

COLLECTING WATER-QUALITY SAMPLES FOR DISSOLVED METALS-IN-WATER

U.S. Environmental Protection Agency, Region 6

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Section 1 Preparation of Field and Laboratory Equipment

Cleaning equipment (i.e. sample bottles, pump tubing, etc.) to be used for clean chemistry applications, both in the field and in the laboratory, is a critically important procedure. Improperly prepared equipment can result in a wasted sampling or analysis efforts and the need for re-sampling and re-analysis. Both problems can result in significant project cost over-runs. It is very important that the procedures described in this SOP be followed carefully and completely at all times.

1.1 Apparatus and Materials

As a minimum, all cleaning should be done in a laboratory reserved for low-level metals work. To the greatest extent possible, the final rinses of each piece of equipment should be done in a clean bench or clean room.

4. High density polyethylene (HDPE) or polypropylene (PP) tubs (preferably with covers) to be used for detergent washing of all equipment and acid soaking of larger items.
5. Wide mouth HDPE or PP jars or carboys for acid soaking smaller items.
6. Various sizes of larger, clear low density polyethylene (LDPE) plastic bags, kept dust free, for covering equipment at various stages during the cleaning process.
7. Sample bottles (LDPE or teflon) of various sizes (i.e. 30 ml to 8 liter).
8. Teflon™ (FEP) tubing.
9. C-flex brand peristaltic pump tubing.
10. Various sizes of plastic cable ties to seal bags at various stages during the cleaning process.
11. Dust-free (e.g. tyvek type) laboratory coats and hair covers to be worn during all stages of the cleaning process.
12. Powder-free gloves to be worn during all stages of the cleaning process.

1.2 Reagents

1. Acids used in the cleaning steps must be ACS reagent grade or better. The ability to achieve acceptable bottle and sampler blanks (i.e. all elements below the detection limit required by the data quality objectives) should be the determining factor for the grade of acid used.
 - ✓ Hydrochloric acid (~10%): Add 270 ml concentrated HCl to 400 ml Type II water and dilute to 1 liter
 - ✓ Nitric acid (1:1): Add 500 ml concentrated HNO₃ to 400 ml Type II water and dilute to 1 liter.
2. Reagent water with metal levels not detectable by ICP-MS. Water should be monitored for impurities. Sources of ultra-pure water, including distilled-deionized, sub-boiling quartz distilled, and Milli-Q, should be compared periodically to select the cleanest water for calibration standard and sample preparation.
3. Ultrapure ammonium hydroxide redistilled from ACS reagent grade material.

1.3 Equipment Cleaning Procedures

1.3.1 Teflon™ Tubing

1. If the tubing has been used previously, cut a small piece of Handy-wipe to fit snugly in tubing.
2. Wipe air valve by DIW container off to get any loose debris off.
3. Attach tubing to air valve and turn on with just enough air pressure to push the Handy-wipe through slowly.
4. Repeat this step 3 times.
5. Clean the outside of the tubing with micro cleaner and designated clean scrubber. Cable tie each set of tubing together, and attach a small piece of clean No. 24 c-flex tubing to each tubing set.
6. Carefully remove tubing that is feeding DIW (distilled water) container.
7. Attached tubing with a cable tie and cover tubing with a plastic bag.
8. Cut a small hole in the bottom of the bag to have access to the tubing.
9. Attach a small piece of clean No. 24 c-flex tubing on tubing set to DIW tubing and flush at appropriate feeding rate.
10. After tubing set has been flushed out thoroughly, empty DIW out of tubing and place in clean bag. Label bag as to stage of cleaning.
11. Once all tubing sets have been flushed, emptied and bagged, return DIW tubing to the container and cover it with plastic.
12. Using designated micro solution bottle, cover top with plastic bag and 6" of No. 24 c-flex micro tubing.
13. Pump micro solution to capacity through tubing leaving no air bubbles. With a small piece of clean No. 24 c-flex attach one end of tubing to another.
14. Place tubing in clean Rubbermaid bag, label and let sit for at least one day.
15. Rinse 6" of No. 24 c-flex micro tubing with DIW before storing.
16. To flush solution out of tubing follow directions 3 - 7.
17. Cover top with plastic bag and 6" of No. 24 c-flex nitric tubing.
18. Pump nitric solution to capacity through tubing leaving no air bubbles.
19. With a small piece of clean No. 24 c-flex nitric attach one end of tubing to another.
20. Place tubing in clean Rubbermaid bag, labeling it and letting it sit for at least 2 days.
21. Rinse 6" of No. 24 c-flex nitric tubing with DIW before storing.
22. Follow steps 3-4 when flushing nitric solution out of tubing.
23. After tubing has been flushed out thoroughly, empty DIW out of tubing and place it in a clean and labeled ice bag.
24. Then close the bag with a cable tie.
25. Store all clean tubing sets in a Rubbermaid bag, in the cleanroom.
26. Be sure to label amount of tubing sets on bag for inventory.

