

Standard Operating Procedure

Sampling Surface Water Quality in Lotic and Wetland Systems

Commonwealth of Kentucky
Energy and Environment Cabinet
Department for Environmental Protection
Division of Water

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DOCUMENT REVISION HISTORY

Version and Effective Date	Page(s) Revised	Revision Explanation	Revision Author
Version 3.0 January 2022	Entire Document	Add wetlands sampling (DOWSOP03021), pole sampler, bucket sampling, and Ortho-P Quick guide. Remove section on rod-and-reel sampler use, replace with updated weighted bottle sampler for bacteria sampling. Add language about sample location versus sample gear. Add details on sample preservation and collection of QC samples. Add Table 3: Troubleshooting. Add information to Table 2 – preservation and bottle volumes/types. Add details to all sections. Add pre-filtering method and include more detailed DOC filtering instructions. Update references and grammatical edits. Remove 40 CFR from appendix and replace with instructions for parameters not covered, images of sample gear, Reference Method table, filtering Quick Guide, and QC COC.	Rebecca E. Clark and Mary Rockey
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Version 1.0 3/15/2010	Title Page	Added Clark Dorman, WQB Manager	
Version 1.0 3/15/2010	Pg. 15	Updated the following sentence: "In order to pass QA testing, laboratory analysis results for all analytes should be less than the method detection limit (MDL)." Changed the requirement from "one half (1/2) the MDL" to "less than the MDL".	
Version 0.0 4/13/09	Entire Document	Replaces in part "Kentucky Ambient/Watershed Water Quality Monitoring SOP, August 2005"	Jessica Schuster

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1.0 SCOPE AND APPLICABILITY

This document provides instruction for the collection, preservation, and handling of surface water quality grab samples in wetland and lotic systems that are collected by Kentucky Division of Water (DOW) field personnel for field screening and laboratory analysis of ambient conditions. Sample collection for some analytical methods require specialized preparation and procedures that are not outlined in this document. Before sampling begins, check the requirements of all project sample parameters to ensure this is the appropriate document (see Chapter 40 Section 136 of the Code of Federal Regulations (CFR)). In particular, this document should not be used for the collection of samples for Per- and Polyfluoroalkyl Substances (PFAS) analyses.

2.0 SUMMARY OF METHOD

This document summarizes surface water sampling methods performed by various DOW programs. On the occasion, that DOW field personnel determine that any of the procedures described in this manual are inappropriate, inadequate, or impractical, the variant procedure will be documented in field log books or field observation sheets, along with a description of the circumstances requiring its use.

This manual should be considered a dynamic document that is reviewed and updated as new procedures and methods are used.

3.0 DEFINITIONS AND ACRONYMS

ASTM: American Society for Testing Materials

CaCO₃: Calcium Carbonate

CBOD: Carbonaceous Biochemical Oxygen Demand

CFR: Code of Federal Regulations

COC: Chain of Custody

DI: De-ionized Water

DEPS: Division of Environmental Program Support

DOC: Dissolved Total Organic Carbon

DOW: Kentucky Division of Water

E. coli: *Escherichia coli*

EPA: United States Environmental Protection Agency

HCl: Hydrochloric Acid

HDPE: High Density Polyethylene

HNO₃: Nitric Acid

H₂SO₄: Sulfuric Acid

KDEP: Kentucky Department for Environmental Protection

K-WADE: Kentucky Water Assessment Data for Environmental Monitoring

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LDPE: Low Density Polyethylene
LIMS: Laboratory Information Management System
LOD: Limit of Detection
LOQAM: Laboratory Operations and Quality Assurance Manual
MDL: Method Detection Limit
NB: Nalgene® Bucket
Ortho-P: Dissolved Orthophosphate (as P)
PCB: Polychlorinated biphenyls
PFAS: Per- and Polyfluoroalkyl Substances
PPE: Personal Protective Equipment
PTFE: Polytetrafluoroethylene, or Teflon®
QA: Quality Assurance
QAC: Quality Assurance Coordinator
QAO: Quality Assurance Officer
QAPP: Quality Assurance Project Plan
QC: Quality Control
SOP: Standard Operating Procedure
TSB: Tryptic Soy Broth
UPW: Ultra-pure De-ionized Water
UV: Ultraviolet
WBS: Weighted Bottle Sampler

Reagent Water: reagent water is a general term used to describe the type of water required for quality control (QC) samples and equipment rinsing. In this SOP it is most commonly de-ionized water (DI) or ultra-pure de-ionized water (UPW). Reagent water requirements depend upon the parameter/analyte of interest and is designated in the analytical method.

4.0 HEALTH & SAFETY STATEMENT

All field staff should review *Worksite Hazard Assessment Guidance Document, Water Quality Branch* (DOW, 2017). If working in or around wetlands, the *Health and Safety Plan for Wetlands Monitoring and Assessment Program* should also be reviewed and carried with each field team (DOW, 2019). In addition, each employee will be individually trained by his/her supervisor, or designee, to perform assigned job tasks safely, prior to his/her performing the task.

Field staff working in and around potentially contaminated surface waters should receive an immunization shot for Hepatitis A in accordance with KDEP Policy SSE-708. In addition, staff should receive immunization for Hepatitis B and tetanus, to aid in the prevention of contracting those pathogens. All field staff must also be trained in CPR, First Aid, and Bloodborne Pathogens in accordance with KDEP Policy SSE-711.

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Personal protective equipment (PPE) should be used when sampling including, but not limited to: site-appropriate wading boots, personal floatation device, latex or nitrile gloves, and cold weather clothing.

Monitoring may include field activities during all stages of the hydrologic cycle, including high discharge/flood stage conditions. It is recommended that field staff use the buddy system and personal floatation devices when collecting samples during high flow conditions. If high discharge conditions are determined unsafe by any field activities staff, do not sample during that time.

5.0 CAUTIONS AND INTERFERENCES

The usefulness and validity of environmental data are highly dependent upon proper sample collection procedures. Proper sampling technique, paired with precise and accurate analytical measurements, is a fundamental element of any monitoring program. The following precautions shall be considered when collecting surface water samples.

- This SOP specifically addresses surface water grab samples (an individual sample collected at single location and time) that are taken from streams and wetlands. It may not be appropriate to use the methods presented in this document for other types of water sampling, or for all parameters. Other methods are discussed in separate SOPs (e.g. sampling lakes and any type of composite sampling).
- This SOP specifically addresses the most common parameters sampled by DOW, be sure to determine any special considerations for all study parameters. Sample collection methods for some parameters may be discussed in separate SOPs (e.g. PFAS).
- Samples should always be stored in a secure location to prevent tampering.
- All samples should have appropriate chain of custody (COC) documentation and COCs must remain with all samples.

It is important to remain cognizant of and limit potential sources of contamination when sampling. Gloves must always be worn when collecting a sample and prior to performing any filtering. Immediately cap all bottles after filling with the sample water and double check that the caps are completely secured on the sample bottles prior to storing in a cooler.

Before sampling, consider the requirements for each sample bottle. Some samples have special requirements, such as:

- Leaving no headspace (e.g. alkalinity, acidity)
- Using only glass bottles (e.g. pesticides, herbicides, low-level mercury, dissolved total organic carbon (DOC))
- Using an amber bottle (e.g. chlorophyll *a*, DOC, pesticides, herbicides)

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- Restricting pre-rinsing of the bottle (e.g. bacteria and pesticides)
- Requiring a pre-cleaned or otherwise pre-treated bottle (e.g. bacteria, low-level mercury, DOC)
- Using specified reagent water for QC samples or rinsing equipment (see section 11.0 for details)
- Having unique preservation requirements and holding times (see Table 2 and Appendix B of this document; or Appendix L of the Division of Environmental Program Support (DEPS) Laboratory Operations and Quality Assurance Manual (LOQAM) (2020) or 40 CFR 136 Table II for more detail)
- Having additional special precautions to avoid sample contamination (e.g. low-level mercury - see reference methods (U.S. Environmental Protection Agency (EPA) Method 1631E (EPA, 2002) and EPA Method 1669 (EPA, 1996)) for details.

6.0 PERSONNEL QUALIFICATIONS

All personnel involved in surface water quality sampling will meet at least the minimum qualifications for their job classification. In addition, all field staff will be trained in the proper water sampling collection and preservation techniques. Training will continue on-the-job through interaction with experienced field personnel and continued outside training when educational opportunities become available.

7.0 EQUIPMENT AND SUPPLIES

A list of supplies that may be required for surface water sampling can be found in Table 1.

Table 1. Surface water sampling equipment and supplies for typical DOW sampling programs.

Sample Bottles	Applicable Parameter/Variable Group
60 mL (2 oz.) Glass wide-mouth amber bottle with PTFE-lined cap	Dissolved total organic carbon (DOC)
60 mL (2 oz.) HDPE wide-mouth square bottle	Dissolved orthophosphate (as P) (ortho-P)
120 mL (4 oz.) Sterile plastic container with Na ₂ S ₂ O ₃ tablets	Bacteria (<i>E. coli</i>)
250 mL (8 oz.) HDPE narrow-mouth amber bottle	Chlorophyll <i>a</i>
250 mL (8 oz.) Sterile plastic containers	Bacteria (<i>E. coli</i>) (QC sample)
250 mL (8 oz.) Glass round amber narrow-mouth bottle w/ Teflon®-lined Closure/Low Particle Protocol	Low-level Mercury
500 mL (17 oz.) HDPE wide-mouth Jar	Metals, Nutrients, Acidity/Alkalinity
1 L (32 oz.) HDPE wide-mouth bottle	Bulk
1 L (32 oz.) Glass amber narrow-mouth bottle	Herbicides, Pesticides/PCBs
Chemical Preservatives	Applicable Parameter/Variable Group
15 mL LDPE Dropper Bottle 1:1 HCl (Hydrochloric Acid)	Low-level Mercury
3.5 mL vial w/ 1 mL 1:1 H ₂ SO ₄ (Sulfuric Acid)	Nutrients, DOC
3.5 mL vial w/ 2 mL 1:1 HNO ₃ (Nitric Acid)	Metals

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Sampling Equipment	Applicable Parameter/Variable Group
47 mm magnetic filter funnel	Orthophosphate (as P), DOC
1 L Nalgene® flask	Orthophosphate (as P), DOC
Solid rubber stopper or cap (to fit 1 L Nalgene® flask, above)	Orthophosphate (as P), DOC
Peristaltic or vacuum pump	Orthophosphate (as P), DOC
Teflon® or Tygon tubing	Orthophosphate (as P), DOC
Weighted Bottle Sampler Setup	Direct grab ¹ , when needed
Pole Sampler	All, when needed
Nalgene® Bucket (or equivalent)	All ¹ , when needed
Sampling Supplies	Applicable Parameter/Variable Group
0.45 µm, 47mm sterile or non-sterile mixed cellulose ester filter	Orthophosphate (as P)
0.45 µm mixed cellulose ester capsule filter	Orthophosphate (as P)
0.45 µm, 47mm Nylaflo® or PES membrane filter	DOC
0.45 µm PES capsule filter	DOC
0.8 µm, 47mm Supor 800 PES membrane filter	DOC and ortho-P pre-filtering
0.7 µm glass fiber filter 47mm	Chlorophyll a
De-ionized water (DI)	Field and Rinsate Blanks
Ultra-pure de-ionized water (UPW)	Low-level Mercury Trip Blanks
Meter stick or other depth measuring device	Wetlands
Field sheets/Chain of Custody forms	All
Ice	All
Plastic food storage bags	All
Powderless latex/nitrile gloves	All
Sample storage coolers (hard-side and/or backpack)	All
Waterproof pens, Sharpies®, and pencils	All
Waterproof bottle label (such as Avery 5520, 5523)	All
Cable ties/Snapper Band	All, when needed

¹Nalgene® bucket may not be appropriate for all parameters. Some parameters (e.g. *E. coli*) require sample collection directly into the sample container. In those instances, a weighted bottle sampler, which allows direct sample collection, should be used.

