

CHAPTER 5

COLLECTING WATER SAMPLES

General Principles

Collect water samples at the same location for both bacteriological and chemical analysis. If meeting holding times for water and bacteriological samples is an issue, field measurements (including flow) may be taken first. See Chapter 3 for details.

If other work is being done at the site—for example, measuring flow, collecting sediment samples, collecting biological samples, or habitat assessment activities—make sure to collect representative samples from an undisturbed area of the stream.

If in doubt about containers, holding times, or preservation measures, call the laboratory receiving the samples.

Required Equipment

See Chapter 9 for the list of basic SWQM equipment.

Depth of Sample Collection

If the water depth at the sampling point is **less than 0.5 m**, collect samples at a depth equal to one-third of the water depth measured from the water surface.

If the water depth is **greater than 0.5 m**, collect samples at a depth of 0.3 m below the surface.

Where to Collect Samples

Collect water samples at the centroid of flow, if the stream appears to be completely mixed from shore to shore. The *centroid* is defined as the midpoint of that portion of the stream width which contains 50 percent of the total flow. For stream samples, the centroid of flow must be accessible for sampling physicochemical parameters, either by wading, from a bridge, or from a boat.

Stream samples are generally collected upstream of a bridge to avoid any influence bridge runoff might have on whether the sample is representative. Sampling from the shoreline of any water body is the least acceptable method unless containers can be filled away from the bank. If shoreline sampling is necessary, avoid backwater areas and stagnant pooled areas in flowing streams. Take care to avoid contaminating the sample with debris from the bank. Collect reservoir and bay samples from boats.

Collecting Water Samples from a Bridge

When it is **not** possible to collect samples directly from a water body, use a discrete sampling device (bailer, Van Dorn bottle). In general, discrete sampling devices are safer and easier to use than a bucket and are the preferred method. However, if a discrete sampler is not available, a plastic bucket may be used. This technique generally applies to sample stations located at bridge crossings where access is an issue.

Rinse the sampling device at least three times with ambient water before collecting the final sample. Pour slowly to avoid creating bubbles. When filling sample containers, pour the water into them; dipping sample containers into the bucket could introduce contamination. Always collect bacteriological samples first.

Collecting Water Samples and Field Measurements from the Same Container

In certain rare circumstances, where personal safety is an issue and the goal is to reduce the time on a bridge, the collector may use a single container for both water samples and field measurements. In that case, rinse the plastic bucket or other appropriate container and the multiprobe instrument at least three times with water from the site. For more information, see Chapter 3, “Field Measurements from a Bucket.”

When collecting samples and field measurements from a single container of sample water, always collect the bacteria sample before the multiprobe instrument is placed in the container—carefully, so that the sample water is not agitated. Gently pour water into the bacteria-sample container. After field measurements have been recorded, pour sample water into containers. To avoid contamination, do not immerse water-sample containers in the bucket.

Collecting water samples under this scenario is only appropriate for conventional water chemistry sampling. It is **not** appropriate for collecting metals or organic samples.

Collecting Water-Chemistry Samples

In most water bodies, near-surface water is considered representative of the water mass. Collect a water sample by directly immersing the container beneath the water surface to a depth of 0.3 m. Sites accessed by bridge can be sampled with a plastic bucket, disposable bailer, or Van Dorn bottle. If using a bucket or bailer, take extreme care to avoid contaminating the sample with debris from the rope and bridge. Be sure to rinse the sample-collection device between stations. Rinse at least three times with ambient water from the next station.

See Table 5.2 for sample volumes, containers, preservatives, and holding times. Also refer to Table A7.3 of the *SWQM QAPP* for a list of methods used to analyze water samples (see Appendix A).

Conventional Parameters

Examples of routine (baseline) conventional parameters include alkalinity, total suspended solids (TSS), chloride, sulfate, nitrite + nitrate, total Kjeldahl nitrogen (TKN), ammonia, total phosphorus (TP), total organic carbon (TOC), and chlorophyll *a*. Laboratory measured total dissolved solids (TDS) and orthophosphate (OP) are not routine parameters. Both laboratory analyzed TDS and field-filtered OP may be sampled and analyzed as needed for specific purposes. Since TSWQS criteria for TDS were developed using specific conductance data and, to be consistent, TDS is calculated using specific conductance.

