only need to be cooled on ice (commonly referred to as Unfixed or No Fix) can also be placed on wet ice at this time.

### **Fixation**

Some samples will need to be fixed with acids before being stored. Samples that are preserved with Sulfuric Acid should always be preserved before samples that are preserved with Nitric Acid. This is because the volatile Nitric Acid vapors may contaminate Nutrient samples and give false Nitrogen results. If you do accidentally preserve the Nitric Acid sample first, then move away from that area when fixing the Sulfuric Acid (e.g., the opposite end of the vehicle or 20 feet away).



Figure -2. Example of sample being preserved with Nitric Acid.

**Holding**

With the exception of fecal coliform, all samples should be delivered to the lab within the holding times specified in "Standard Methods for the Examination of Water and Wastewater", 18<sup>th</sup> Edition

**Preservation Methods and Holding Times.**

**Table -1. Preservation Methods and Holding Times**

<b>Parameter</b>	<b>Preservation</b>	<b>Max. Holding Time</b>
Fecal Coliform	Cool <10 °C, 0.0008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	6 hours. (24 hours for TMDL/WAB samples)
Acidity	Cool ≤4 °C	14 days.
Alkalinity	Cool ≤4 °C	14 days.
Ammonia, Ammonium	Cool ≤4 °C, H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days.
Chloride, Bromide	None required	28 days.
Kjeldahl (TKN) and Organic N	Cool ≤4 °C, H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days.
Chromium VI	Cool ≤4 °C, pH = 9.3–9.7	28 days.
<b>Mercury (CVAA)*preferred method*</b>	<b>HNO<sub>3</sub> to pH&lt;2</b>	<b>28 days.</b>
Mercury (CVAFS)	5 mL/L 12N HCl or 5 mL/L BrCl	90 days.
Total Metals (except Boron, Chromium VI, and Mercury) Aluminum, Barium, Calcium, Iron, Magnesium, Manganese, Sodium, Strontium	HNO <sub>3</sub> to pH<2	6 months
Dissolved Metals (except Boron, Chromium VI, and Mercury)	Filtered, HNO <sub>3</sub> to pH<2	6 months
Nitrate	Cool ≤4 °C	48 hours.
Nitrite	Cool ≤4 °C	48 hours.
Nitrate-Nitrite (NO <sub>2</sub> -NO <sub>3</sub> -N)	Cool ≤4 °C, H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days.
Total Orthophosphate	Cool ≤4 °C	48 hours.
Dissolved Orthophosphate	Filtered, Cool ≤4 °C	Filter within 15 minutes; 48 hours.
Phosphorous, Total	Cool ≤4 °C, H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days.
Total Solids, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Iodide, Specific Conductance, Lab pH	Cool ≤4 °C	7 days.
Sulfate	Cool ≤4 °C	28 days.