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8.0 STEP-BY-STEP PROCEDURE

8.1 Sample Container and Identification

Several analyses may be performed using source water from one sample bottle (referred to as the variable group). All analytical parameters in one bottle must require the same sample bottle type and sample preservative type. In addition, when requesting multiple analyses from one sample bottle it is important to ensure that there is adequate volume in the sample bottle to complete all analyses and required QC. Variable group bottles should be delivered to the lab within the shortest holding time for the group of analytes. An example list of variable groups, bottle types, minimum required volume, and sample preservation requirements can be found in Table 2. The specific analytes within each variable group will vary depending upon project objectives and should be outlined in specific quality assurance project plans (QAPPs) (or their sub-documents) and must be described on the COC documentation. A full list of DEPS sample parameters and their required volumes, bottles, holding times, and preservation can be found in Appendix L of the DEPS LOQAM (2020).

Parameters not included in Table 2 may have collection method considerations not included in this SOP. When using this SOP to collect samples not specifically mentioned, any modifications to the procedure must be outlined in the QAPP (see Appendix A).

Information for every sampled site should be recorded on the bottle; either directly on the bottle surface, or on a waterproof bottle label. All marking should be done in black, permanent ink (Sharpie® marker, fine or medium point, or the equivalent). If the bottle is a QC sample of any type, the type should be clearly marked on the label.

At a minimum, the following information should be recorded on each sample bottle and/or label:

- Site ID
- Site Location
- County
- Date of Collection (formatted dd/mm/yy)
- Time of Collection (formatted in 24 hour)
- Sample Collectors (initials, full names maintained in QAPP)
- Analysis Parameters or Variable Group (i.e. Bulk, Nutrients, Metals, etc.)
- Preservation Method

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Table 2. List of variable groups (and parameters commonly analyzed from each group) sampled by DOW, along with their collective required volume, bottle type, preservation, and any special handling information. See Appendix B for DEPS method number and EPA approved reference method for listed parameters. For details about specific parameters, or parameters not listed here, see Appendix L of the latest DEPS LOQAM (2020) or 40 CFR 136.

Variable Groups	Parameters ¹	Bottle Volume and Required Type for Group	Preservation ¹	Special Handling	Holding Time ¹
Alkalinity	Acidity, Alkalinity as CaCO ₃ , Bicarbonate as CaCO ₃ , Carbonate as CaCO ₃	500 mL plastic (or glass)	Cool to ≤6°C	No headspace	14 days
Bulk	CBOD, Bromide, Chloride, Conductivity, Fluoride, Nitrate, Nitrite, Orthophosphate, Sulfate, Total Dissolved Solids, Total Suspended Solids, Turbidity	1 L plastic (or glass)	Cool to ≤4°C	none	Varies for parameters listed
Chlorophyll <i>a</i>	Chlorophyll <i>a</i> , Phycocyanin	250 mL plastic amber	Cool to ≤4°C	Must be filtered within 24 hours of sample collection (in field or in lab); sample is the filter	24 hours
DOC	Dissolved total organic carbon (DOC)	60 mL glass amber bottle with PTFE seal, pre-cleaned	H ₂ SO ₄ pH<2 (1 mL); Cool to ≤4°C	Filter in the field, sample is the filtrate; trip blank required	28 days
Dissolved Orthophosphate	Orthophosphate (as P)	60 mL plastic (or glass)	Cool to ≤4°C	Filter in the field, sample is the filtrate	48 hours
Bacteria	<i>Escherichia coli</i> (<i>E. coli</i>), Fecal Coliforms	120 mL sterile container, plastic or glass	Cool to <10°C	Do not pre-rinse bottles; direct sampling method required	8 hours
Herbicides	Herbicides (e.g. Acifluorfen, Bentazone, Dinoseb, Pentachlorophenol) and Caffeine	1 L amber glass bottle with PTFE seal	Cool to ≤6°C	Equipment rinsate blank required if sampling device is used	7 days
Low-level Mercury ²	Low-level Mercury	250 mL pre-cleaned glass with PTFE lined caps in bag	5 mL/L 12N HCl pH<2 (1.25 mL)	UPW trip blank required	28 days
Metals	Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Hardness, Iron, Lead, Manganese, Magnesium, Mercury, Molybdenum, Nickel, Potassium, Selenium, Silver, Sodium, Thallium, Vanadium, Zinc	500 mL plastic (or glass)	HNO ₃ (1:1) pH<2 (2 mL); Cool to ≤4°C	none	28 days or 6 months (depends on parameter)
Nutrients	Ammonia, Nitrate-Nitrite, Total Kjeldahl Nitrogen, Total Organic Carbon, Total Phosphorus	500 mL plastic (or glass)	H ₂ SO ₄ pH<2 (1 mL); Cool to ≤4°C	none	28 days
Pesticides and PCBs	Pesticides (e.g. Atrazine, Chlorpyrifos, Endosulfan, Permethrin, Propachlor, Simazin) and PCBs	1 L amber glass bottle with PTFE seal	Cool to ≤4°C	Do not pre-rinse; equipment rinsate blank required if sampling device is used	7 days

¹See DEPS LOQAM (2020) and specific reference methods for details on holding times and preservation for water chemistry parameters listed. Chlorophyll and bacteria analyses follow DOW SOPs DOWSOP03048 (DOW, 2020) and DOWSOP03025 (DOW, 2018a), respectively.

²Some parameters require strict contamination control measures during sample collection that are not fully outlined in this SOP. Refer to 40 CFR 136 and EPA approved methods (EPA 1631E (EPA, 2002) and EPA 1669 (EPA, 1996)) for full requirements.

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8.2 Sample Collection

Depending on the varying conditions during a sample collection event, samples may be collected from different locations relative to the waterbody and using a variety of sample collection gear. Sampling gear may be direct (sample is collected directly into the sample container) or indirect (sample is collected into a secondary container, which is then used to fill the sample container(s)).

Sample collection locations include:

- 1) wading,
- 2) sampling from the bank,
- 3) sampling from a bridge, and
- 4) sampling from a boat.

From any of those locations the following sampling gear or method may be used:

- 1) sample collection by hand (dipping the sample container directly into the stream or wetland to collect sample water),
- 2) pole sampler (where a sample container is attached to the end of a pole which is extended to the desired sampling location),
- 3) weighted bottle sampler (sample container is secured into a weighted sampler which is lowered into the water at the sample collection location), and
- 4) Nalgene® bucket (or equivalent) (a clean bucket is lowered into the sample water at the desired location and filled with sample water which is then used to fill the sample containers – this is the only method described in this SOP that is indirect).

Which location and type of sampling gear used depends on the project objectives and sampling station conditions and is at the discretion of the field technicians collecting the sample. Directly filling a sample container with sample water is always preferred, and in some cases (e.g. bacteria) may be required. Project sampling method priorities and/or limitations should be described in project study plans.

Water samples should be collected at mid-depth. If samples are unable to be collected at mid-depth, collection depth should be recorded on datasheets and included in data entry.

8.2.1 Wetland Considerations for Grab Sampling

If surface water is present in the assessment area it must meet the following criteria in order to be sampleable:

- Deep enough to collect a sample without fouling the water (about 15 cm). Sample collection may be attempted at shallower depth, however, extreme care must be taken to not allow contamination from disturbed sediments. If samples are contaminated with sediments, bottles can be emptied and re-rinsed with un-disturbed sample water

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and collection can be attempted again. However, if final samples are contaminated with sediments, the sample should be discarded and the site marked as “not sampleable” on the field form (also, see Table 3, (8) and (9)).

- Not fouled from wading, sampling, or otherwise accessing the site (i.e., water clarity should be representative of the natural condition of the wetland, which may include turbid water that results from flooding),
- Collector(s) can sample from a safe location (i.e., surface water is ≤ 1 meter deep, substrate is relatively stable).

The preferred sampling location is in an area that is representative of the assessment area as a whole. If standing water is not present at the most representative location within the assessment area, samples may still be collected from a location that is representative of the habitat where standing water is present. In this situation, the collector should note why the sampling location selection deviated from the preferred location.

The sampling location should be near the center of the water body and away from inlets and outlets with flowing water if these features are not representative of the assessment area. If flowing water is representative of the area containing standing water, sampling may occur in these areas.

The preferred sampling method is using a pole sampler from the edge of the wetland. Approach the edge of the standing water area but do not enter the water to avoid disturbing sediments, falling in, or fouling the water and potentially contaminating or otherwise compromising the quality of the water sample. If it is not possible to sample from the edge, collect samples from within the wetland, but at a location that does not disturb the substrate.

Collect samples from a location that is completely free of surface debris or floating vegetation. If surface debris or vegetation are present, slowly and carefully push it aside with the pole sampler. Use care not to disturb bottom sediments when collecting or pushing aside surface debris or vegetation. If bottom sediments become disturbed, move to another representative location.

8.2.2 Grab Samples for Water Chemistry

Wading for Water Chemistry

Lotic (in stream): Grab samples should be collected in the centroid of flow in a section of stream in which indicators of complete mixing are evident. The sampler should face upstream and approach site from downstream ensuring no disturbed streambed sediment contaminates the sample. If additional work is planned upstream of the sample site, the water samples should be collected prior to any other sampling or upstream of any disturbance. If neither of those options are possible, samples may be collected a reasonable amount of time after any

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streambed disturbance. A reasonable amount of time is dependent upon instream conditions and should be determined using best professional judgement. Care should be taken not to displace the preservative if the bottle is pre-preserved.