Nutrient Sample Collection

Due to an increased focus on nutrient impacts in Texas and the U.S., states are facing an increasing need to collect additional data on parameters to help assess and control eutrophication. Most researchers working with nutrient impacts argue for the use of TP rather than OP for defining trophic status, conducting TMDLs, looking for trends in eutrophication, and setting water quality criteria (the EPA's national guidance criteria are expressed as TN and TP). When evaluating and controlling nutrient loadings, loads can only be effectively expressed as TP.

Recent efforts by the TCEQ include: (1) developing methods to estimate percent aquatic vegetation coverage in streams, (2) improving quantification levels for total phosphorus (TP) and potentially total nitrogen (TN), and (3) acquiring additional routine data on TN (TKN and nitrate/nitrite).

Collecting data to determine total nutrients is important to fully characterize the trophic condition of water bodies and to directly relate the effect of nutrient loadings to instream conditions. Core parameters should include paired nitrogen parameters nitrate, nitrite (or nitrate + nitrite), ammonia, and TKN as well as TP and Secchi-disk transparency.

Orthophosphate (optional)

A separate sample for orthophosphate (OP) must be filtered in the field within 15 minutes of collection. The sample must be filtered using a 0.45 μ filter. This is needed to separate dissolved and suspended forms of orthophosphate. The parameter code for field-filtered OP is 00671.

OP Sampling Supplies

The most cost-effective and least time-consuming method uses a 60 mL Luer Lock syringe, a 25 mm 0.45 μ syringe filter, and a 60 mL Nalgene bottle. The equipment does not have to be sterile but must be clean and protected from potential contaminants. Keep unused supplies in plastic bags or another container.

The Whatman GD/X syringe filter is designed for highly turbid samples. A single filter contains a prefiltration stack with layers starting at 10 μ to the final 0.45 μ filter (see Figure 5.1). This filter processes 3 to 7 times more sample volume, which decreases hand pressure and increases efficiency for hard-to-filter samples. However, as with any method, there can be limitations and it may not be as effective in all areas of the state. Sample collection may require multiple filters. Alternative filtration methods may be substituted, as long as filtration is performed within 15 minutes of collection using a 0.45 μ filter.

OP Sample Collection Method

Draw the ambient water into a clean 60 mL Luer Lock syringe by pulling back on the plunger. Fill the syringe to the 60 mL mark. Attach a new GD/X syringe filter to the syringe by screwing it onto the tip (see Figure 5.1). Push in on the syringe plunger to start filtering the sample until it starts to come out of the filter. Place the end of the filter over the sample container and filter the sample directly into its container. If flow through the filter slows and increased pressure is required, replace the filter and continue until the required volume is collected. The volume may vary depending on the lab performing the

analysis but in general a minimum of 50 mL is required. Discard any used filters. The syringes may be reused if cleaned following appropriate protocols.

Sample Containers and Volumes

Sample containers should be new, unused, clean polyethylene containers or glass jars or used laboratory cleaned containers. Prior to sample collection, collectors should rinse containers three times with ambient water and discard water away from the sample location. However, new, unused containers or those cleaned in a laboratory may be used without rinsing. You must remain consistent with whichever method is chosen. See Table 5.2 for suggested sample containers and volumes.

Note: If using cubitainers, do not inflate them by blowing into them.

Routine conventional parameters require at least three containers. Routine parameters require one unpreserved sample (alkalinity, chloride, sulfate, fluoride, nitrate + nitrite, TSS, and VSS), one preserved sample (ammonia, TKN, TOC, TP), and one unpreserved for chlorophyll *a*. Collect the chlorophyll *a* sample in a wide-mouth amber container or place the container in an amber-colored plastic bag.

