**Ozarks Environmental and Water Resources Institute (OEWRI)**
**Missouri State University (MSU)**

Standard Operating Procedure for:

# Water Sample Collection

Ozarks Environmental and Water Resources Institute
Missouri State University
Roy Blunt Hall 343
901 South National Avenue
Springfield, MO 65897

Prepared by: Brianne Edwards Date: 11/27/2023
OEWRI Research Specialist

Approved by: Robert Pavlowsky Date: 11/27/2023
OEWRI Director

November 27th, 2023


# Table of Contents

**Identification of the method**
Collection of water samples.

**Scope of the method**
This standard operating procedure provides Missouri State University (MSU) field and laboratory personnel with guidance on the procedure for collecting, preserving, and transporting water samples. Information is also provided for the proper completion of sample collection forms.

**Summary of method**
Water samples are collected in bottles appropriate for each analyte. Sampling personnel should be aware that collecting water samples can be hazardous and that following these procedures should minimize personal risks. Sample bottles are dipped into stream flow either by hand, at the end of a sampling pole, or within a depth integrated sampler. A preservative is added to the bottle if needed; the bottle is sealed and placed into a cooler with ice. Information about the sample (for example, collection time, temperature, preservative, etc.) is recorded on the sample collection form and bottle label.

**Definitions**
1) Deionized water: water that does not contain cations (Na, Ca, Fe, Cu) or anions (Cl and Br).
2) Chain of Custody (COC): used to describe the written record of the collection, possession, and handling of samples.
3) Field Duplicate (FD): two separate samples collected during the same site visit, from the same location in the stream, and within <5 minutes of one another. Both samples are treated identically throughout field and laboratory procedures. Analyses of field duplicates indicate the effects of natural variations in actual water quality parameters; variations in sample collection procedures, preservation, and storage; and are used to analyze the precision of instantaneous sample collection.
4) Field Blank (FB): an aliquot of deionized water added to an empty sample container while at a sampling site and then treated as a regular sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all pre-analysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.
5) Natural water flush: water at the sampling site that is used to rinse the sample bottle three times before sample collection.
6) Grab sampling: water samples collected by hand where the bottle is dipped into the current with the mouth of the bottle upstream. The sample should be

collected within the thalweg of the channel and the bottle should be allowed to fill near the middle of the water column.

7) Depth integrated sampling: water samples are collected with a DH-48 or a DH-76 sampler using one continuous vertical motion throughout the entire water column without pausing when the channel bed is reached.
8) Cross-channel depth-integrated sampling: water samples are collected using depth integrated sampling techniques at equal width increments across the entire surface width of the channel.
9) Composite sampling: a technique whereby water samples are combined, regardless of collection type, thoroughly homogenized, and treated as a single sample.
10) Thalweg: the deepest point of the channel.

**Health and safety**

1. When wading in streams where water depths may be 1 meter deep or more, wear a life preserver and/or remove hip boots or chest waders. Currents can force wading field workers into deep water and water-filled boots can make swimming difficult.
2. When walking through densely vegetated areas along streams, be sure to look for and avoid toxic plants like poison ivy. Be sure to wear appropriate insect repellent and protective clothing for protection from mosquitoes, chiggers, and ticks. In addition, probe areas in your path with a walking stick to warn and disperse venomous snakes like the cottonmouth and copperhead, which may inhabit riparian areas.
3. Field staff should protect themselves from water borne illness by wearing disposable gloves, and avoid touching their eyes, nose, and mouth.
4. Clean off with disinfectant soap and water after wading in streams. This is particularly important for streams that drain livestock areas, sewage treatment plant effluents, and other obvious pollution sources.
5. Under no circumstances should you drink the water from any stream.
6. Concentrated sulfuric and nitric acid are both highly corrosive.
    a. Use protective gloves during handling. Review the MSDS for additional information and safety concerns regarding the acids used to preserve the samples based on the analyte of concern.
    b. Fresh concentrated nitric acid and sulfuric acid will be transferred to a clean precise volume dispenser for each sampling event. Arrangements should be made with the laboratory manager prior to field activities for this action to take place.

c. Any nitric or sulfuric acid not used in the field will be disposed of properly by the laboratory manager.

**Personnel qualifications**

Water samples will be collected by Missouri State University (MSU) field and laboratory personnel who have received appropriate training from experienced personnel, prior coursework, and field experience regarding the collection of grab samples, and who are familiar with all of MSU's sample handling and labeling procedures and appropriate SOPs.