Wetland: See section 8.2.1 for detailed wetland sampling considerations. If sampling while wading (pole sampler is preferred), enter the water slowly and step carefully to minimize disruption of sediment. Sampler should be careful to avoid collecting water impacted by the plume of sediment disturbed. Similar to wading in streams for sample collection, if there is noticeable water flow within the wetland, the sampler should face the direction of flow, and approach the sample location from “downstream”. If additional work is planned “upstream” of the sample location, water samples must be taken first.

The following procedure for collecting grab samples should be followed:

- Don gloves.
- For containers requiring rinsing:
 - Fill the bottle ~¼ full.
 - Loosely cap, shake the bottle, and discard water downstream. Repeat for a total of three rinses.
- Do not rinse pre-treated or specialized sampling bottles unless specified.
- *Lotic:* Sample at mid-depth from a well-mixed area in stream (generally mid-channel or, if possible to determine, the thalweg of the stream reach).
- *Wetland:* See section 8.2.1 for sampling location details.
- Remove cap, point mouth of bottle down and submerge fully, when the desired depth is reached, rotate the bottle to point away from the sampler (upstream if lotic), allow the bottle to fill, lift the bottle from the water.
- Bottles should be filled to the base of the neck except for when collecting for acidity and/or alkalinity, which should have no headspace. See section 8.2.3 for details.
- If waterbody is too shallow to fill bottle while submerged, fill as much as possible while submerged, ensuring the minimal amount for analysis is obtained (see also Table 3, (8)).
- Cap bottle.
- All samples should be preserved within 15 minutes of collection according to the requirements outlined in 40 CFR 136 (Table II, footnote 2). See section 8.3 for details.

Pole Sampler for Water Chemistry

If a stream is not able to be safely waded, grab samples should be obtained with a pole sampler (diagram in Appendix C). For wetlands, using a pole sampler is the preferred sampling gear. Samples taken using the pole sampler should be obtained using the following steps:

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- Don gloves.
- For containers requiring rinsing, it is easiest to rinse containers from the bank prior to using the pole sampler:
 - Fill the bottle ~¼ full.
 - Loosely cap and shake the bottle and discard water. Repeat for a total of three rinses.
- Rinse the bottle holder end of the pole sampler three times with native water.
- Using zip ties or a snapper band, attach one bottle to the bottle holder at the end of the pole sampler.
- Uncap bottle and extend the pole to the desired length in order to reach the desired sampling location.
- Submerge the bottle to desired depth (typically mid-depth for water chemistry samples, ~10cm sub-surface for bacteria), fill with water, swing full bottle to the bank, and cap. *Care should be taken not to displace the preservative if the bottle is pre-preserved.*
- Fill water chemistry bottles to the base of the neck except for when collecting for acidity and/or alkalinity, which should have no headspace. See Section 8.2.3 for details.
- Cap bottle.
- Repeat this method with each sample bottle.
- All samples should be preserved within 15 minutes of collection according to the requirements outlined in 40 CFR 136 (Table II, footnote 2). See section 8.3 for details.

Weighted Bottle Sampler for Water Chemistry

When a stream is not wadeable or accessible from the bank or by boat, direct grab samples can be obtained by lowering a weighted bottle sampler (WBS) from a bridge (see Appendix D). Safety vests should be worn, so that collector is visible to passing motorists. Collectors should not collect samples from bridges with high traffic volume or if the situation is considered unsafe. This method is specifically designed to allow direct sampling from a bridge where required. Samples taken using a weighted bottle should be obtained using the following steps:

- Don gloves.
- Rinse the WBS three times with reagent water.
- Using cable ties or a snapper band, attach bottle(s) to WBS (*if WBS has the capacity to fill multiple bottles at once, ensure that all bottles have the same rinsing and sample location and depth requirements*).
- For bottles that require rinsing, uncap bottle(s) and gently lower the WBS (avoid overhanging vegetation) to the desired sampling location (a well-mixed area in the stream; if possible to determine, the thalweg of the stream reach).
 - Allow the bottle(s) to fill at least ¼ full.
 - If unable to tip bottles while suspended: carefully raise the WBS, cap bottle(s), shake to rinse, and discard rinse water. Repeat for a total of three rinses.

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- If able to tip bottles while suspended: shake to rinse, discard rinse water by inverting bottles. Repeat for a total of three rinses.
- To obtain sample water, carefully lower uncapped bottles in WBS to the desired sampling location.
- Submerge the bottle(s) to desired depth, allow time to fill with sample water, and carefully pull the WBS up, being careful not to touch the sampler against the surface of the bridge or overhanging vegetation to avoid sample contamination.
- Bottles should be filled to the base of the neck except for when collecting for acidity and/or alkalinity, which should have no headspace. See Section 8.2.3 for details.
- Cap bottle.
- Repeat this method with each sample bottle.
- All samples should be preserved within 15 minutes of collection according to the requirements outlined in 40 CFR 136 (Table II, footnote 2). See section 8.3 for details.

Nalgene® Bucket for Water Chemistry

When a stream is not wadeable, or accessible from the bank or by boat, grab samples may be obtained by dropping a Nalgene bucket (NB) from a bridge. Safety vests should be worn, so that collector is visible to passing motorists. Collectors should not collect samples from bridges with high traffic volume or if the situation is considered unsafe. Collecting the water sample should be done before *in situ* data is collected to prevent contamination of the sample.

Note: secondary collection vessels cannot be used for samples to be analyzed for bacteria. Decisions about the acceptability of using an indirect sampling method for other parameters should be discussed in project study plan.

The following procedures should be used to obtain samples using a NB:

- Affix an appropriate length of clean rope for the collection site to the bucket handle.
- Rinse bucket three times with ¼ bucket full of reagent water.
- Gently lower the bucket (avoid overhanging vegetation) to the desired sampling location (a well-mixed area in the stream; if possible to determine, the thalweg of the stream reach).
- Obtain a partial bucket of water.
- Raise bucket just above the stream surface and shake to rinse.
- Repeat rinsing process for a total of three rinses.
- Lower bucket back into the stream and obtain a full bucket of water in the desired location (a well-mixed area in the stream; if possible to determine, the thalweg of the stream reach).
- Pull bucket up, being careful not to touch the bucket against the surface of the bridge or overhanging vegetation to avoid sample contamination.

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- Once the sample has been safely obtained, don gloves and begin rinsing the sample bottles (that require rinsing) with the sample water by pouring a small amount of water from the bucket into the sample bottle.
 - Fill each bottle $\sim\frac{1}{4}$ full.
 - Loosely cap and shake each bottle and discard water. Repeat for a total of three rinses.
- Gently swirl the bucket before pouring sample water into each container to ensure the water is well mixed. Avoid touching the sample bottle with the bucket when pouring.
- Bottles should be filled to the base of the neck except for when collecting for acidity and/or alkalinity, which should have no headspace. See section 8.2.3 for details.
- Cap bottle(s).
- If more water is required to fill all required sample bottles, lower the bucket and obtain another bucket full of water.
- All samples should be preserved within 15 minutes of collection according to the requirements outlined in 40 CFR 136 (Table II, footnote 2). See section 8.3 for details.

8.2.3 Special Instructions for Filling and Capping Bottles

Unless bottles specifically require no headspace, sufficient air space for mixing should be present in capped bottles. If bottles are overfilled, sample water may be poured off to reach the desired level before capping (except where prohibited by analytical method).

To fill a bottle with no headspace:

- Under water:
 - while the bottle is submerged and upright, submerge the cap and turn it upside down to release any bubbles that may be in the lid, then cap the bottle while still submerged.
- If the water is too shallow to fully submerge, or if bottle was filled using a pole sampler, WBS, or Nalgene Bucket
 - fill the bottle to the highest extent – if possible, over-fill to create a convex meniscus,
 - if plastic, loosely cap bottle and **gently** squeeze to expel air while tightening cap (*caution – expelling air with this method will negatively impact sample volume*).
 - If glass, carefully cap over-filled bottle.

After filling, invert the bottle to check for air bubbles. If detectable air is present, additional sample water should be added or the bottle should be re-filled (unless bottle rinsing is prohibited, in which case a new bottle should be used to collect a new sample).

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8.2.4 Filtrate Samples

Some analyses may require the collector to filter the water sample prior to delivering it to the lab. Kentucky Division of Water currently utilizes two techniques for filtering water samples: vacuum and peristaltic. A quick reference for vacuum filtering can be found in Appendix E.

The following should be taken into consideration when collecting filtered samples:

- Gloves should be worn while processing samples to prevent cross contamination.
- Filtering apparatus should be set up in such a manner to prevent environmental contamination (if filtering at the vehicle, turn vehicle off; use a relatively clean, flat, stable surface, and keep parts in clean plastic bags until use).
- Each filtered analyte has specific filter requirements. Dissolved orthophosphate requires a phosphate-free 0.45µm pore size membrane filter. DOC requires a 0.45µm pore size membrane filter that does not significantly contribute nor remove carbon from the sample. Pall Supor® membrane filters were selected based on DOC research by Karanfil, et.al. (2003) and Khan and Subramania-Pillai (2006); these filters are also phosphate-free.
- DOW filters by parameter/purpose are:
 - Pre-filter (when needed) for both DOC and Othro-P: 0.8 µm, 47mm Supor® 800 (PES) membrane filter
 - DOC: 0.45 µm, 47mm Nylaflo® or Supor® 450 (PES) membrane filter
 - Dissolved orthophosphate (as P): 0.45µm 47mm mixed cellulose ester filter
- Samples must be filtered prior to adding preservatives.
- Samples should be filtered and preserved within 15 minutes of collection according to the requirements outlined in 40 CFR 136 (Table II, footnote 2).
 - Consider the travel time from a sample site to the vehicle and the time needed to filter samples. If necessary, carry filter equipment (in clean plastic bags) to the sample site.
- These directions are specific to collecting filtrate for dissolved orthophosphate (as P) and DOC. Filtering for any other analyte may require additional steps or precautions.
- Filtered samples are typically taken from the “Bulk” parameters bottle. However, care should be taken to ensure that the volume requirements for bulk analyses are met. A separate bottle may be dedicated to the collection of sample water for filtering, if necessary. Which sample bottle is used to provide water for filtering depends on project decisions and should be defined in program management or project study plans.
- Pre-filtering sample water using a larger pore size filter is appropriate if the water is extremely turbid or if initial filtering efforts using the 0.45 µm fail. Two filter flasks are required when pre-filtering.