1.3.2 Bottles (125 ml to 1 liter)

1. Fill the bottles to capacity with micro solution, either directly from previous bottle rotation or make a new solution.
2. Shake and let sit in sealed, labeled bags for **at least one day**.
3. Empty bottles of micro solution in new set of bottles for rotation. To rinse fill bottles 1/4 full with DIW, cap, shake, and empty. **Do this 3 times**.
4. To transport all bottles in and out of the cleanroom be sure they are in clean and labeled Rubbermaid bags.
5. Next fill the bottles to capacity with 50% nitric solution. It is preferable that this procedure is done in a cleanroom hood. The bottles should be capped tightly. Let bottles sit in nitric solution for **at least 2 days**.
6. Empty bottles of nitric solution, either into new bottles in rotation or into designated nitric solution bottles.
7. **Rinse bottles as described in step 3.** If using a cleanroom, be sure to transport all bottles in and out of the cleanroom in clean and labeled Rubbermaid bags.

8. Next fill the bottles to capacity with 10% HCl (hydrochloric) solution. It is preferable that this procedure is performed in a cleanroom hood. The bottles should be capped tightly.
9. Let bottles sit in HCl solution for **at least two days**.
10. Empty bottles of HCl solution either into new bottles in rotation or designated HCl solution bottles.
11. **Rinse bottles as described in step 3.** If using a cleanroom, be sure to transport all bottles in and out of the cleanroom in clean and labeled Rubbermaid bags.
12. Dry bottles with the lids on. Let them dry **at least one day**.
13. Package dry bottles in a Ziplock bag. One gallon size for 1-liter, quart size for 500 ml and 250 ml.
14. Store bottles in a large Rubbermaid bag, labeling amount of bottles on bag for inventory.

1.3.3 Bottles (30 or 60 ml)

1. Place (72, one box) uncapped bottles and lids in clean double ice bag.
2. Fill bag with new micro solution about 1/2 full.
3. Cable tie the bag and label it, make sure there are no air bubbles.
4. Place in a clean Nalgene container and let sit for one day.
5. Empty bottles and lids in a clear Nalgene container.
6. Rinse the bottles and lids **three times with DIW**.
7. Place bottles and lids in designated container of 50% nitric solution, in the acid hood and let them sit for **at least 2 days**.
8. After sitting for 2 days remove bottles and lids by placing them in clean Nalgene container. **Rinse 3 times with DIW**.
9. Place bottles and lids in designated container of 10 % HCl solution, in the acid hood. Let sit for **at least 2 days**.
10. Remove bottles and lids by placing them in Nalgene container. Also, **rinse 3 times with DIW**. With the lids on the bottles dry them in the clean room in front of the HEPA filter. Let dry **at least 1 day**.
11. Package the dry bottles in a labeled Ziplock bag.
12. Store in a large Rubbermaid bag, labeling the amount of bottles on the bag for inventory.

1.3.4 Bottles (2 liters or larger)

1. Wash exterior with Micro solution and designated clean chemistry scrubber.
2. Fill bottles to capacity with micro solution.
3. Shake, label, and let sit in cable tied bags **at least 1 day**.
4. Empty bottles of micro solution.
5. Rinse bottles 1/4 full with DIW, cap, shake and empty. Do **this 3 times**. When transporting all bottles be sure they are in clean and labeled Rubbermaid bags.
6. Next fill bottle to capacity with 50 % nitric solution. Make sure procedure is done under vent hood, cap tightly.
7. Let bottles sit in the nitric solution **at least 2 days**.
8. Empty bottles of nitric solution, either in new bottles in rotation or in designated nitric solution bottles.
9. Rinse bottle as described in step 5. When transporting be sure they are in clean and labeled bags.
10. Next fill bottle to capacity with 10 % HCl solution. Make sure procedure is performed under vent hood, cap tightly.
11. All bottles with HCl solution should be labeled. Let bottles sit in HCl solution **at least 2 days**.
12. Rinse bottle as described in step 5. When transporting bottles make sure they are in clean and labeled bags.
13. Dry the bottle with lid on.
14. Package dry bottles in labeled ziplock bags.

1.3.5 Cartridge filters

Fill cartridge filters with 10% HCl solution and seal using pre-cleaned No. 24 c-flex tubing. Place in a clean plastic bag and let sit for **at least 3 days**.

1. Flush cartridge filter with 1 liter of reagent water and re-seal with tubing and let sit **at least 1 day**.

2. Flush filter with 2 liters of reagent water. Leave filter full.
3. Add 1 ml of ultrapure ammonium hydroxide to filter and re-seal with c-flex tubing. Let filter sit for **at least 3 days** before being used for sampling.
4. Filter **must still be flushed with at least 0.5 to 1 liter** of the water to be sampled to insure not residual acid is left in the filter prior to the final sample being collected.

1.3.6 Equipment Quality Control

With each cleaning batch of tubing (i.e. typically 10 sets) or bottles (i.e. typically 24-72) a blank is taken. For bottle blanks, reagent water is added to a randomly selected bottle under clean conditions. For tubing sets, reagent water is pumped through the tubing and into a pre-cleaned bottle. The bottle is then treated as a dissolved water sample and analyzed by ICP-MS. If the bottle or sampler blanks show detectable amounts of any element of interest, the batch of affected equipment is re-cleaned.