**Equipment and supplies**

1. Field Notebook, Pen, and Permanent Marker: for recording sample site information and to complete the sample bottle labels.
2. Global Positioning System (GPS): to locate sample sites
3. Cooler with ice and bottle rack: for storage and transport of samples from the field to the lab.
4. Fresh Concentrated Sulfuric Acid (H2SO4) in a precise volume dispenser: for preservation of nutrient samples. (Caution: highly corrosive. Handle with gloves)
5. Fresh Concentrated Nitric Acid (HNO3) in a precise volume dispenser: for preservation of metals samples. (Caution: highly corrosive. Handle with gloves)
    a. Fresh concentrated nitric acid will be delivered to a clean precise volume dispenser for each sampling event.
    b. Arrangements should be made with the laboratory manager prior to field activities for this action to take place.
    c. Any nitric acid not used in the field will be disposed of properly by the laboratory manager. (Caution: highly corrosive. Handle with gloves)
6. Protective Gloves: for protection against chemicals and from water borne contaminants.
7. Sample Container: appropriate for the analytes of concern and that have been *visually checked for cleanliness by both the laboratory manager* during the release of the containers from the laboratory *as well as the field technician before taking the containers into the field*.
    a. Always take an additional sample container into the field.
    b. Always keep sample containers capped after inspection to prevent contamination. Containers used most often have a capacity of 500 ml and are made of HPDE plastic.
    c. The project supervisor will determine the appropriate size and type of sample containers to use for the project.

8. DI Water: for the field blank (FB).
    a. Rinse two clean sample containers three times each with DI water in the laboratory.
    b. Fill one of the containers with DI water and cap. Transfer this DI water to the other pre-rinsed container in the field for the field blank.
    c. Most project managers prefer that the location of the field blank preparation be noted in the field notes or on the chain of custody (COC) as well.
9. US DH-48 or US DH-76 Depth-integrating Suspended Sediment Sampler
    a. These samplers are used to collect depth integrated samples and are designed to continuously extract a sample as they are lowered from the water surface to the channel bed and returned to the surface at a constant rate of travel.
    b. DH-48 and DH-76 collection is described in the Sample Collection Procedures section.
10. Sampling pole: used to extend the reach from shore by 5 to 10 feet depending on the length of the pole. This sampling pole is used for collecting grab samples with wider or faster flowing streams.
11. Chain of Custody Forms: used to describe the written record of the collection, possession, and handling of samples.
    a. Chain of custody (COC) forms are located in the OEWRI laboratory and should be completed as described in the Chain of Custody SOP (OEWRI-SOP-001).

**Reagents and standards**

1. Fresh concentrated nitric acid ($HNO_3$)
2. Fresh concentrated sulfuric acid ($H_2SO_4$)
3. DI water

**Quality control**

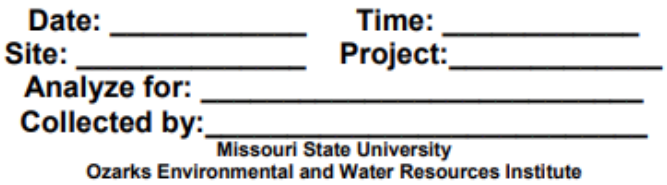
Field blanks and duplicates should be prepared and analyzed when required for each sampling site to ensure no contamination has occurred. The chain of custody forms should be completed as described in the Chain of Custody SOP (OEWRI-SOP-001). Chain of custody (COC) forms are located on a board in the OEWRI Laboratory.

**Sample preservation and storage**

1) Sample preservation: samples are acidified to pH<2, put on ice during transport, and are stored in a refrigerator at the laboratory to retard biological action, retard hydrolysis of chemical compounds and complexes, reduce volatility of constituents, and reduce absorption effects.
2) Sample preservation is determined by the water quality parameters of interest. If the samples are collected for nutrient analyses, then $H_2SO_4$ should be used to acidify those samples. Nitric acid is used to acidify samples collected for metal analyses.
3) Samples collected to determine suspended solid or dissolved fraction parameters do not require acidification.

**Sample Collection Procedures**

Every sample container must have a sample label (see below for example). The label should be completed using indelible ink before placing the bottle into the stream (i.e., it is easier to write on a dry label than a wet one).




**A. Sample Documentation**

1) For each sample, record the date, site ID, sample type, matrix, container type, preservative, time of collection, and the collector's initials on the Chain of Custody form (See OEWRI-SOP-001 Chain of Custody for explanation of how to complete the form).
2) Additionally, record the date, site ID, time collection, and any other information required in the field notebook. Ambient hydrologic conditions such as stream flow and precipitation should be recorded in the field notebook as well, as specified by the project QAPP.