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Vacuum Technique

- Collect the sample using appropriate sample methodology.
- Triple rinse funnel, funnel filter base, and flask with reagent water.
- Single rinse the forceps with reagent water.
- Attach filter base to flask and connect the tubing from the vacuum pump.
- Use clean forceps to place appropriate filter onto funnel filter base.
- Pour 100 mL reagent water into funnel (Khan and Subramania-Pillai, 2006).
- Filter, rinse flask, and discard reagent water filtrate.
- Invert the bottle of sample water several times to mix.
 - This step can be skipped if no other, non-filtered analytes will be tested from this bottle.
- Pour 50 mL of the sample water into funnel (Karanfil et al., 2003).
 - This volume can be reduced to 25 mL under conditions of extreme turbidity.
- Filter, rinse flask, and discard sample water filtrate.
- Pour enough sample water into the funnel to provide enough finished sample for rinsing the sample bottle and for analysis (100-150 mL per analyte bottle).
 - If pre-filtering, add 50 mL to allow for second filter rinse.
- Filter and:
 - If pre-filtering, remove funnel apparatus and insert reagent water-rinsed stopper into pre-filtering flask. Begin process again at step 2 with a second flask and use the appropriate final filter.
 - If final filtering, continue with the next step.
- Fill an appropriate sample bottle $\frac{1}{4}$ with the sample water filtrate.
- Loosely cap bottle, shake vigorously, and discard rinse water.
- Repeat for total of three rinses.
- Fill the sample bottle with filtered sample water to the appropriate level.
 - The base of the bottle shoulder (to allow for water expansion during freezing) for orthophosphate samples.
 - The base of the bottle neck for DOC samples (to allow for mixing).
- Cap bottle.
- Preserve sample accordingly.
- All samples should be preserved within 15 minutes of collection according to the requirements outlined in 40 CFR 136 (Table II, footnote 2). See section 8.3 for details.

Peristaltic Pump Technique

- Collect the sample using appropriate sample methodology.
- Triple rinse tubing inside and out with reagent water.
- Set up peristaltic pump and attach tubing.
- Attach appropriate capsule filter to one end of the tubing.

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- Place the free end of the tubing in a reagent water source (*not the same container used for filling QC blank samples*). Hold the filter end over a waste container. Turn on the pump and run at least 100 mL of reagent water through the tubing and through the filter in order to rinse (Khan and Subramania-Pillai, 2006).
- Leaving the pump running, remove the tubing from the reagent water source and drain as much of the fluid remaining in the system as possible. Shaking the capsule filter may facilitate removal of the entrained water.
- Invert the bottle of sample water several times to mix.
 - This step can be skipped if 1) this is not a composite sample, and 2) no other, non-filtered analytes will be tested from this bottle.
- Place the free end of the pump tubing into the bottle containing the sample water.
- Filter about 50 mL of sample water into the waste container (Karanfil et al., 2003).
 - This volume can be reduced to 25 mL under conditions of extreme turbidity.
- If bottle requires pre-rinsing, transfer capsule filter over an empty sample bottle opening and filter enough to fill ¼ full. Cap and shake bottle to rinse and discard rinse water. Repeat for a total of three rinses.
- Transfer capsule filter over the rinsed sample bottle and fill to the appropriate level.
 - The base of the bottle shoulder (to allow for water expansion during freezing) for orthophosphate samples.
 - The base of the bottle neck for DOC samples (to allow for mixing).
- Cap bottle.
- Preserve sample accordingly.
- All samples should be preserved within 15 minutes of collection according to the requirements outlined in 40 CFR 136 (Table II, footnote 2). See section 8.3 for details.

8.2.5 Bacteria Samples

Water samples collected for analyzing bacteria should be collected in the centroid of flow in a section of stream where complete mixing is evident. The sampler should face upstream and approach the site from downstream ensuring no disturbed streambed sediments contaminate the sample. If additional work is planned upstream of the sample site, the water samples must be taken first, or collected upstream of any instream disturbance. Gloves must always be worn to minimize cross contamination.

Bottles may be pre-preserved with sodium thiosulfate. While not required for surface water samples, it may be appropriate to use it in some situations (if sampling in areas where chlorine levels are suspected to be high), and care should be taken while sampling to make sure the preservative is not lost. The presence of this preservative in ambient samples without elevated chlorine levels will not negatively impact sample results.

The following procedure for collecting water for bacteriological analysis should be followed:

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In stream or Pole Sampler

Note: if using a pole sampler, follow the same directions described below, only attach the bottle to the bottle holder at the end of the pole sampler (as described in Section 8.2.2 above) prior to extending the bottle to the desired sampling location.

- Use sterile and pre-labeled sample bottles. Do not pre-rinse prior to collecting the sample.
- Point the mouth of the bottle directly over the surface of the water. If the bottle contains a preservative, angle the mouth so as not to spill the preservative.
- Dip and draw the bottle approximately 10cm beneath the water surface, and through the water column in one swift motion, such that the bottle is filled to the inscribed 'fill line'.
- Do not pour off excess water if the bottle is filled above the 100 mL fill line.
- If adequate volume is not obtained on first effort, do not reuse the bottle. Use a new, un-contaminated bottle and repeat the procedure.
- Close and secure the sample bottle lid immediately.
- All samples should be preserved within 15 minutes of collection according to the requirements outlined in 40 CFR 136 (Table II, footnote 2). See section 8.3 for details.

Weighted Bottle Sampler

If a stream is not wadeable then a weighted bottle set-up should be used following the methodology described below (see Appendix D). Gloves should always be worn to minimize cross contamination.

- Use sterile and pre-labeled sample bottles. Do not rinse prior to collecting the sample.
- Insert and secure the sample bottle directly to the weighted bottle sampler.
- Lower the bottle to a well-mixed area of the stream.
- Collect sample by approximating a 'sweeping' motion upstream through water.
 - The object of the 'sweeping' motion is to minimize contamination from the sampling equipment, minimize the collection of surface scum, avoid spilling the sample, all while sampling at a sub-surface depth. Whatever technique a sampler uses to maximize these objectives is acceptable.
- Pull bottle up, being careful not to touch the bottle against the surface of the bridge or overhanging vegetation to avoid sample contamination.
- Do not pour off excess water if the bottle is filled above the 100 mL fill line.
- If an adequate volume is not obtained on first effort, do not reuse bottle; use a new, un-contaminated bottle and repeat the procedure.
- Close and secure the sample bottle lid immediately.
- All samples should be preserved within 15 minutes of collection according to the requirements outlined in 40 CFR 136 (Table II, footnote 2). See section 8.3 for details.

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8.3 Sample Preservation

All surface water samples should be collected in the appropriate bottles and preserved in the correct manner, as dictated by 40 CFR 136. Sample preservation should occur within 15 minutes of collection in the field (40 CFR 136, Table II, footnote 2), including placement in a cooler with wet ice. All labels on sample containers that have been preserved with chemicals must include the type of preservative used.

Refer to the *Sample Control and Management SOP* (DOW, 2021) for specific requirements for sample preservation documentation as it pertains to chain-of-custody records.

8.3.1 Acid Preservation

When samples require the addition of an acid preservative, the following steps should be followed:

Pre-measured Aliquot Technique

- Don gloves.
- Carefully open one sample container.
 - If there is not sufficient headspace for mixing, pour a small amount of sample water out of the bottle (after mixing) before adding acid.
 - If the lid must be set down, place it top down on a clean surface.
- Carefully open the lid to the acid container and pour contents into the sample bottle without touching the inside of the sample bottle.
 - Replace cap on acid vial prior to disposing in a waste container.
- Securely re-cap the sample bottle and invert several times to mix.
- Remove and dispose of gloves.

Dropper Bottle Technique

- Don gloves.
- Carefully open one sample container.
 - If there is not sufficient headspace for mixing, pour a small amount of sample water out of the bottle (after mixing) before adding acid.
 - If the lid must be set down, place it top down on a clean surface.
- Gently shake acid dropper bottle, carefully open the lid and invert acid container over the sample bottle without touching the inside of the sample bottle.
- With the acid dropper bottle held vertical (not held at an angle), gently squeeze and count the number of drops that fall into the sample bottle until the appropriate volume has been added.
- Securely re-cap the acid bottle.
- Securely re-cap the sample bottle and invert several times to mix.
- Remove and dispose of gloves.

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Pipet Technique

- Don gloves.
- Carefully open one sample container and place lid top down on a clean surface.
 - If there is not sufficient headspace for mixing, pour a small amount of sample water out of the bottle (after mixing) before adding acid.
- Carefully open the lid to the acid container and place lid top down on a clean surface.
- Insert clean pipet into acid bottle and withdraw required amount of acid.
- Hold pipet tip over the sample container (do not place it in the water or touch the inside of the bottle) and release or drop the required amount of acid into the sample container.
- Securely re-cap the acid container and dispose of any used items such as a used pipet tip in an appropriate waste container.
- Securely re-cap the sample bottle and invert several times to mix.
- Remove and dispose of gloves.

8.3.2 Wet Ice Preservation

All samples should be placed upright in a cooler of wet ice for preservation and transport. Wet ice should be of sufficient quantity to cover all of the bottles (and small enough to be able to fill spaces between bottles) and maintain a temperature of 4°C from the time of sample collection until samples are delivered to the laboratory or prepared for shipment. Additional ice may need to be added if outdoor temperatures are very high or storage times are long (e.g. overnight). The use of ice packs as a substitute for wet ice should be avoided.

8.4 Sample Storage and Transport

Samples should be stored in containers that are free of possible contaminants. Sample bottles may be placed inside of sealed food grade plastic bags prior to being stored on ice in coolers if cross contamination is deemed a strong possibility (e.g. low level mercury).

Check that caps are secure before placing bottles upright in a clean, undamaged cooler. If the cooler has a plug, make sure it is securely sealed. Refer to the *Sample Control and Management SOP* (DOW, 2009) for specific requirements about sample storage and transport, including further details about sample shipment.

8.5 Chain of Custody

All surface water samples should be accompanied by accurate and traceable sample COC documentation. Refer to the *Sample Control and Management SOP* (DOW, 2021) for specific requirements.

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9.0 TROUBLESHOOTING

A list of problems that could occur while sampling surface water quality in lotic systems and the recommended solutions are listed in Table 3. Field staff should always use best professional judgement when problems occur while sampling.