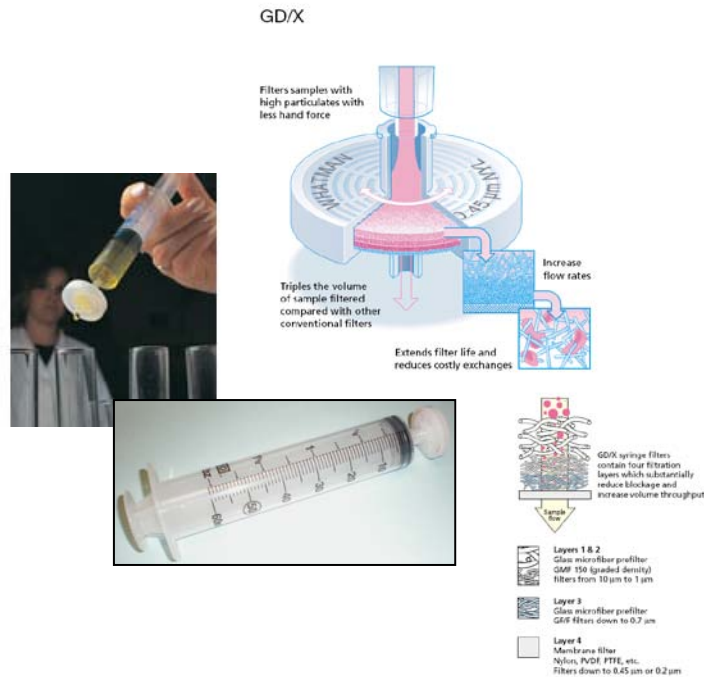


Figure 5.1. Whatman GD/X syringe filter and filtration apparatus.

Container Label

Label each container with enough information to allow the lab to associate the sample with the request for analysis tag or chain of custody; key sample information includes identifiers such as *Station ID#*, *Sample Tag ID#*, *preservative*, *sample date*, and *station description*.

Sample Preservation

Ice. Samples must be placed on ice immediately after collection. Place all samples that require cooling only on ice before preserving other samples with acid. Sufficient ice will be needed to lower sample temperature to $< 6^{\circ}\text{C}$ but not to the freezing point. Sample temperature must be maintained at $< 6^{\circ}\text{C}$ until delivery to the laboratory. This may mean repacking samples prior to shipment.

Samples that are hand delivered to the laboratory the same day of collection may not meet the $< 6^{\circ}\text{C}$ requirement. In this case, the samples are considered acceptable if there is evidence that chilling has begun, such as arrival on ice.

Take care at all times during collection, handling, and transport to prevent exposure of the sample to direct sunlight. For cubitainers, try to remove excess head space.

Acid. Label samples requiring preservation with sulfuric acid (H_2SO_4) in a way that lets the laboratory know that acid has been added. For example, put an **X** on the container cap to signify that acid was used for preservation, or label container “2 mL H_2SO_4 added.” Add approximately 2 mL of 1:1, analytical reagent grade H_2SO_4 to each liter of sample to be analyzed for ammonia, total Kjeldahl nitrogen, total phosphorus, and total organic carbon. This amount is adequate to reduce the pH to less than 2. Invert about several times before placing the sample on ice, in the dark. Maintain the temperature at $< 6^{\circ}\text{C}$ until arrival at the laboratory.

Preservation with acid must occur in the field within 15 minutes of collection.

Samples must be cooled to $< 6^{\circ}\text{C}$ but should never be frozen. See Table 5.2.

Safety note: Wear safety glasses when working with acids. Transport acids in a secure container that will prevent spills. Always carry sodium bicarbonate (baking soda) with acids to use in case of spills. Clean up all spills and splashes. Have a supply of freshwater nearby: it comes in handy if acid is spilled on the skin.

Field QC Samples

Field splits (FS) are collected with every 10th conventional water sample. If fewer than 10 samples are collected in a month, submit one set of field splits for that month. Field blanks are not routinely required but may be inserted into the sample regime if needed for a specific reason. Submit QC sample results for field splits are submitted to the TCEQ for storage in SWQMIS using the *monitoring type code* “FS.” See Chapter 10 for detailed information on field QC samples.