Section 2 Sampling Methods

The following sections describes grab sampling for metals-in-water and trace elements. The protocols most widely accepted at this time, especially when using the parts-per-billion ($\mu\text{g/L}$) analytical levels, require the use of “clean” sampling procedures. These sampling procedures help reduce (to the extent possible given current resources) the amount of contamination introduced when collecting water-quality samples in the field. “Clean” sampling procedures involve: (1) using equipment that is constructed of non-contaminating materials and that has been cleaned rigorously before field work and between field sites; (2) handling equipment in a manner that minimizes contamination; (3) collecting, processing, and handling samples in a manner that prevents contamination; and (4) routinely collecting quality-control (QC) samples.

2.1 Grab Sampling

A grab sample is collected in an open container from a single point at, or near, the stream/river/lake/reservoir surface. Grab samples can be collected with a suspended or hand-held polypropylene (Nalgene™) 5-gallon container, disposable bailer, or narrow, open-mouth bottle. If the grab sample is collected by hand-held methods, the sampler should wade where the sample will be collected (preferably at the centroid of flow or mid-channel) and immerse a hand-held narrow-mouth bottle. The sampler should stand downstream of the bottle as it is being filled. Care must be taken to avoid collecting particles that are re-suspended as the result of wading. Various examples of grab samples include: dip, discrete, and pump samples. Dip samples and grab samples and containers (of the appropriate non-contaminating material) such as Nalgene™ buckets or cubitainers are used for grab samples. Discrete or point samples are collected by either (1) lowering a sampler to a specified depth and collecting a sample by first opening, then closing the samplers, or (2) using a single stage sampler, which fills when stream stage rises to a pre-determined height. Thief-type samplers and some pumps are the samplers most often used to collect samples by method 1 above. Although these samplers are designed primarily to sample still waters, they can be adapted to slowly flowing water. Single-stage samplers used in method 2 above include crane-type devices and are useful at stations on flashy streams or other locations where it is difficult to reach a station to manually collect samples. Pump sampling is typically accomplished with suction lift or submersible pump systems designed to collect water-quality samples.

For routine water-quality samples where near-surface water is representative of the water mass, a water sample can be collected by directly immersing the container beneath the water surface to a depth of 1 ft. A bucket can be used to collect a sample if the mixed surface layer is very shallow or accessible only from a bridge. If a bucket is used, caution should be taken to avoid contaminating the sample with debris from the rope and bridge. Care must be taken also to rinse the bucket between stations. In slow-moving rivers, reservoirs, and estuaries, the depth in the mixed layer can be determined from field measurements by locating the thermocline or an abrupt change in specific conductance. In tidally-influenced waterbodies, the mixed surface layer is defined as that portion of the water column from the surface to the depth at which the specific conductance is 6,000 $\mu\text{S/cm}$ greater than the specific conductance at the surface. For mixed surface layer samples (depth >1 ft.), pre-rinse one of the following sample devices at least once with native water before using: submersible pump tube, Kemmerer, or Van Dorn. A minimum volume of 3

L should be collected from each site. Sample containers do not have to be rinsed with site water. Care should be taken at all times during sample collection, handling, and transport to prevent exposure of the sample to direct sunlight. Summary information on sample processing, preservation, and holding times for grab sampling methods, including dissolved metals in water, is contained in Tables 2 and 3.

2.2 Clean Hands/Dirty Hands Techniques for Water-Quality Sampling Overview

“Clean” sampling procedures, including Clean Hands(CH)/Dirty Hands (DH) techniques, are required when collecting samples for metals and other trace elements. CH/DH techniques separate field duties and dedicate one individual as “clean-hands” to tasks related to direct contact with the sample. These techniques are summarized below:

1. CH/DH techniques require two people working together.
2. At the field site, one person is designated as “clean hands” (CH) and the second person as “dirty hands” (DH). Although specific tasks are assigned at the start to CH or DH, some tasks overlap and can be handled by either, as long as contamination is not introduced into samples.
3. Both CH and DH wear appropriate non-contaminating, disposable, powderless gloves during the entire sampling operation and change gloves frequently, usually with each change in task (wearing multiple layers of gloves allows rapid glove changes).
4. **CH takes care of all operations involving equipment that comes into contact with the sample; for example, CH:**
 - ✓ Handles the surface-water sample bottles
 - ✓ Handles the discharge end of the surface-water sample tube or line
 - ✓ Prepares clean work space (either inside vehicle or laboratory prep area)
 - ✓ Sets up processing and preservation chambers
 - ✓ Sets equipment inside chambers (i.e., sample bottles, filtration, and preservation equipment)
 - ✓ Works exclusively inside chambers during collection, processing, and preservation.
 - ✓ Changes chamber covers, as needed
 - ✓ Sets up field-cleaning equipment and cleans equipment
5. **DH takes care of all operations involving contact with potential sources of contamination; for example, DH:**
 - ✓ Works exclusively exterior to processing and preservation chambers
 - ✓ Prepares and operates sampling equipment, including pumps and discrete samplers, peristaltic pump switch, pump controller, and manifold system
 - ✓ Operates cranes, tripods, drill rigs, vehicles, or other support equipment
 - ✓ Handles the compressor or other power supply for samplers
 - ✓ Handles tools such as hammers, wrenches, keys, locks, and sample-flow manifolds
 - ✓ Handles single or multiparameter instruments for field measurements
 - ✓ Handles stream-gaging or water-level equipment
 - ✓ Sets up and calibrates field-measurement instruments
 - ✓ Measures and records water levels and field measurements