Table 3. Troubleshooting

Problem	Solution
(1) A sample bottle is spilled during acid preservation.	<ul style="list-style-type: none"> • If the spill occurs prior to preservation, the volume of the sample after the spill reaches the neck of the sample bottle, and the likelihood of contamination is low, proceed with preserving the sample. • If the spill occurs prior to preservation and the volume does not reach the neck of the bottle, sampling should be repeated using the same bottle (unless bottle re-use is specifically prohibited). Triple rinse the bottle and follow the appropriate sampling procedure. • If the spill occurs after preservation, sampling should be repeated with a new bottle following the appropriate sampling procedure.
(2) Field staff does not have enough bottles to collect all the samples and is unable due to time and or distance to go back and get more supplies.	<ul style="list-style-type: none"> • Program management or project study plans should specify if any of these solutions are preferred, or unacceptable. If possible, contact the project coordinator for a decision before sampling. • If issue is noticed towards the end of a sampling run, a site could be dropped from the sampling trip, so that all the samples are collected at most of the sites. • A specific variable group (bottle) could be chosen to be dropped, if noticed at the beginning of the sampling run, and crossed off from all the stations on the COC. • If on an overnight sampling trip, contact closest regional office or closest WQB office and see if someone is available to deliver the necessary supplies. • Alert program coordinator of the error, so that they can determine whether resampling is necessary.
(3) Preservative is lost from a pre-preserved sample container.	<ul style="list-style-type: none"> • When sampling for bacteria in streams and wetlands, the sodium thiosulfate tablet is not required. If it is lost during sample collection, the sample can still be used. • If projects use other pre-preserved bottles, guidance from analytical reference methods should be determined and detailed in project plans.
(4) Field staff were unable to preserve the samples within 15-minute time requirement.	<ul style="list-style-type: none"> • Program management or project study plans should specify if any of these solutions are preferred, or unacceptable. • If possible, go back and collect new samples. • If not possible to collect new samples, mark the COC with a time flag, which DOW can enter into K-WADE during data entry, or cross off the COC and discard samples.

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Problem	Solution
(5) Field staff forgot DI/UPW or DI/UPW not available when gathering supplies for field day.	<ul style="list-style-type: none"> • For DI, find a store to purchase distilled water. It can be used as a substitute for DI in blanks and when filtering. • There is no suitable substitute for UPW, if required. • Use of any water other than the required reagent water must be noted on the COC. • If DI/UPW is unavailable while you are getting supplies ready for your field day refer to the study plan for the sites you are collecting and see if it would be possible to move your field blank to another sampling event. <ul style="list-style-type: none"> ○ It is best to make the study's program coordinator aware of your deviation from the study plan. This solution only works for sampling events that do not involve filtering or rinsing equipment.
(6) Field staff forgot DI for <i>E. coli</i> field blank.	<ul style="list-style-type: none"> • When there is no other alternative, unopened bottled water can be used for an <i>E. coli</i> field blank. • Purchase a bottle of water from a store near your sites or use a sealed bottle of bottled water that field staff has on hand for drinking water. • Use of any water other than the required reagent water must be noted on the COC.
(7) Filtering turbid water to collect filtrate (does not apply to <i>Chlorophyll a</i> filtering – see DOWSOP03048 (DOW, 2020).	<ul style="list-style-type: none"> • If sample water appears especially turbid, collect water for filtering in a separate sample bottle so that it does not need to be mixed before filtering (this may allow some of the heavier solids to settle in the bottle). • Pre-filter using the larger pore size filter (Supor 800) according to directions in this SOP. • When filtering turbid water it is best to use smaller increments in the event that you need to change the filter. • If the filter becomes so clogged with particles that you can't continue filtering, use the following procedures to change the filter: <ul style="list-style-type: none"> ○ Remove the funnel apparatus from the flask and carefully pour off any sample water left in the funnel, remove the used filter and discard, set aside. ○ Use any existing filtrate to triple rinse and fill the filter sample bottle. ○ Rinse filter funnel and flask with reagent water. ○ Place a new filter on the funnel base and rinse the filter with 50 mL of reagent water followed by 25 mL of sample water (see 8.2.3, Vacuum Technique) before continuing with filtering sample water in small increments. • If at any time unfiltered water contaminates the filtered sample, discard sample and begin filtering sample from the start.
(8) Water is too shallow to completely fill sample bottle	<ul style="list-style-type: none"> • In streams - sample collection may be shifted up or downstream according to project directives to find a deeper area of well-mixed water. • If sample bottles cannot be filled to the required level a bottle of the same material can be used to collect sample water and pour into another sample bottle (HDPE used to fill HDPE, and glass used to fill glass). There must also be no restrictions on pre-rinsing the bottle used for pouring (i.e. do not use a pesticide bottle, which should not be pre-rinsed, to fill another glass bottle, however, you could use an herbicide bottle to fill a pesticide bottle.) If this method is used, it should be noted on the field form and/or COC.

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Problem	Solution
(9) Site becomes disturbed from sampling activities prior to or during sample collection.	<ul style="list-style-type: none"> Do not collect sample water that has been contaminated with disturbed sediments from collection activities or other nearby human or animal activities. If in a stream: move upstream of disturbance within the sample reach (do not move above a significant tributary or other instream/watershed feature such as a point discharge or dam). Describe the new location and reasons for moving sample location on the field datasheet and/or COC. If in a wetland: if possible, move to an undisturbed area of the wetland that meets the requirements of sample collection objectives. Describe the new location and reasons for moving sample location on the field datasheet and/or COC.
(10) Dogs	<ul style="list-style-type: none"> If you are working a site and you encounter a friendly dog while working with multiple field staff, it is best if one staff member keeps the dog away from the other staff member who is collecting or preserving samples. If dogs enter the sample area and disturb sediments, be sure to collect samples from an undisturbed spot at the sample location, or move to another area, if needed. If you touch the dog with gloved hands prior to collecting or preserving samples make sure that you don a clean pair of gloves before you continue, so as not to inadvertently contaminate the sample. If you encounter an aggressive dog, do not attempt to begin, or abort in-progress sampling at the location. In K-WADE you will enter the data as not sampled due to unsafe location, and make comments explaining the situation in the station visit comments.
(11) Thunderstorms	<ul style="list-style-type: none"> Do not sample during thunderstorms. Check the weather; if possible wait out the storm in a safe location. Do not attempt to sampling if thunder has been detected in the previous 30 minutes. If the storms have set in and you can't wait it out, cross sites off COC. Depending on schedule and program guidelines, you may be able to reschedule the trip to the station. Consult with program coordinator, if necessary. Entire sampling trip may need to be repeated. If site cannot be revisited at another time, enter sites in K-WADE as not collected due to unsafe conditions. Note thunderstorms in the station comments.

10.0 DATA AND RECORDS MANAGEMENT

Results of water chemistry analyses performed by DEPS will be stored in their Laboratory Information Management System (LIMS) and a certified report will be sent to the sample collector, project coordinator, and program supervisor.

Results of bacteriological analysis performed by Water Quality Branch (WQB) personnel will be recorded as described in *Enzyme Substrate Test for the Detection of Total Coliforms and Escherichia coli in Ambient Waters* (DOW, 2018a).

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The results of water chemistry and bacteriological analyses performed by other laboratories should be mailed (physically and/or electronically) to the project coordinator.

Chain of Custody records for all samples delivered to the DEPS laboratory for analysis shall be retained using the guidelines established in *Standard Operating Procedure for Sample Receiving and Custody* (DEPS, 2014). Chain of Custody documents will be scanned and emailed to the sample collector. The custodian of the samples will keep and file the original COCs as stated in *Standard Operating Procedure for Sample Receiving and Custody* (DEPS, 2014). Copies of the original COC documentation submitted for shipped samples should be made prior to shipping the samples.

Copies of the original COC documentation submitted to contract laboratories shall be obtained at the time of delivery of the samples. These COC copies should be stored in project folders under the custodianship of the project coordinator or other designee.

11.0 QUALITY CONTROL AND QUALITY ASSURANCE

11.1 Quality Control

The types of quality control samples collected for various projects must be specified in the QAPP. The purposes of QC samples are to provide information on background conditions, isolate site effects, evaluate contamination during sample transit, or to evaluate field and laboratory variability. Types of QC samples may include:

Field Duplicate: Samples collected at the same time and place under identical conditions and treated identically throughout field and laboratory procedures. Results provide an estimate of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Split Sample: A sample created by initially collecting twice as much volume as is normally collected and then apportioning, after mixing, into two sets of containers. This type of sample is used to assess analysis variability.

Field Blank: A sample that is prepared in the field using the sample collection gear to fill an identical clean container with reagent water. This blank should be treated as a sample in all respects, including exposure to sampling site conditions, storage, preservations, and all analytical procedures. The sample is used to assess potential contamination from the environment (i.e. sample handling, container, or preservative), not associated with the source being sampled.

Field Rinsate Blank/Equipment Blank: A sample used to assess the possible contamination level of equipment that is field cleaned and re-used on-site. The sample is taken by rinsing field cleaned equipment with reagent water and collecting the rinse

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water to be submitted for analyses of all constituents that are normally collected using that piece of equipment.

Trip Blank: A sample used to assess the potential contamination level of sample storage containers during transit.

11.1.1 Field Duplicate Collection Procedure

When collecting a field duplicate QC sample, follow the exact same procedures for collecting the field sample. Ideally, the sample bottles will be submerged and filled at the same time. If concurrent sampling is not possible, the duplicate sample should be collected in the same location, at the same depth, and immediately following the field sample collection for that parameter group. Field duplicate bottles should be labeled as such and preserved in the same manner and at the same time as the associated field sample.

11.1.2 Field Blank Collection Procedure

To determine the appropriate reagent water to use, refer to Table 4 in section 11.2.2 or the associated analytical methods. Use regular sample bottles or high density polyethylene (HDPE) carboy, that have been triple rinsed with reagent water prior to filling, to transport reagent water as practicality dictates. Ensure sufficient volume to triple rinse and fill all QC sample bottles, and to rinse any equipment, as needed.

Bring reagent water bottles to the sampling site along with the regular sample bottles for the site and a matching set of bottles for the field blanks. Handle the empty field blank bottles in a similar manner as the regular sample bottles (e.g. if you carry the sample bottles in a backpack, the field blank bottles should be carried there as well).

'Direct Fill' Method

This method is used to create field blank samples any time one of the 'direct fill' sampling methods is used. These include grab samples collected by wading or using a pole sampler, WBS, or from a boat.

- Immediately before or immediately after collecting the field samples, prepare the field blank(s).
- Don a new pair of gloves.
- For containers requiring rinsing:
 - Fill the bottle ~¼ full with reagent water.
 - Loosely cap and shake the bottle and discard water. Repeat for a total of three rinses.
- Do not rinse pre-treated or specialized sampling bottles unless specified.
- If using equipment such as a pole sampler or WBS, attach empty field blank sample bottle to the equipment.