**B. Pre-sampling Field Procedures**

1) Do not disturb the water upstream of the sampling location. If this does happen, then allow sufficient time and flow to pass for stream to clear itself before collecting a sample.
2) Collect representative samples from flowing water and in the thalweg or at a location determined by the project supervisor.

3) Fill and flush the sample container three times with natural water from the sampling site. Discard the rinse water downstream.
4) Field technicians should avoid skimming the water surface or disturbing sediment in the channel bed during collection.

**C. Sampling Methods**

**1) In *shallow* streams (< 0.2 m):** point grab samples are collected in the sample bottle by dipping the bottle below the water surface (Figure 1).
   1. Fill the bottle to just below the neck.
   2. A sampling pole can be used for sample collection from approximately 5 - 10 feet from the shoreline. The sample container is attached to the pole which is extended to collect the sample.

**2) In *deeper* streams (> 0.2 m and < 0.5 m):** water column grab samples can be collected.
   1. Dip the bottle into the water with the opening pointed down to exclude water (Figure 2).
   2. Slowly, begin to turn the opening up while moving the bottle up through the water column.
   3. The bottle should be almost full when the bottle is removed from the stream.
   4. If the bottle is completely full, then it is probable that the bottle was full before reaching the top of the water column. In this case, recollect the sample using a faster speed through the column.

**3) When the *depth of water in the channel is* > 0.5 m*:*** use a DH-48 or a DH-76 depth-integrating sampling device to collect depth integrated samples.
   1. The DH-48 is designed to collect water samples that are wadable. The wading rod is attached to the sampler body.
   2. A nozzle is threaded into the front of the sampler, and it extends into the sample container (Figure 3a). The channel width, depth, and flow rate as well as the volume of the sample container will dictate which size of nozzle to use.
      i. The nozzle size determines the correct submersion time during sample collection. Make sure that the nozzle is firmly in place and determine its size.
   3. Air in the sample container escapes through a vent tube in the back of the sampler body. Flow (water velocity) and nozzle size determine the correct submersion time during sample collection.
      i. Use Figure 3b to determine the correct submersion time to take a proper volume of water for the sample.

4. While in the field, insert a sample container into the sampler body by turning the spring loaded clamp. Return the clamp to its original position to seal the sample container again the gasket.
5. Collect a sample by submerging the sampler body into the water using one continuous vertical motion throughout the entire water column without pausing when the channel bed is reached (Figure 3c).
    i. The sample should be collected within the thalweg of the channel and the sampler should be raised and lowered until the bottle is full, which occurs when bubbles are no longer escaping from the bottle.
6. When the bubbles stop coming to the surface, pull the sampler body from the water and tilt it upright to keep the water sample in the container. Turn the spring loaded clamp and remove the bottle. Cap the bottle and return to the stream bank.

**4) <u>Width-Nested Depth-Integrated Sampling:</u>** Water samples are collected using depth integrated sampling techniques at equal width increments throughout the entire surface width of the channel. Samples can be collected from a bridge using the DH-76 and following these procedures:

1. Cross sections are measured at a straight-sided wade-able section of stream, with reasonably smooth, laminar flow.
2. The selection of the location of the channel section to be profiled for depth-integrated sampling should consider accessibility and logistics; aims of the study; absence of backwater conditions due to downstream impoundments, back flooding rivers, and tides; and channel flow is slightly converging or constant in cross-section without areas of near-zero velocity or eddies.
3. After the channel section is located, a tape measure is pulled tightly across the stream and anchored on both sides with stakes or surveyor's pins. The zero reading on the tape is staked on the left bank of the channel and tape readings increase toward the right bank. The left and right sides of the channel are determined by looking downstream.
4. The width of the water surface is divided into at least 3 subsections with each side of a subsection called a "vertical" (Figure 4).
5. Collect a sample at each vertical using depth-integrated sampling techniques described in the Collection Procedures and record the horizontal location on the tape.

6. One continuous vertical motion should be used to collect water throughout the entire water column at the midpoint of each increment without pausing when the channel bed is reached.
7. Samples taken at each increment can be analyzed separately or can be combined to produce a composite sample for the site.

**5) Composite sampling:** Water samples (regardless of collection type) are combined, thoroughly homogenized, and treated as a single sample.