2.3 Metals and Trace Elements Sampling Overview

The following field practices are recommended when sampling for metals and trace elements:

1. Think contamination: be aware of and record potential of contamination at each field site.
2. Wear appropriate non-contaminating, disposable, powderless gloves.
 - (a) Change gloves before each step during sample collection (and processing).
 - (b) Avoid hand contact with contaminating surfaces (such as equipment, coins and food).
3. Use equipment constructed of materials that are relatively inert with respect to targeted analytes. Metal samplers must be epoxy-coated to prevent trace element contamination.
4. Use only equipment that has been cleaned according to prescribed procedures. Sampling processing equipment should be kept covered (when not dispensing sample).

5. Field rinse equipment, but only as directed. Some equipment for some analytes should not be field rinsed.
6. Use correct sample-handling steps:
 - (a) Minimize the number of sample-handling steps
 - (b) Use CH/DH techniques as required for parts-per-billion (ppb or $\mu\text{g/L}$) trace element sampling.
 - (c) Adapt CH/DH techniques for all sample types, as required to obtain data of known quality.
 - (d) Train for and practice field techniques under supervision before collecting water samples on your own
7. Collect and process samples in a clean enclosure such as a dedicated water-quality field vehicle or field processing chamber. Metallic objects, dirt, oil residue, engine exhaust, and food can all be sources of contamination. Sample processing chambers can be fashioned from a polyvinyl chloride frame and clear plastic bag.
8. Filter samples for *dissolved trace elements* and *metals* as soon as practical after collection with disposable, tortuous path, capsule filter (effective size of $0.45\ \mu\text{m}$; 15 mm diameter or larger, Gelman Supor™ 12175, or equivalent [Ref. EPA Method 1669]). A variable speed, battery-operated pump fitted with a peristaltic pump head that forces the sample through Tygon™ or Teflon™ tubing is recommended. Filtered samples should be preserved with (1+1), ~7.7N Ultrex™, Ultrapure Reagent nitric acid (HNO_3), to a $\text{pH} \leq 2.0$. Normally, 3 mL of (1+1) acid per liter should be sufficient to preserve the sample. For field purposes, the nitric acid can be stored on quantities of 2 mL in polypropylene vials.
9. Collect a sufficient number of appropriate types of QC samples. QC samples should be reviewed to determine if cleaning procedures are sufficient and contamination has been minimized.

Specific details regarding grab sample collection methods, preservation, storage, and handling requirements are summarized in Tables 2 and 3.

2.4 Dissolved Metals-in-Water Collection Technique

Collecting metals-in-water requires two people. One person, designated as “Clean Hands,” is the only one in direct contact with the sampling container, tubing, and filter (or anything that touches the ambient or blank water). The second person, or “Dirty Hands,” sets up the apparatus and operates the pump. Both CH and DH wear powder-free latex gloves during the sample collection process.

Sample Collection

At the site, DH sets up the pump while the CH takes a bottle from the plastic bag and places it in a “container holder.” A container holder can be anything nonmetal that supports the bottle, freeing up the collector’s hands. CH takes the end of the tubing with the filter attached out of the bag and places it in the pump head. The outlet end is approximately 18 inches from the pump. The other end is long enough to easily reach beneath the surface water. DH closes the pump head, locking the tubing in place.

CH takes the other end of the tubing, removes the plastic cover from the end of the tubing and places it in a “tubing holder.” The tubing holder can be a PVC pipe, or something similar (nonmetallic), can be used to hold and extend the tubing beneath the water surface.

DH immerses the intake tube directly into the water and operates the pump to flush the tube and filter with the filter held upright. CH removes the cap from the sample container to fill with filtrate leaving some head space. CH puts the cap back on the container and places it back in the plastic bag. Whenever CH touches the boat or equipment, which may be contaminated, gloves should be changed immediately.

Sample Preservation

If not using a commercially purchased pre-acidified container, filtered metals-in-water samples should be preserved with (1+1), ~7.7N Ultrex™, Ultrapure Reagent nitric acid (HNO₃), to a pH ≤ 2.0. Normally, 3 mL of (1+1) acid per liter should be sufficient to preserve the sample. For field purposes, the nitric acid can be stored in quantities of 2 mL in polypropylene vials. Holding times for acid preserved samples is six months except for mercury which is 28 days. After collecting the sample and adding the preservative, the container is placed back in a plastic bag for shipping. This is to prevent possible contamination from other samples in the ice chest.

Trivalent Chromium due to the complexity of the preservation method, it is advised that the sample we shipped to the laboratory unpreserved.