Metals-in-Water Samples

Basic metals-in-water monitoring focuses on the TSWQS for the protection of aquatic life.

Routine Status Monitoring for Metals

For routine status monitoring (sometimes called “TSWQS metals”), collect samples for *dissolved* and *total metals*. Routine dissolved metals include arsenic, cadmium, chromium, copper, iron, lead, magnesium, manganese, nickel, silver, and zinc. Routine total metals include only selenium and mercury.

Routine metals-in-water samples are not collected during periods of abnormally high turbidity associated with high or flood flows. Samples with high turbidity are unstable, making it difficult to collect a representative grab sample of soluble metals. High suspended solids can also interfere with the sample analysis. However, metals should be collected at sites that are normally turbid, but special-study sampling may be an exception. For example, wet-weather sampling is likely to include some samples with high turbidity.

Delay sampling for metals for at least 48 hours following a heavy rainfall.

Sample-Collection Depth

Collect metals-in-water samples from a depth of 0.3 m, using a peristaltic pump or other pumping system. Near-surface water is considered representative of the water mass in all water-body types. For determining compliance with numerical toxic-substance standards, a sample taken at the surface (as previously defined) is adequate.

Sampling Equipment and Preparation

Total- and dissolved-metals equipment preparation and cleaning procedures are based on EPA Method 1669 (EPA 1996). Metals-in-water sampling materials must be cleaned and prepared by a laboratory that can perform adequate quality-control checks (for example, equipment and bottle blanks). See Table 5.1 for components of a standard metals-in-water sample-collection kit.

The following applies to the information in Table 5.1:

- Disposable supplies must not be reused. This includes filters, gloves, storage bags, and ground cloths.
- Resuable supplies must be properly cleaned before reuse.
- Bottles may be used new without additional cleaning if they are certified pre-clean and metals free, and a blank is run from each lot.
- Materials should be stored and transported in dust-free containers, such as plastic bags, included in laboratory-prepared sampling kits.
- Materials such as gloves, storage bags, and plastic wrap, may be used new without additional cleaning unless the results of the equipment blank pinpoint any of these materials as a source of contamination. In that case, either a different supplier must be obtained or the materials must be cleaned.

Field Filtration

Sample filtration for dissolved metals *must be performed in the field within 15 minutes of collection* and with extreme care to avoid contamination. If samples are allowed to sit for an extended period of time, metals will settle out or adhere to the sides of the plastic container. Pump and filter samples directly into their container.

Table 5.1. Components of a standard metals-in-water sample-collection kit.

Item	Use	Cleaning	Storage	QC Check
Reusable Supplies				
250 mL plastic bottles	dissolved-metals blank, dissolved-metals sample, total-metals sample, total metals blank)	HNO ₃	dust-free containers	Upon opening a new box of bottles, one in every 100 bottles are checked for contamination by filling with purified reagent water and submitting for analysis by ICP, ICP-MS, or CVAFS. The water must not show metals concentrations above the reporting limits.
250 mL glass or Teflon bottles	mercury blank and sample	HNO ₃	dust-free containers	
Peristaltic pump	dissolved-metals sample	Pump modules do not require cleaning. However, nearly all peristaltic pumps contain a metal head and metal controls. Touching the head or controls necessitates changing of gloves before touching the tubing and/or cartridge filter.		equipment blank
1 L bottle of blank water	field blank	Metals-free deionized water	dust-free containers	Used for field and equipment blanks.
Disposable Supplies				
0.45 μ metals-free cartridge filter	dissolved-metals samples	Not required. Purchase certified pre-cleaned and bagged samples	dust-free containers	Record lot number. Upon opening a new lot of filters, one in every 100 filters are checked for contamination by filling with purified reagent water and submitting for analysis by ICP, ICP-MS, or CVAFS. The water must not show metals concentrations above the reporting limits.
plastic (3' × 3')	ground cloth	Not required		equipment blank
60 mL plastic syringe	dissolved-metals sample	Not required. Purchase certified pre-cleaned	dust-free containers	equipment blank
Teflon tubing (for use with peristaltic pump)	dissolved-metals sample	Soaking in 5–10% HCl solution for 8–24 hours, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with mercury-free air or nitrogen	double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.	equipment blank
powder-free gloves	sample collection	Not required	dust-free containers	equipment blank