1. Collect samples using the appropriate sampling method.
2. Dispense equal volumes of each sample collected into one sample container.

**6) Field Blank Preparation**

1. Rinse two clean sample containers three times each with DI water in the laboratory. Fill one of the containers with DI water and cap. Transfer this DI water to the other pre-rinsed container in the field for the field blank.
2. Use only containers that were specifically rinsed with DI water 3 times prior to field activities.
3. Label appropriately and include the site abbreviation where the field blank was prepared if required by the project manager.

**D. Sample Preservation**

1) Add preserving acid to each sample, duplicate, and field blank immediately after collection or preparation.

2) Do not acidify samples collected specifically for total suspended solid or dissolved fraction analyses. Total suspended solid samples do not require acidification and dissolved fraction samples are acidified after filtration.

3) Fresh concentrated sulfuric acid ($H_2SO_4$) is used to preserve samples collected for nutrient analyses. Fresh concentrated nitric acid ($HNO_3$) is used to preserve samples collected for metal analyses. Fresh acid will be delivered to a clean precise volume dispenser for each sampling event.

   a. Arrangements should be made with the laboratory manager prior to field activities for this action to take place.

4) Any acid not used in the field will be disposed of properly by the laboratory manager. (Caution: highly corrosive. Handle with gloves).

5) Use the precise volume dispenser to deliver 2 ml of acid into the samples, duplicates, and field blanks by squeezing the dispenser once to fill the inner chamber with acid and then tipping and squeezing a final time to deliver acid to the sample container.

6) There is no need to check the pH of the samples; 2 ml will make the sample pH <2 which is adequate to preserve surface water samples collected in the Ozarks.

**E. Sample Transportation, Storage, & Documentation**

1) Sample containers are capped and placed on ice in a cooler for transport to the laboratory.
2) The samples will be kept in the possession of Missouri State University personnel who collected the samples until the samples are transferred to a laboratory refrigerator (OEWRI laboratory located in Blunt Hall 125) with the appropriate Chain of Custody forms.
3) Chain of custody (COC) forms should be completed as described in the Chain of Custody OEWRI-SOP-001.
4) Field notebooks and copies of the COC forms should be stored by the project manager in a file dedicated to the project for which samples are collected.
5) The original COC will be stored in a file and kept in the quality control manager's office.

**Pollution Prevention**

Volumes of reagents made should mirror the number of samples being analyzed. These adjustments should be made to reduce waste. Any nitric or sulfuric acid not used in the field will be disposed of properly by the laboratory manager.

**Waste Management**

All waste from these procedures shall be collected and disposed of according to existing waste policies within the MSU Geography, Geology, and Planning Department.

**References**

OEWRI. Standard Operating Procedure for: Chain of Custody. OEWRI-SOP-001. Ozarks Environmental and Water Resources Institute, Missouri State University. 2022. https://oewri.missouristate.edu/_Files/OEWRI_SOP001_COC_01202022.pdf

**Tables, Diagrams, and Flowcharts**

Figures illustrating sampling methods and instrumentation can be found on pages 12-14.