Hexavalent Chromium acidification alters the hexavalent form of chromium, a separate (unacidified) sample must be submitted if hexavalent chromium is to be analyzed. Filter, add 1 mL NaOH per 125 mL of sample. Submit a minimum of 500 mL sample. The sample is collected, placed on ice, and shipped to the laboratory in time for analysis to begin within 24-hours of collection. The laboratory should be notified when a hexavalent chromium sample will arrive. Hexavalent chromium is not usually analyzed on unfiltered samples.

Sample Container Label

Label each container with the tag number and the type of sample. Since the sample has been filtered and preserved, this information should be noted on the laboratory analyses request form.

Field Blanks and Replicates

Field blanks should be prepared immediately before collecting and processing an environmental sample at a selected site. All equipment should have been cleaned, either in the field or preferably in the laboratory following guidelines outlined in this guidance. The water used for field blanks should be metals free. Equipment need not be cleaned nor filters changed between processing the field blank and the environmental sample. However, certain pieces of equipment should be cleaned or changed if they have obviously been contaminated or if there is a significant potential for contamination. The sequential replicates are collected as you would collect a normal sample.

The sample collection method outlined for dissolved metals-in-water samples is followed for the field blank with the following exceptions:

CH opens a container of blank water (metals-free DI water). DH removes the plastic cover from the end of the tubing and inserts the tubing into the blank water container. DH holds the tubing in place.

CH takes the plastic cover off the other end of the tubing. DH turns on the pump and flushes a small amount of water through the filter to purge it for dissolved metals.

CH removes the cap from the sample container and uses the pump to fill with metals-free DI water. CH puts the cap back on the container and places it in the plastic bag.

2.5 Companion Samples for Metals-in-Water

Request a hardness analyses whenever metals-in-water are to be analyzed from an inland site (estuaries sites do not require hardness analysis). Typically, the hardness can be calculated from the analysis of calcium and magnesium. Sample holding time for unpreserved samples is 2 days under refrigeration. Hardness samples can be preserved giving longer holding times, but they must be filtered before the acid preservative is added. Filter, then preserve with 2 mL of concentrated H_2SO_4 or 5 mL of concentrated HNO_3 per liter of sample.

Section 3 Types of Quality-Control Collection Requirements for Metals-in-Water

Three types of QC samples are routinely collected for metals-in-water studies. Blanks and spikes are used to estimate bias. Replicates are used to estimate variability.

A **blank** is a water sample that is intended to be free of the analytes of interest. Blank samples are analyzed to test for bias that could result from contamination of environmental samples by the analytes of interest during any stage of sample collection, processing, and analysis. A field blank is prepared in the field and used to demonstrate that: (1) Equipment has been adequately cleaned to remove contamination introduced by samples obtained at previous sites; (2) sample collection and processing have not resulted in contamination; and (3) sample handling and transport have not introduced contamination. In addition, because the field blank is treated like an environmental sample at the laboratory, it includes potential contamination introduced during laboratory handling and analysis.

A **field blank** is used to demonstrate that the sample-collection and sample-processing equipment are not introducing contamination. Field blanks can be prepared using individual pieces of the collection and processing equipment. For example, a sample prepared by exposing the blank solution just to the filter apparatus would be a filter blank. In metals-in-water, the only type of field blank that is routinely prepared is by filtering a quantity of metals free water through the tubing and filter apparatus. This is used to determine whether the tubing and filter are introducing contamination into the sample.

A **trip blank** is a sample of analyte-free water that is prepared in the laboratory or in the office. It is transported, unopened, to the field with other sample containers and is shipped to the laboratory for analysis with the collected samples. Trip blanks are used to identify contamination that might occur during

sample transport and analysis rather than as a result of sample collection and processing in the field. Because the primary source of this contamination is airborne, trip blanks are normally prepared for VOCs.

Replicates are two or more samples collected or processed so that the samples are considered to be essentially identical in composition. **Split replicates** are prepared by dividing a single volume of water into multiple samples. These replicates provide a measure of variability introduced during sample processing and analysis. **Concurrent replicates** are multiple samples collected from an environmental matrix as closely as possible to the same location and time. These replicates account for the variability measured by split replicates and the additional variability introduced by sample collection. Depending on sampling procedures, concurrent replicates also might include an unknown amount of short-term environmental variability. **Sequential replicates** are multiple samples collected at the same location, but at slightly different times, generally one right after the other. These replicates provide a measure of the same sources of variability as concurrent replicates and the additional variability associated with short-term environmental fluctuation.

For purposes of this SOP, the term “replicate” is used to refer to all similarly collected or processed samples. The term “primary environmental sample” and “duplicate environmental sample” are used to identify particular samples in a replicate pair.

3.1 Field Blanks

Field blanks should be prepared immediately before collecting and processing an environmental sample at a selected site. All equipment should have been cleaned, either in the field or preferably in the laboratory following guidelines outlined in this guidance. The water used for field blanks should be metals free. Equipment need not be cleaned nor filters changed between processing the field blank and the environmental sample. However, certain pieces of equipment should be cleaned or changed if they have obviously been contaminated or if there is a significant potential for contamination.