Labeling the Sample Container

Do not write directly on the sample container. Use a labeling material that will not contaminate the sample. Write the sample information on the plastic bag holding the sample container. Provide enough information for the laboratory receiving the sample to easily match it to the analysis request or chain of custody (for example, date, location, type of sample). For the dissolved metals-in-water sample indicate that the sample has been field filtered.

Sample Preservation

Metals-in-water samples are preserved with a 1 : 1 HNO₃/H₂O solution made from metals-grade HNO₃ and metals-free deionized water. To eliminate potential contamination in the field, metals-in-water samples are shipped to the lab unpreserved. Samples are preserved upon arrival at the laboratory. The lab will add acid to bring the pH down to < 2. The holding time for acid-preserved samples is six months, except for mercury—28 days.

Companion Samples for Metals in Water

Request total-hardness analysis whenever metals in water are to be analyzed from an inland site (estuarine sites do not require hardness analysis). Typically, hardness can be calculated from the analysis of calcium and magnesium. The same sample used for total metals may also be used for hardness.

If a *total-metals sample* is collected, submit a sample for total suspended solids (TSS) if not already requested in a companion sample for routine water chemistry.

See Table 5.2 for sample volumes, containers, preservatives, and holding times for hardness and TSS samples.

Clean Hands / Dirty Hands Sampling

Total- and dissolved-metals sampling procedures are based on EPA Method 1669 (EPA 1996).

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 require two people working together. At the field site, one person is designated as *CH* and the second as *DH*. Although specific tasks are assigned at the start, some tasks overlap and can be handled by either *CH* or *DH* as long as no contamination is introduced into samples. Both *CH* and *DH* wear non-contaminating, disposable, powder-free gloves during the entire sampling process and may change gloves frequently as the tasks change. Specifically, *CH* changes gloves between samples and whenever anything not trace-metals clean has been touched.

CH takes care of all tasks involving direct contact with the sample bottle and transfer of sample from the collection device to the bottle. *CH* generally works inside a clean area, usually inside a large plastic bag near the water body (see Figure 5.2) or inside a vehicle. *DH* works outside of the clean area on tasks such as preparing the sampler, operating sampling equipment, and all other activities that do not involve direct contact with the sample.

If two people are not available, metals-in-water samples may be collected by an individual who changes gloves when switching between *CH* and *DH* tasks.

Avoiding Contamination

The key to collecting a good metals-in-water sample is to avoid potential sources of contamination. Collect samples upstream from bridge crossings. Whenever possible, collect samples facing upstream and upwind to minimize contamination. Other sources of contamination to avoid include airborne dust, automobile exhaust, cigarette smoke, and nearby corroded and rusty bridges, pipes, poles, or wires. Mark sample information on the plastic bag and not on the bottle.



Figure 5.2. Collecting a dissolved-metals sample with a TCEQ Clean Metals Kit.

Look for ways to reduce the number of sample handling steps. This is not generally an issue when collecting a sample with a peristaltic pump, tubing, and a 0.45 μ cartridge filter. A large volume of water can be processed quickly filling sample containers directly from the water body.

However, using a 60 mL syringe requires multiple steps to fill the syringe and filter sample to obtain the appropriate volume. The potential for introducing unwanted contaminants is high. An efficient way to reduce the number of sample handling steps is to use a larger laboratory-prepared container to collect the sample. An empty blank water container can be used to collect the ambient water sample. This supplies a large volume of sample allowing the entire filtering process to be done inside the clean area. Refer to “TCEQ Houston Laboratory Clean Metals Kit—Sampling Procedure,” below, for additional information on this collection method.

Metals-in-Water Collection Procedures

Metals sampling procedures are based on EPA Method 1669 (EPA 1996). The following section outlines sample collection using the traditional EPA Method 1669—peristaltic pump, tubing, and cartridge filter.