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- Fill each field blank bottle with reagent water to the base of the neck except for when collecting for acidity and/or alkalinity, which should have no headspace, and cap. See Section 8.2.3 for details.
- Record the sample time on the COC and be sure to indicate that it is a field blank on both the bottle and the COC.
- Field blanks should be preserved, transported, and stored in the same way as the regular sample bottles.

Nalgene® Bucket Method

note: this method may serve as a field blank or an equipment rinsate blank

Blanks for samples collected using a NB should be performed using the following procedure:

- Immediately after collecting the field sample(s), prepare the field blank(s).
- Don a new pair of gloves.
- Rinse NB three times with ¼ bucket full of reagent water.
- For containers requiring rinsing:
 - Fill the bottle ~¼ full with reagent water.
 - Loosely cap and shake the bottle.
 - *In order to conserve sample water, the rinse water can be used in all sample bottles, in succession.*
 - Discard rinse water.
 - Repeat for a total of three rinses.
- Do not rinse pre-treated or specialized sampling bottles unless specified.
- Fill bucket with sufficient reagent water to fill each blank bottle.
- Gently swirl the bucket before pouring blank water into each container to ensure the water is well mixed. Avoid touching the sample bottle with the bucket when pouring.
- Fill bottle to the base of the neck except for when collecting for acidity and/or alkalinity, which should have no headspace, and cap. See Section 8.2.3 for details.
- Record the sample time on the COC and be sure to indicate that it is a field blank on both the bottle and the COC.
- Field blanks should be preserved, transported, and stored in the same way as the regular sample bottles.

11.1.3 Trip Blank Collection Procedure

Trip blanks for DOW are typically only used when collecting low-level mercury and DOC (low-level mercury blanks require UPW). However, trip blanks may be used with any parameter and in those instances, alternate reagent water may be required. To determine the appropriate reagent water to use, refer to Table 4 in section 11.2.2 or the associated analytical method.

Trip blank bottles should be prepared in the lab prior to departure for field sampling. The trip

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blank should be stored in the same cooler as the sample bottles for the entire sampling trip. If multiple coolers are used during the sampling trip, the trip blank must be placed in each cooler for a portion of the sampling trip and shipment.

- Don gloves.
- For containers requiring rinsing:
 - Fill the bottle $\sim\frac{1}{4}$ full with appropriate reagent water (see Table 4).
 - Loosely cap and shake the bottle and discard water. Repeat for a total of three rinses.
- Do not rinse pre-treated or specialized sampling bottles unless specified.
- Fill bottle to the base of the neck with reagent water except for when collecting for acidity and/or alkalinity, which should have no headspace, and cap. See Section 8.2.3 for details.
- Trip blanks should be preserved, transported, and stored in the same way as the regular sample bottles.

11.1.4 Filtering Equipment Rinsate Blank Procedure

Equipment rinsate blanks for filtering equipment should be performed using the following procedure:

Note: If this procedure is completed prior to the filtering of sample water, this filter and set-up can be used for filtering sample water without further rinsing with reagent water.

Vacuum Technique

- Triple rinse funnel, funnel filter base, and flask with reagent water.
- Single rinse the tubing (inside and out) and forceps with reagent water.
- Attach filter base to flask and connect the tubing from the vacuum pump.
- Use clean forceps to place appropriate filter onto funnel filter base.
- Pour 50 mL reagent water into funnel.
- Filter, rinse flask, and discard reagent rinse water.
- Pour enough reagent water into the funnel to provide enough finished water for rinsing the rinsate blank bottle and for analysis (100-150 mL).
- Filter and fill an appropriate sample bottle $\frac{1}{4}$ with the filtered reagent water.
- Loosely cap bottle, shake vigorously, and discard rinse water.
- Repeat for total of three rinses.
- Fill the sample bottle with filtered reagent water to the appropriate level and cap.
 - The base of the bottle shoulder (to allow for water expansion during freezing) for orthophosphate samples.
 - The base of the bottle neck for DOC samples (to allow for mixing).
- Preserve sample accordingly.

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- All samples should be preserved within 15 minutes of collection according to the requirements outlined in 40 CFR 136 (Table II, footnote 2). See section 8.3 for details.

Peristaltic Pump Technique

- Triple rinse tubing inside and out with reagent water.
- Set up peristaltic pump with tubing.
- Attach appropriate capsule filter to one end of the tubing.
- Place the free end of the tubing in a reagent water source (*not the same container used for filling QC blank samples*). Hold the filter end over a waste container.
- Filter about 100 mL of reagent water into the waste container (Khan and Subramania-Pillai, 2006).
- If bottle requires pre-rinsing, transfer capsule filter over an empty rinsate blank bottle opening and filter enough to fill ¼ full. Cap and shake bottle to rinse and discard rinse water. Repeat for a total of three rinses.
- Fill the blank bottle with filtered reagent water to the appropriate level and cap.
 - The base of the bottle shoulder (to allow for water expansion during freezing) for orthophosphate samples.
 - The base of the bottle neck for DOC samples (to allow for mixing).
- Preserve sample accordingly.
- All samples should be preserved within 15 minutes of collection according to the requirements outlined in 40 CFR 136 (Table II, footnote 2). See section 8.3 for details.

11.2 Quality Assurance

11.2.1 Cleaning Field Equipment

The following procedures have been adapted from Chapter A3 of the *USGS National Field Manual* (Wilde, 2004) and the *USGS Field Guide for Collecting and Processing Stream-Water Samples for the National Water-Quality Assessment Program* (Shelton, 1994) and vary depending upon the types of samples that are collected using the equipment. If the following cleaning procedures are insufficient, see the aforementioned references for more in-depth cleaning procedures. All detergent used for cleaning equipment must be certified phosphate-free. Cleaning may be needed if contamination is suspected (e.g. rinsate or field blank does not meet acceptance criteria) or known (e.g. sample water was not promptly rinsed from sampling or filter equipment and dried upon the surface, fowling is visible, storage and/or transport conditions were contaminated).

Two HDPE washbasins are available and should be pre-cleaned using the same technique (one labeled “Detergent Wash” and one labeled “DIW”). Prepare a clean surface for drying equipment by either following the same technique below or placing clean aluminum foil (dull side up) on the surface.

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Orthophosphate and DOC Filtering Equipment

During routine field sampling a prompt and thorough triple rinse with reagent water should be sufficient to maintain decontamination of the filter funnel, flask, and pump tubing. However, when the filter funnel, tubing, flask, and reagent water storage bottles need to be cleaned use the following technique.

Detergent Wash and Tap Water Rinse

- Don gloves.
- Place equipment in “detergent wash” basin and soak equipment in a 0.1 - 0.2 percent phosphate-free detergent/tap water mix for 10-30 minutes.
- Fill tubing with solution and keep submerged for 10-30 minutes.
- Scrub exterior and interior surfaces of equipment.
- Rinse thoroughly with warm tap water to remove detergent residue and place in clean “reagent water” basin.

Reagent Water Rinse

- Don a new pair of gloves.
- Rinse all equipment and tubing thoroughly with reagent water.
- Place onto a clean surface to dry.

Clean Equipment Storage

- Store filter equipment in a clean bin. Use clean plastic bags to minimize contamination during storage and transport.

Weighted Bottle Samplers

Weighted bottle samplers must be inspected and documented each week of use to ensure that the equipment is working properly. The samplers should be inspected for any areas where paint may be chipping away to eliminate/reduce the chance of contaminating metals samples and should be repainted with epoxy-based paint as needed.

During routine field sampling, a prompt and thorough triple rinse with reagent water should be sufficient to maintain decontamination of weighted bottle samplers. However, when the WBS need to be cleaned, use the following technique.

Detergent Wash and Tap Water Rinse

- Don gloves
- Place WBS in a basin labeled “detergent wash” and soak equipment in a 0.1-0.2 percent phosphate-free detergent/tap water mix for 10-30 minutes

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- Scrub exterior and interior surfaces of equipment
- Rinse thoroughly with warm tap water to remove detergent residue and place in clean “reagent water” basin.

Reagent Water Rinse

- Don a new pair of gloves
- Rinse with reagent water
- Place onto a clean surface to dry

Clean Equipment Storage

- Store WBS in a clean bucket

Pole Sampler, Storage Containers, Coolers, and Other Equipment

Equipment and storage bins/containers used to house equipment within vehicles may need to be cleaned and can be cleaned following the directions outlined above. If the items are too large to soak in a basin, use the following method:

Detergent Wash and Rinse

- Don gloves.
- Use a scrub brush and tap water rinse to remove surface dirt and films.
- Clean with phosphate-free detergent, allowing 30-60 seconds of contact time with detergent, before rinsing with tap water.
- Rinse again with reagent water.
- Place onto a clean surface to dry.

For soft items that can be laundered, a small amount of fragrance free detergent should be used.

11.2.2 Sampling Supplies

Proper documentation for supplies (e.g. recording lot numbers and expiration dates), running appropriate blanks on supplies, discarding expired supplies, and reporting to the appropriate branch quality assurance coordinator (QAC) and/or DOW quality assurance officer (QAO) the results of any problems and corrective actions is the responsibility of the designated Supply Manager.

Sample bottles shall be stored in such a manner to prevent unintentional contamination. Boxes of bottles shall remain closed until their use is required. Bottles are to be stored within original shipping containers and should not be stored on bare floors. Loose bottle caps must be stored in sealed containers or re-sealable storage bags. Any certified, pre-cleaned bottles should be stored with lids sealed from supplier.

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Water Chemistry Sample Bottles, Filters, and Acids

Contamination levels may be tested for every new lot of sample bottles, filters, and acid preservatives. Bottles that are not certified pre-cleaned may be triple-rinsed and filled with the appropriate reagent water and preserved appropriately. Certified pre-cleaned bottles should not be triple-rinsed prior to being filled with reagent water and preserved appropriately. When checking for bottle or preservative contamination, bottle should be labeled as “bottle blank” or “preservative blank”, respectively, and the lot number and bottle type should be designated on the bottle and COC (Appendix F).

Because of lot-to-lot variation in filters, testing each lot of filters for DOC interference is recommended (Karanfil, et.al, 2003; Khan and Subramania-Pillai, 2006). To test filters for DOC contribution, a filter rinsate blank for 3 filters (EPA Method 415.3) from each lot should be created in the lab following the steps in 11.1.5 using the appropriate reagent water and bottles from the same lot. The bottles should be labeled “filter blank” and the filter and bottle lot number recorded on the bottle and COC (Appendix F). In addition, an un-filtered blank should be created using a bottle from the same lot and the same reagent water, for comparison. This sample should be labeled “water blank” and the bottle lot number recorded on the bottle and COC (Appendix F).