3.2 Replicates

Replicates for analysis of metals-in-water are produced by splitting a single, large volume of water, collected from the waterbody, into two samples (one primary and one duplicate). The split replicates will allow assessment of sources of variability (sample processing, handling and analysis) that can be controlled by field and laboratory procedures. Sequential replicates are collected for the purpose of estimating the magnitude of variation of the sample.

Replicates should be targeted at sites and times where concentrations of at least some target analytes are expected to exceed detection limits. If concentrations of all target analytes are expected to be less than detection, collection of replicates should be deferred until conditions are more favorable for detection or canceled since non-detect information will not provide the requisite information to estimate the magnitude of variation of the sample. Attempt to collect replicates over the range of detectable concentrations expected within the study area, but give greater emphasis to collecting replicates at high concentrations. Replicate samples need not be collected uniformly throughout the sampling period or at all surface water sites; however, they should be scheduled to cover a wide range of hydrologic conditions.

3.3 Quality Control (QC) Data Assessment Guidelines

Analyses of field/equipment blanks associated with the equipment preparation and field sampling are required to demonstrate freedom from contamination introduced during the equipment cleaning and actual sampling. The following sections describe the required types, procedures, and criteria for analyzing field and equipment blanks.

- 3.3.1 Analyze the field blank(s)(samples collected from the same site at the same time) shipped with each set of samples. Analyze the blank immediately before analyzing the samples in the batch.
- 3.3.2 If the metal of interest or any potentially interfering substance is found in the field/equipment blank at a concentration equal to or greater than the method limit (ML), or

greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes.

- 3.3.3 Alternatively, if a sufficient number of field/equipment blanks (three minimum) are analyzed to characterize the nature of the field/equipment blank, the average concentration plus two standard deviations must be less than the regulatory compliance level or less than one-half the level in the associated sample, whichever is greater.
- 3.3.4 If contamination of the field blanks and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken before the next sampling event.
- 3.3.5 Both the **field** and **equipment blanks** are defined in Section 3.0

3.3.6 Data Use and Acceptability

Regardless of the field sampling method(s) used, all data will be deemed acceptable and used for Section 303(d) and 305(b) decisions unless the data has been deemed unacceptable due to the stated QC guidelines, Sections 3.3.2 and 3.3.3. If the data does not meet the QC guidelines, it will be censored (disregarded) for use in Section 303(d) and 305(b) decisions.

3.3.7 Toxicity Assessment Guidelines

Those samples that are deemed acceptable based on the stated QC guidelines will be assessed as follows in making designated use attainment decisions:

Fully Supporting - For any one pollutant, no more than 1 exceedance of acute criteria (State's criteria maximum concentration) within a 3-year period and no more than 1 exceedance of chronic criteria (State's criteria continuous concentration) within a 3-year period.

Table 1. Collection frequencies for routine quality-control samples

[- -, denotes no samples required]

Constituent or group	Number of quality-control samples per total number of environmental samples (at all surface-water sites, each year)			
	Field blanks	Trip blanks	Replicate field matrix spikes	Replicates
Dis. Metals-in-water	1 in 10 samples ^②	- -	- -	1 in 10 ^① samples
Trace elements	1 in 10 samples	- -	- -	1 in 10 ^① samples

①A minimum of three **sequential replicates** will be collected. However, if, in the judgement of the project manager, the concentrations of all target analytes are expected to be less than detection, collection of replicates will be deferred until conditions are more favorable for detection or canceled since non-detect information will not provide the requisite information to estimate the magnitude of variation of the sample.

②If the metal of interest or any potentially interfering substance is found in the field/equipment blank at a concentration equal to or greater than the method limit (ML), or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes. Alternatively, if a sufficient number of field/equipment blanks (three minimum) are analyzed to characterize the nature of the field/equipment blank, the average concentration plus two standard deviations must be less than the regulatory compliance level or less than one-half the level in the associated sample, whichever is greater.

Table 2. General Guidelines for selecting equipment on the basis of construction material and target analyte(s)

[✓, generally appropriate for use shown; Si, silica; Cr, chromium; Ni, nickel; Fe, iron; Mn, manganese; Mo, molybdenum; CFC, chlorofluorocarbon; B, boron]

Construction material for sampling equipment		Target analyte(s)	
Material	Description	Inorganic	Organic
Plastics¹			
Fluorocarbon polymers ² (other varies available for differing applications)	Chemically inert for most analytes	✓ (potential source of fluoride)	✓ (Sorption of some organics)
Polypropylene	Relatively inert for inorganic analytes	✓ (not appropriate for Hg)	Do not use
Polypropylene (linear)	Relatively inert for inorganic analytes	✓ (not appropriate for Hg)	Do not use
Polyvinyl chloride (PVC)	Relatively inert for inorganic analytes	✓ (not appropriate for Hg)	Do not use
Silicone	Very porous. Relatively inert for most inorganic analytes	✓ (potential source of Si)	Do not use
Metals			
Stainless steel 316 (SS 316)	SS-316-metal having the greatest corrosion resistance. Comes in various grades. Used for submersible pump casing.	✓ (Potential source of Cr, Ni, Fe, and possible Mn and Mo) Do not use for surface water unless encasted in plastic.	✓ Do not use if corroded ³
Stainless steel 304	Similar to SS-316, but less corrosion resistant	Do not use	✓ Do not use if corroded ³
Other metals: brass, iron, copper, aluminum, galvanized and carbon steels	Refrigeration-grade copper or aluminum tubing are used routinely for collection of CFC samples	Do not use	✓ Routinely used for CFCs Do not use if corroded ³
Glass			
Glass, borosilicate (laboratory grade)	Relatively inert. Potential sorption of analytes	✓ Do not use for trace element analyses. Potential source of B and Si	✓