Total-Metals Sample

At the site *DH* opens the outer, dirty bag holding the total-metals sample bottle while avoiding contact with the clean inner bag (if present). *CH* opens the inner bag (if present) and pulls out the sample bottle. *CH* does not touch anything but the sample bottle, the cap, and the water being sampled. *CH* opens the bottle, making sure not to lay the cap on any surface while off the bottle.

For a total-metals sample, fill the container directly from a water body or from a precleaned sample collection device. To reduce contamination, containers can be filled and capped under the surface of the water. Allow enough space for the addition of acid. Samples are preserved by the laboratory performing the analysis. *CH* places the container

back in the plastic bag and sealed by *DH*. The holding time for preserved metals samples is six months.

Follow the same process for a total-mercury sample. Allow enough space for the addition of acid. Mercury samples are preserved by the laboratory doing the analysis. The holding time for a preserved mercury sample is 28 days.

Dissolved-Metals Sample

At the site, *DH* sets up the pump, while *CH* places the bottle in a *container holder*—anything nonmetal that supports the bottle, freeing up the collector's hands. *DH* opens the bag containing the filter. *CH* takes an end of the tubing and attaches the 0.45 μ cartridge filter making sure the flow arrow points in the correct direction. The filter end is approximately 18 inches from the pump, and the other end is long enough to easily reach beneath the water surface. *DH* closes the pump head, locking the tubing in place.

DH pulls the dissolved-sample container from the cooler and opens the outer, dirty bag while avoiding contact with the clean inner bag (if present). *CH* opens the inner bag (if present) and pulls out the sample bottle. *CH* does not touch anything but the sample bottle, the cap, and the water being sampled.

DH immerses the intake tube directly into the water and operates the pump. *CH* allows the ambient water to flush the tube and filter with the filter held upright. This allows water to run over the filter and remove any dirt or dust particles that might be on the filter. *CH* removes the cap from the sample bottle, holds the filter over the container opening, and allows the container to fill, leaving some head space. *CH* puts the cap back on the bottle and places the bottle back inside the plastic bag. *DH* seals the bag and places it in the ice chest.

Whenever *CH* touches the boat or equipment, which may be contaminated, *CH* should change gloves immediately.

As an alternative method, use a 0.45 μ cartridge filter and a 60 mL syringe to collect a dissolved-metals sample. For details on using this method, refer to “TCEQ Houston Laboratory Clean Metals Kit—Sampling Procedure,” below.

TCEQ Houston Laboratory Clean Metals Kit—Sampling Procedure

The TCEQ Houston Laboratory currently supplies *Clean Metals Kits* to TCEQ personnel and some CRP partners. The following are procedures, based on EPA Method 1669 (EPA 1996), for collecting samples using the TCEQ Houston Lab Clean Metals Kit. Each kit comes with supplies to collect dissolved metals, total metals, total mercury, and the associated blanks. The Clean Metals Kits are prepared according to the Houston Lab standard operating procedure no. 7, “Preparation of Clean Kits for Collection of Trace Metals Samples.”

Note: Not all of the supplies in the kit may be required for all sampling events. Return unused supplies to the lab as described in “Sample Handling and Shipping,” below.

Sampling Kits

Ideally, metals sampling will be pre-planned and appear on the CMS. TCEQ personnel and other monitors using the Clean Metals Kits should notify the TCEQ lab of the number of kits and the delivery schedule that will be required for the coming fiscal year. Then, the kits must be ordered from the TCEQ lab prior to samplings, allowing at least two weeks for kit preparation and delivery. A limited number of kits are often available for instantaneous orders. The TCEQ lab supplies an order form for kits. The shelf life of a kit is approximately one year, provided the kit has remained sealed and there is no visible deterioration of components. Individual kits are enclosed in two plastic bags and shipped in a clean plastic ice chest. A kit contains all equipment and bottles for proper collection of samples from one site for the analyses of dissolved metals, total metals, and mercury. The kit also contains the metals-free water and bottles for the collection of required QC blanks.