*Figure 1. Point grab sampling method.*

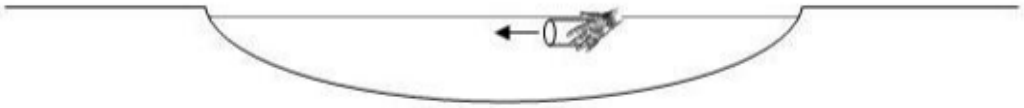


*Figure 2. Water column grab sampling method.*

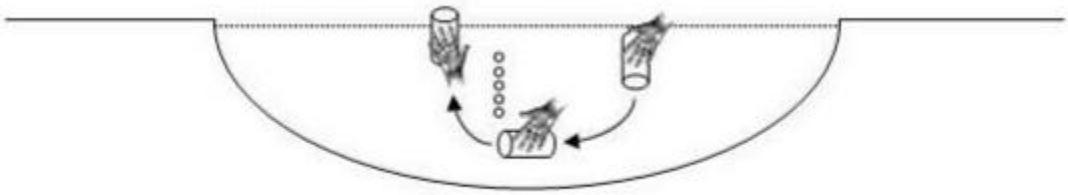


*Figure 3a. Depth-integrated sampler (DH-48).*

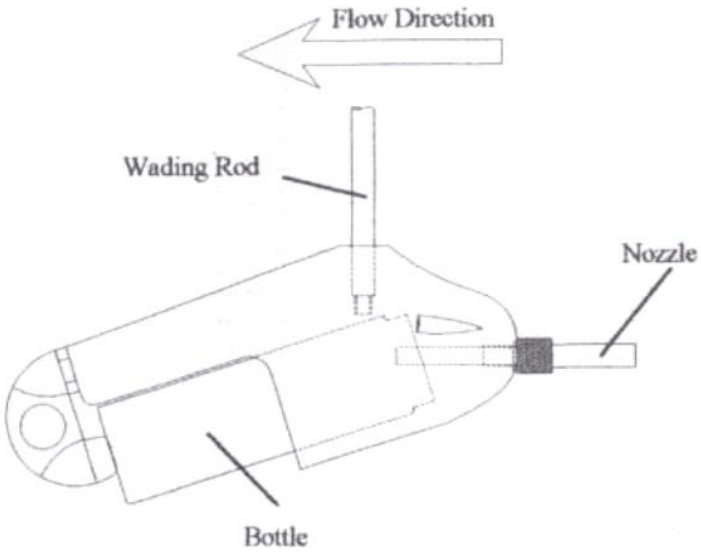


*Figure 3b. Estimated submersion time graph.*

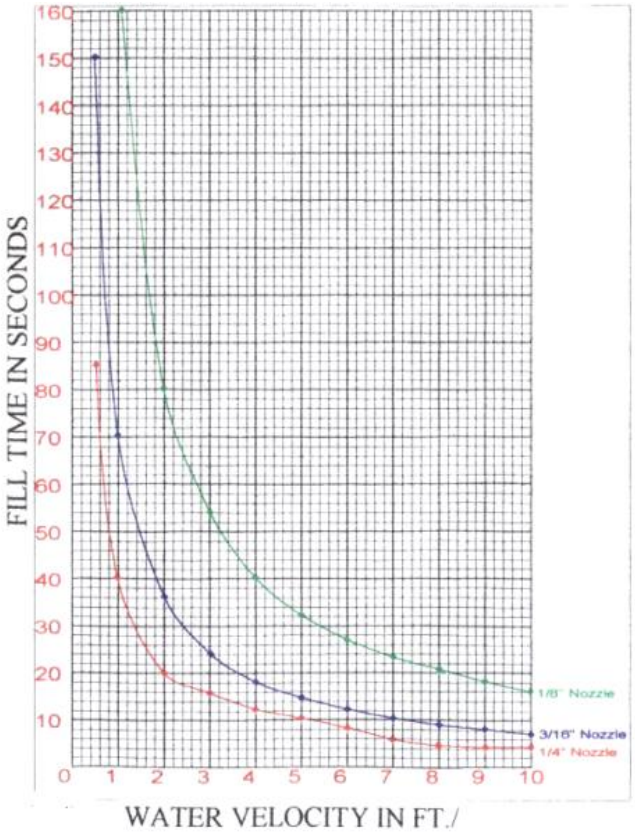



*Figure 3c. Depth-integrated sampling method.*

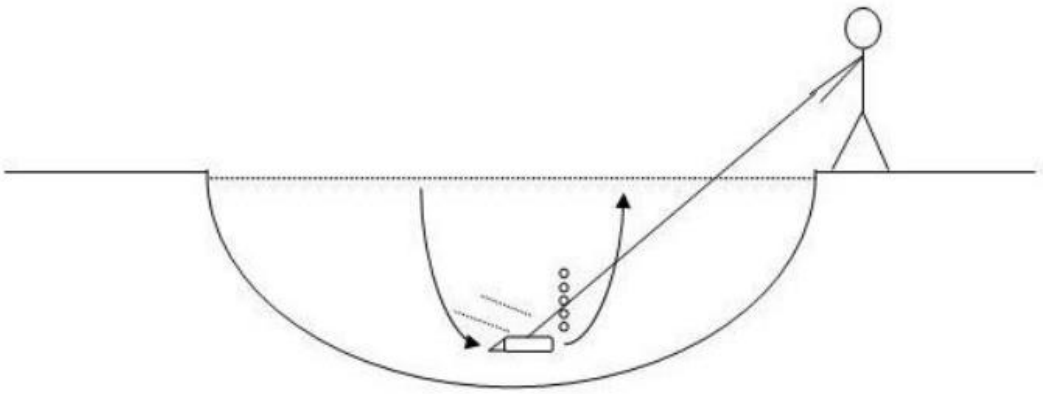


*Figure 4. Width-nested depth-integrated sampling method.*