¹Plastic used in connection with inorganic trace-element sampling should be uncolored or white. Tubing used for trace metal sampling should be cleaned by soaking in 5-10 percent HCl solution for 8-24 hours, rinsing with reagent water (metals free) and allowed to air dry in mercury-free environment. After drying, the tubing is doubled-bagged in clear polyethylene bags, serialized with a unique number, and stored until used.

² Fluorocarbon polymers include materials such as Teflon™, Kynar™, and Tefzel™ that are relatively inert for sampling inorganic or organic analytes. Only fluoropolymer should be used for samples that will analyzed for mercury because mercury vapors can diffuse in or out of other materials, resulting in either contaminated or biased results.

³ Corroded/weathered surfaces are active sorption sites for organic compounds.

Table 3. Summary of grab sample collection methods, preservation, storage and handling requirements

PARAMETERS	CONTAINERS	SAMPLE VOLUME (mL)	PRESERVATION	MAXIMUM HOLDING TIME
WATER				
ROUTINE WATER SAMPLE				
Alkalinity	Cubitainer or Glass	100	Cool to 4 °C, dark	14 days
Total Suspended Solids/Suspended Solids	Cubitainer or Glass	400	Cool to 4 °C, dark	7 days
Chloride (Cl)	Cubitainer or Glass	100	None required	28 days
Sulfate (SO₄)	Cubitainer or Glass	100	Cool to 4 °C, dark	28 days
Orthophosphate (OPO₄)	Cubitainer or Glass	150	Filter ASAP; Cool to 4 °C, dark	48 hours
Nitrate + Nitrite (NO₃ + NO₂)	Cubitainer or Glass	150	1-2 mL conc. H ₂ SO ₄ to pH <2, and Cool to 4 °C, dark	28 days
Ammonia (NH₃)	Cubitainer or Glass	150	1-2 mL conc. H ₂ SO ₄ to pH <2, and Cool to 4 °C, dark	28 days
Total Phosphorus (TPO₄)	Cubitainer or Glass	150	1-2 mL conc. H ₂ SO ₄ to pH <2, and Cool to 4 °C, dark	28 days
Total Organic Carbon (TOC)	Cubitainer or Glass	100	1-2 mL conc. H ₂ SO ₄ to pH <2, and Cool to 4 °C, dark	28 days
Chlorophyll a	Quart cubitainer	1,000	Cool to 4 °C, dark	Filter 48 hours Filters may be stored frozen up to 30 days
Nitrite	Quart cubitainer	50	Cool to 4 °C, dark	48 hours
Total Dissolved Solids	Quart cubitainer	250	Cool to 4 °C, dark	7 days
Hardness	Quart cubitainer	250	2 mL conc. HNO ₃ to pH<2; Cool to 4 °C, dark OR 2 mL conc. H ₂ SO ₄ to pH <2; Cool to 4 °C, dark	6 months
ROUTINE WATER SAMPLE COLLECTION PROCEDURE				
<ul style="list-style-type: none"> ◦Label container before collection with a unique sample identifier number, Station Location, Date and Sample Type ◦Place an X on the container lid to identify the acidified sample. ◦Open containers by pulling apart. Pre-rinsing cubitainers with ambient water is not necessary. ◦Fill each container with ambient water by submerging container approximately one foot below the surface mid-stream until filled. ◦Place sample on ice immediately. Acidify the X container as soon as possible. ◦Place on ice and ship as soon as possible. 				

Table 3. Summary of grab sample collection methods, preservation, storage and handling requirements–Continued