The types of analyses that may be performed for each bottle type and the type of reagent water that should be used (DI or UPW) is listed in Table 4. In order to pass quality assurance (QA) testing, laboratory analysis results for all analytes should be less than the Limit of Quantification (LOQ). All holding times and preservation methods should follow the guidelines described in 40 CFR 136.

If acceptance criteria are exceeded in a bottle that was preserved with acid, an additional sample where the same acid lot is tested in a bottle from a different lot, or the same bottle lot is tested with a different acid lot may be required to determine the source of contamination.

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Table 4. Sample bottle QA requirements for commonly used bottles and analyses in DOW.

Bottle	Parameters	Preservative	Reagent Water
500 mL HDPE wide-mouth Nalgene® Jar	Acidity, Alkalinity as CaCO ₃ , Bicarbonate as CaCO ₃ , Carbonate as CaCO ₃	Cool to ≤6°C on wet ice	DI
1 L Natural HDPE round	CBOD, Bromide, Chloride, Conductivity, Fluoride, Nitrate, Nitrite, Orthophosphate, pH, Sulfate, Total Dissolved Solids, Total Suspended Solids, Turbidity	Cool to ≤4°C on wet ice	DI
250 mL Narrow-mouth HDPE Amber Bottle	Chlorophyll <i>a</i> , Phycocyanin	Cool to ≤4°C on wet ice	DI
60 mL Wide Mouth Amber Glass Bottle, PTFE cap	Dissolved total organic carbon (DOC)	H ₂ SO ₄ pH<2; Cool to ≤4°C on wet ice	DI
60 mL Nalgene® narrow mouth, high-density polyethylene bottle	Orthophosphate (as P)	Cool to ≤4°C on wet ice	DI
120 mL sterile container, plastic or glass	<i>E. coli</i> , Fecal Coliforms	Cool to <10°C on wet ice	DI
1L (32 oz.) Boston round amber, PTFE cap	Herbicides, Pesticides, and PCBs	Cool to ≤6°C on wet ice	DI
8 oz.(approx.250 mL) round amber narrow-mouth bottle w/Teflon®-lined Closure/Low Particle Protocol	Low-level Mercury	40 drops (5mL/L) 12N HCl	UPW
500 mL HDPE wide-mouth Nalgene® Jar	Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Hardness, Iron, Lead, Manganese, Magnesium, Mercury, Molybdenum, Nickel, Potassium, Selenium, Silver, Sodium, Thallium, Vanadium, Zinc	HNO ₃ (1:1) pH<2; Cool to ≤4°C on wet ice	DI
500 mL HDPE wide-mouth Nalgene® Jar	Ammonia, Nitrate-Nitrite, Total Kjeldahl Nitrogen, Total Organic Carbon, Total Phosphorus	H ₂ SO ₄ pH<2; Cool to ≤4°C on wet ice	DI

Bacteria Sample Bottles

Bacteria sample bottles require three specific QA measures before sampling can occur. The procedures are listed below:

1. Sterility Check

The sterility of each new lot of sample containers must be tested prior to use following these procedures:

- Randomly select one sample container from each lot.
- Pour 25 mL of single strength sterile Tryptic Soy Broth (TSB) into the sample bottle.
- Incubate the bottle and Broth for 48 hours at 35°C.

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- Check for cloudiness, indicating the growth of bacteria.
- If no growth occurs then the lot passes the sterility check and can be used for sampling.
- If growth occurs, repeat the procedure.
- If the lot fails twice, discard the lot of bottles and test a new lot of bottles.
- Record results in the QA logbook.

2. Volume Check

The volume of each new lot of sample containers must be tested prior to use to ensure that the accuracy of the 100 mL fill line is within +/- 2.5 mL.

- Fill a sample bottle from the new lot to the fill line with water.
- Pour the contents into a 100 mL graduated cylinder.
- Record the difference in the QA logbook.

3. Fluorescence Check

Sample containers must be checked for fluorescence if total coliform and *E. coli* are analyzed using an enzyme substrate test (e.g. IDEXX's Colilert®)

- Add 100 mL of DI to a sample container.
- Observe for fluorescence using a 6 watt, 365 nm, long-wave ultraviolet (UV) lamp.
- If there is fluorescence, discard the lot of bottles, and test a new lot of bottles.
- If fluorescence does not occur, then the bottle lot passes the fluorescence check and can be used for sampling.

11.2.3 Reagent Water

If DI or UPW is made in-house, water blanks for all standard analytes should be submitted for contaminant analyses on a quarterly basis, or at least following the replacement of filters, whichever is more frequent. Bottles should be labeled as "water blank" and the bottle and preservative lot numbers and clear identification of the water source should be designated on the bottle and COC (Appendix F). All holding times and preservation methods should follow the guidelines described in 40 CFR 136. Records of blank results will be kept electronically and a hard copy should be stored in an appropriate laboratory QA/QC logbook. If the water is purchased commercially, all records of certification will be stored in the QA/QC logbook. Testing and reporting to the appropriate branch quality assurance coordinator (QAC) and/or DOW quality assurance officer (QAO) the results of any problems and corrective actions is the responsibility of the Microbiology Lab Manager.

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De-ionized Water

De-ionized (DI) water is tap water that has been treated by passing through a standard de-ionizing resin column filter. De-ionized water used by DOW should meet the specifications listed in Table 5.

Table 5. QA criteria for de-ionized water (based on ASTM 2018, in part).

Analyte	QA Criteria
Specific Conductivity	≤5 micromhos/cm at 25°C
pH	5.0 to 8.0 at 25°C
Total Organic Carbon	No limit
Sodium ¹	<0.500 mg /L
Chloride ¹	<0.600 mg/L

¹ Due to laboratory analysis restrictions, criteria is based on DEPS's Limit of Detection (LOD)

Ultra-Pure De-ionized Water

Ultra-pure de-ionized water should meet the following conditions: The water must not contain detectable total recoverable metals or dissolved ions above one half (1/2) the MDL as defined by laboratory analysis, the water must meet the criteria in Table 5, and the water must meet the following criteria (ASTM, 2018):

Conductivity = ≤1.0 micromhos/cm at 25°C;

Total Organic Carbon¹ = <0.20 mg/L.

¹ Due to laboratory analysis restrictions, criteria has been based on DEPS's Limit of Detection (LOD)

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13.0 APPENDICES

13.1 Appendix A: Parameter Questions

Suggested list of additional information needed to sample any parameter not specifically addressed in this SOP. It may still be inappropriate to sample some parameters using this SOP (e.g. PFAS). The following information should be found in 40 CFR 136, laboratory QA documents and SOPs, and analytical reference methods. The following table may be populated and included in QAPP documents for each additional parameter not listed in this SOP:

Variable Group	Parameters	Bottle Volume and Required Type	Preservation	Special Handling and QC Requirements	Holding Time	DEPS SOP and Reference Method
[Name of Group] ¹	[list of parameters to be analyzed within this group/bottle] ²	[bottle type and volume] ³	[required preservation method] ⁴	[list all special handling and unique QC requirements] ^{5,6}	[holding time] ⁷	[found in DEPS LOQAM Appendix C]

¹Variable group applies when multiple parameters are collected from the same bottle.

²Only parameters with the same bottle, preservation, and handling requirements should be combined into a single bottle.

³Ensure that the bottle contains sufficient volume for all parameters and their laboratory QC requirements. Additional requirements may include bottle material, bottle opacity, bottle volume, size of bottle opening (e.g. wide-mouth or narrow-mouth), and bottle cap material. In addition, list if the bottle must meet special requirements such as sterility, pre-cleaning, and being pre-preserved.

⁴Preservation requirements should be outlined in 40 CFR 136 Table II, laboratory documentations (e.g. DEPS LOQAM (2020) Appendix L), and analytical methods. Include the type and volume of acids and the desired resulting pH, if required. And, include the required temperature if sample should be cooled.

⁵Special handling includes considerations such as: leaving no headspace, restrictions on pre-rinsing the bottle, requiring direct sample collection or the prohibition of specific sampling gear, required filtering or other special handling of sample at the collection location, specified sampling location/depth, special precautions against contamination.

⁶Required QC samples and reagent water. Determine the reagent water requirements for collecting QC samples and rinsing equipment. Also, list if any atypical QC samples are required, such as a trip blank.

⁷If more than one parameter will be analyzed from the same bottle, the parameter with the shortest holding time should be listed here.

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13.2 Appendix B: Reference Methods for Parameters in this SOP

Division of Environmental Program Support (DEPS) Laboratory method numbers and their 40 CFR 136.3 approved reference methods for parameters included in Table 2 of this document and commonly analyzed by DOW surface water programs.

Variable Groups	Parameters ¹	DEPS Method ¹	Reference Method ¹	Holding Time ¹
Alkalinity	Acidity	1000	SM 2310B 20 th Ed.	14 days
	Alkalinity (Alkalinity as CaCO ₃ , Bicarbonate as CaCO ₃ , Carbonate as CaCO ₃)	1020, 1030, 1040	SM 2320B 20 th Ed.	14 days
Bulk	CBOD-5	2040	SM 5210B 20 th Ed.	24 hrs (grab) 48 hrs (composite)
	Anion Scan (Part A: Bromide, Chloride, Fluoride, Nitrate (as N), Nitrite (as N), Orthophosphate (as P), Sulfate)	\$1180_CALC	EPA 300.0 Rev 2.1	48 hours for full Part A
	Chloride	1100	SM 4500 Cl- D 20 th Ed.	28 days
	Fluoride	1160	SM 4500-F-C 20 th Ed.	28 days
	Sulfate	1425	EPA 375.4	28 days
	Conductivity	1145	EPA 120.1	28 days
	Total Dissolved Solids (TDS)	1340D	SM 2540C 20 th Ed.	7 days
DOC	Total Suspended Solids (TSS)	1320	SM 2540D 20 th Ed.	7 days
	Turbidity	1460	EPA 180.1 Rev 2.0	48 hours
DOC	Dissolved total organic carbon (DOC)	2260D	SM 5310C 20 th Ed.	28 days
Herbicides	Herbicides	\$6231_HERB	SW846; SM 8321B	7 days
	Caffeine, 1,7-Dimethylxanthine	\$6231_CAFF	SW846; SM 8321B	7 days
Low-level Mercury	Low-level Mercury	3320	EPA 1631E	28 days
Metals	Total Recoverable Metals (Calcium, Iron, Magnesium, Potassium, Sodium)	\$3120_MINCALC	EPA 200.7 Rev 4.4	6 months
	Total Recoverable Metals (Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Lead, Manganese, Molybdenum, Nickel, Selenium, Silver, Thallium, Vanadium, Zinc)	\$3130_ALLCALC	EPA 200.8 Rev 5.4	6 months
	Mercury	3340_CALC	EPA 245.1 Rev 3.0	28 days
	Hardness	1220	SM 2340B 20 th Ed.	28 days
Nutrients	Ammonia (as N)	2000	EPA 350.1 Rev 2.0	28 days
	Nitrate/Nitrite (as N)	2120	EPA 353.2 Rev 2.0	28 days
	Total Kjeldahl Nitrogen (TKN)	2280	EPA 351.2 Rev 2.0	28 days
	Total Organic Carbon (TOC)	2260	SM 5310C 20 th Ed.	28 days
	Total Phosphorus (TP)	2205	EPA 365.4 (1974)	28 days
Ortho-P	Orthophosphate (as P)	2160D	EPA 365.1 Rev 2	48 hours
Pesticides/PCBs	Pesticides (e.g. Atrazine, Chlorpyrifos, Endosulfan, Permethrin, Propachlor, Simazine)	\$6441_ALL	EPA ASB 100P	7 days
	PCBs (e.g. Aroclor and Total PCBs)	\$6300_CALC	SW846; SM 8082A	7 days

¹Information from DEPS LOQAM appendices (DEPS, 2020); this appendix does not replace the reference; see the latest version of the DEPS LOQAM for the most accurate information.