PARAMETERS	CONTAINERS	SAMPLE VOLUME (mL)	PRESERVATION	MAXIMUM HOLDING TIME
WATER				

NON-ROUTINE WATER SAMPLES

OIL AND GREASE	Glass container with teflon lined lid rinsed with hexane or methylene chloride	1,000	2 mL conc. H ₂ SO ₄ to pH <2; cool to 4 °C, dark	28 days
PHENOLS	Glass container with teflon lined lid	1,000	2 mL conc. H ₂ SO ₄ to pH <2; cool to 4 °C, dark	28 days
BIOCHEMICAL OXYGEN DEMAND	Gallon cubitainer	> 4,000	Cool to 4 °C; add 1g FAS crystals per liter if residual chlorine present	48 hours
CHEMICAL OXYGEN DEMAND	Quart cubitainer	110	2 mL conc. H ₂ SO ₄ to pH <2; cool to 4 °C, dark	28 days
METALS-IN-WATER				
DISSOLVED (except Hg)	HNO ₃ cleaned quart plastic container	1,000	Filter at sample site with 0.45 micron in-line filter ¹ into ultra-pure ² HNO ₃ preacidified container to pH<2	6 months
DISSOLVED MERCURY	HNO ₃ cleaned quart plastic container	1,000	Filter at sample site with 0.45 micron in-line filter ¹ into ultra-pure ² HNO ₃ preacidified container to pH<2	28 days
TOTAL (except Hg)	HNO ₃ cleaned quart plastic container	1,000	Preacidified container with 5 mL ultra-pure ² HNO ₃ to pH<2	6 months
TOTAL MERCURY (Hg)	HNO ₃ cleaned quart plastic container	600	Preacidified container with 5 mL ultra-pure ² HNO ₃ to pH<2	28 days
HEXAVALENT CHROMIUM (filtered)	Plastic or glass	600	Cool to 4 °C, dark	24 hours; must notify lab in advance

METALS-IN-WATER SAMPLE COLLECTION PROCEDURES

DISSOLVED METALS (includes Hexavalent Chromium)

- Put on **powder-free** latex, polyethylene, or vinyl gloves using Clean Hands/Dirty Hands technique.
- Assemble pump³, tubing, and filter.
- Immerse intake tubing directly into water 1ft. and pump approx. 500 mL of ambient water to flush tubing and filter.
- Fill precleaned, preacidified container with 600-1,000 mL of filtrate leaving some head space.

TOTAL METALS

- Put on **powder-free** latex, polyethylene, or vinyl gloves using Clean Hands/Dirty Hands technique.
- Assemble pump, and tubing without filter.
- Immerse intake tubing directly into water 1ft. and pump approx. 500 mL of ambient water to flush tubing
- Fill precleaned, preacidified container with 600-1,000 mL of filtrate leaving some head space.

NOTES

¹Capsule Filter: 15 mm diameter or larger, tortuous path capsule filters, Gelman Supor™ 12175, or equivalent (Ref. EPA Method 1669).

²Nitric Acid, Ultra-pure, commercially known as Ultrex™, Ultrapure Reagent.

³Pump and pump apparatus—Required for use with the container method. Peristaltic pump—115 a.c., 12 volt d.c., internal battery, variable speed, single head, Cole-Parmer, portable, Masterflex L/S™, Catalog No. H-07570-10 drive with Quick Load pump head, Cat. No. H-07021-24, or equivalent (Ref. EPA Method 1669).

Table 3. Summary of grab sample collection methods, preservation, storage and handling requirements–Continued

PARAMETERS	CONTAINERS	SAMPLE VOLUME (mL)	PRESERVATION	MAXIMUM HOLDING TIME
ORGANICS/PESTICIDES-IN-WATER				
VOLATILE ORGANICS (VOA)	Two 40-mL VOA vials	80	Cool to 4 °C, dark; or 2-4 drops ¹ HCl to pH<2, cool to 4 °C, dark for BTEX	14 days
ORGANICS		1,000	Cool to 4 °C, dark	7 days until extraction and 40 days after extraction
PESTICIDES & HERBICIDES Organophosphorus Pesticides Organochlorine Pesticides Chlorinated Herbicides	1-qt. glass container with teflon lined lid per sample type; <u>must be prerinsed with hexane, acetone, or methylene chloride</u>	Each sample type requires 1,000 mL in a separate container	If chlorine is present, add 0.1 g sodium thiosulfate	
SEMI-VOLATILE ORGANICS				
ORGANICS-IN-WATER COLLECTION PROCEDURES				
<p>Label each container before collection with tag no./unique sample identifier number, Station Location, Date, and “ORGANICS: Organophosphorus Pesticides, Organochlorine Pesticides, or Chlorinated Herbicides” or “SEMI-VOLATILE” (depending on the sample type).</p> <ul style="list-style-type: none"> ◦ Fill to the top. Put in dark and on ice. ◦ Fill quart container(s) to the top. Put in dark and on ice. 				
BIOLOGICAL				
TOXICITY IN WATER	Two 1-gallon cubitainers	8,000 mL	Cool to 4 °C, dark	36 hours
TOXICITY SAMPLE COLLECTION PROCEDURES				
<p>WATER</p> <ul style="list-style-type: none"> ◦ Label containers before collection with Station Location, Date, and Sample Type. ◦ Open cubitainer by pulling apart. Pre-rinsing cubitainers with ambient water is not necessary. ◦ Fill each container with ambient water by submerging container approx. 1-ft. below the surface mid-stream until filled. ◦ Place on ice and ship as soon as possible. <p>NOTES</p> <p>◦ Preserving with HCl, discuss with laboratory personnel; preserved samples may cause damage to analytical equipment. If sample is analyzed within 48 hours, preservation may not be required.</p>				

Prior to preserving with HCl, discuss with laboratory personnel; preserved samples may cause damage to analytical equipment. If sample is analyzed within 48 hours, preservation may not be required.