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13.3. Appendix C: Swing/Pole Sampler

A pole sampler enables the user to reach a well-mixed area away from the bank when the user is unable to wade safely or to avoid disturbing sediments from accessing the sample location.

- The device can be purchased in 6 (extends to 12) and 8 (extends to 24) foot lengths. It is listed as a swing sampler by Forestry Suppliers and Fisher Scientific.
- To extend the pole, twist the two sections in opposite directions until loose, and extend. Once extended to the desired length, tighten by twisting the two sections in the opposite direction as before until snug.
- Bottles should be held to the end-piece while a snapper band or cable tie is secured around the bottle and in the groove of the end piece (see below).
- Cable ties can also be used to attach bottles that are too small for the snapper band.



Photo from Fisher Scientific website: <https://www.fishersci.ca/shop/products/nasco-swing-samplers-2/p-4390491>

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13.4 Appendix D: Weighted Bottle Sampler

A weighted bottle sampler enables the user to collect a direct fill grab sample from a bridge when access by wading or from the bank is not possible or has been deemed unsafe.

- The devices pictured were fabricated by DOW from material easily purchased at local hardware stores, and are shown here as examples. Actual designs in use may vary.
- Cable ties are used to hold bottles in place on the larger basket WBS.
- Ropes can be attached to both the top and bottom of either sampler. When lowered with both ropes attached, the samplers can be manipulated to fill and then empty bottles (for pre-rinsing with native water), or to better control the tilt and orientation of the bottles while filling.



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13.5 Appendix E: Vacuum Pump Technique Field Filtering Quick Guide

DOC and Ortho-P Vacuum Filtering Quick Guide*

*This guide is intended as a set of prompts and reminders while performing this subset of tasks. It is not a replacement for thoroughly reading and understanding the SOP and receiving appropriate training. Refer to *Standard Operating Procedure Sampling Surface Water Quality in Lotic and Wetland Systems* (DOWSOP03015) and review related project study plan requirements.

Supplies:

- | | |
|--|---|
| <input type="checkbox"/> filter flask (2 if pre-filtering) | <input type="checkbox"/> filter forceps |
| <input type="checkbox"/> flask cap (if pre-filtering) | <input type="checkbox"/> labeled 60mL Nalgene for ortho-P |
| <input type="checkbox"/> filter base | <input type="checkbox"/> labeled 60mL amber glass for DOC |
| <input type="checkbox"/> filter tower | <input type="checkbox"/> vacuum pump with tubing |
| <input type="checkbox"/> 0.45µm MCE filters for ortho-P | <input type="checkbox"/> DI wash bottle or carboy |
| <input type="checkbox"/> 0.45µm Nylaflo or Supor filters for DOC | <input type="checkbox"/> gloves |
| <input type="checkbox"/> 0.8µm Supor for pre-filtering | |

Filtering Quick Guide*

1. Label 60mL bottle with site information, date, time, initials.
2. Don gloves.
3. Triple rinse filter flask and tower with DI.
4. Single rinse forceps and tubing with DI.
5. Assemble apparatus, place filter on filter base with forceps
 - a. Pre-filter: 0.8 µm, 47mm Supor® 800 (PES) membrane disc filter
 - b. DOC: 0.45 µm, 47mm Nylaflo® or Supor® 450 (PES) membrane disc filter
 - c. Dissolved orthophosphate (as P): 0.45µm 47mm mixed cellulose ester filter
6. Fill tower with 100mL DI, pump through filter. Shake, dump rinsate.
 - a. If making a Field Blank – do it now unless pre-filtering
 - b. Fill tower with 100 mL DI, pump through filter.
 - c. Triple rinse Blank bottle with rinsate and then fill.
7. Fill tower with 50 mL shaken sample water, pump through filter. Shake, dump rinsate.
8. Fill tower with 100 mL shaken sample water, pump through filter.
9. Triple rinse 60mL sample bottle with filtrate in flask.
10. Fill 60mL sample bottle to bottom of shoulder with filtrate.
 - a. If pre-filtering, return to step 1 and repeat all steps using the appropriate 0.45 µm filter
11. Place 60mL sample bottle in cooler on wet ice.
12. Discard used filter and triple rinse all equipment with DI before storing.

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13.6 Appendix F: QC Chain of Custody

Sample type for all QC samples is "Laboratory Blank". Designations such as bottle blank, preservative blank, filter blank, or water blank should be made clear in the sample name or source description.

QC CHAIN OF CUSTODY (2022)		PROJECT:	Program Code: A51										
Page 1 of 2		TRIP:	Shipment Temp: °C										
Sample Type	Matrix	Sample Name	Source Description and Location	Date (mm/dd/yy) hh:mm (24hr)	1 Nutrients H ₂ SO ₄ Cool to 4°C	2 Bulk Cool to 4°C	3 Alkalinity Cool to 4°C	4 Metals HNO ₃ Cool to 4°C	5 Herbicides Cool to 4°C	6 Pesticides Cool to 4°C	7 Ortho-P Cool to 4°C	8 DOC H ₂ SO ₄ Cool to 4°C	9 Low-level Mercury 5mL/L HCl Cool to 4°C
LB	Grab Water				<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
					pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>
					Total Bottles: _____	DEPS Lab Sample ID: _____							
					<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
					pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>
					Total Bottles: _____	DEPS Lab Sample ID: _____							
					<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
					pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>
					Total Bottles: _____	DEPS Lab Sample ID: _____							
					<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
					pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>
					Total Bottles: _____	DEPS Lab Sample ID: _____							
					<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
					pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>
					Total Bottles: _____	DEPS Lab Sample ID: _____							
					<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
					pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>
					Total Bottles: _____	DEPS Lab Sample ID: _____							
					<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
					pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>
					Total Bottles: _____	DEPS Lab Sample ID: _____							
					<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
					pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>	pH <input type="checkbox"/>
					Total Bottles: _____	DEPS Lab Sample ID: _____							

Sample Type: LB=Lab Blank; Collection Type: Grab, Composite; Matrix: Water

QC CHAIN OF CUSTODY (2022)	PROJECT:	Program Code: A51
Page 2 of 2	TRIP:	Shipment Temp: _____ °C

Preservative Information

Sulfuric Acid (H₂SO₄) Lot #: _____ Exp. Date: _____

Nitric Acid (HNO₃) Lot #: _____ Exp. Date: _____

Hydrochloric Acid (HCl) Lot #: _____ Exp. Date: _____

Sample Collectors (Print First & Last Name): _____

Program Supervisor: _____ Jessica Schuster, DOW _____ Project Coordinator: _____

Relinquished by: (signature) _____	Date: _____	Received by: (signature) _____	Date: _____
Print Name: _____	Time: _____	Print Name: _____	Time: _____
Representing: Kentucky Division of Water	Representing: _____	Representing: _____	Representing: _____
Relinquished by: (signature) _____	Date: _____	Received by: (signature) _____	Date: _____
Print Name: _____	Time: _____	Print Name: _____	Time: _____
Representing: _____	Representing: _____	Representing: _____	Representing: _____

Water Matrix Analyses					
Analyte Group	Parameter	Preservation Method	Analyses Requested	Minimum Volume Container Type	Holding Time
1	Nutrients	H ₂ SO ₄ pH < 2.0, Cool to 4°C	Ammonia (2000), Nitrate/Nitrite (2120), TKN (2280), TOC (2260), Total P (2205)	500mL HDPE bottle	28 days
2	Bulk	Cool to 4°C	CBOD5 (2040); IC Anion Scan (\$1180_CALC); Br-, Cl-, F-, SO ₄ ²⁻ , NO ₃ ⁻ , NO ₂ ⁻ , PO ₄ ³⁻ ; Turbidity (1460); TSS (1320); TDS (1340D)	1 liter HDPE bottle	24 hours
3	Acidity/Alkalinity	Cool to 4°C	Acidity (1000), Total Alkalinity (1020, 1030, 1040)	500mL HDPE bottle	14 days
4	Metals	HNO ₃ pH < 2.0, Cool to 4°C	Hardness (1220), Total Recoverable Metals (\$3130_ALLCALC), ICP Minerals (\$3120_MINCALC), Mercury (3340_CALC)	1 liter HDPE bottle	6 months
5	Herbicides	Cool to 4°C	Herbicides (\$6231_HERB, \$6231_CAFF)	1 liter amber glass bottle, PTFE cap	7 days
6	Pesticides / PCBs	Cool to 4°C	Pesticides Group 2 (\$6441_ALL), PCBs (\$6300_CALC)	1 liter amber glass bottle, PTFE cap	7 days
7	Orthophosphorus (as P)	Cool to 4°C	Dissolved Orthophosphate (as P, 2160D) – FIELD FILTER	50mL plastic only	48 hours
8	Dissolved Organic Carbon	H ₂ SO ₄ pH < 2.0, Cool to 4°C	Dissolved Organic Carbon (DOC, 2260D) – FIELD FILTER	60mL pre-cleaned amber glass bottle, PTFE cap	28 days
9	Low-level Mercury	HCl pH < 2.0 Cool to 4°C	Low-level Mercury (3320)	250mL pre-cleaned amber glass bottle, PTFE cap, bagged	28 days

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