A standard Clean Metals Kit contains the following supplies in a black sample kit box enclosed in 2 (3' × 3') plastic bags with a cable tie:

- 4 250 mL plastic bottles labeled with the sample type (BDM—*blank dissolved metals*, BTM—*blank total metals*, SDM—*sample dissolved metals*, STM—*sample total metals*) and a unique identification number
- 1 125 mL glass bottle (BHG—*blank mercury*)
- 1 250 mL glass bottle (SHG—*sample mercury*)
- 1 packet of supplies (two 5" × 8" bags, two 6" × 4" sheets of Parafilm, cork, one AquaPrep 600 filter, and one 60 mL plastic syringe)
- 1 1 L bottle (BH20—*blank water*)

All Clean Metals Kit supplies are shipped in an ice chest marked for metals samples only. In addition to the black sample kit box the ice chest contains the following supplies:

- 1 plastic bag (3' × 3') to be used as a ground cloth
- 2 plastic containers for shipping glass bottles
- 1 plastic container with Velcro on the bottom to hold the sample bottles while filtering—referred to below as the “Velcro container”
- 1 packet of bubble bags (2)
- 1 sheet of bubble wrap to line the cooler for shipping
- 1 manila envelope to hold the original request form, kit instructions, and two packets of gloves (medium—3 pairs and large—4 pairs)
- 2 binder clips to attach “clean enclosure” plastic bags to black box
- 1 black box (Sampling Kit)
- 1 set of sampling instructions

Using the Sampling Kit

Collect samples upstream from bridge crossings. Whenever possible, sample facing upstream and upwind to minimize contamination. Other sources of contamination to avoid include airborne dust, automobile exhaust, cigarette smoke, and nearby corroded or rusty bridges, pipes, poles, or wires. Mark sample information on the plastic bag, not on the bottle.

Kit Preparation

1. Put on gloves.
2. Lay the ground cloth down.
3. Remove the black box from the cooler and carefully cut the cable ties from both bags.
4. Open the black box and use the binder clips to attach “clean enclosure” plastic bags to the box.
5. Place the cork in the hinge of the black box.
6. Remove the contents from the black box and set them aside.
7. Attach Velcro container to the bottom of the black box.

Collecting Blank Samples

Total Mercury (Hg) Blank

1. Using the *blank mercury bottle* (BHG-), slide the double plastic bags partially down, and place them inside the Velcro container in the black box.
2. Open the *blank water* (BH₂O-) labeled for mercury use.
3. Fill the BHG bottle up to its neck with blank water; recap the bottle, reseal the plastic bags and set them aside.

Total Metals Blank

4. Using the *blank total metals bottle* (BTM-), slide the double plastic bags partially down and place the bottle (still inside the plastic bags) inside the Velcro container in the black box.
5. Open the *blank water* (BH₂O-) designated for metals use.
6. Fill the BTM- bottle up to its neck with blank water; recap the bottle, reseal the plastic bags, and set them aside.

Dissolved-Metals Blank

7. Using the *blank dissolved metals bottle* (BDM-), slide the double plastic bags partially down and place the bottle (still inside the plastic bags) inside the Velcro container in the black box.
8. Open the blank water (BH₂O-) labeled for *Trace Metals* use.
9. Remove the plunger from syringe and insert the syringe tip into the filter. Note the flow direction on the filter.
10. Fill the syringe with blank water and use the plunger to flush the filter with 120 mL of blank water
11. Attach the filter to the top of the BDM- bottle and wrap its neck securely with one piece of Parafilm.
12. Fill the syringe with blank water. Repeat until the bottle is filled to its neck.
13. Remove the filter and Parafilm from bottle. Recap the bottle, reseal the plastic bags, and set them aside.

Collecting Metals Samples

Dissolved Metals

1. Remove the *total metals bottle* (STM-) from its double bags and collect a sample from the water body. An alternative is to empty the one-liter blank-water container

and use the bottle to collect sample for filtering under the protection of the plastic enclosure.

2. Before filtering a dissolved-metals sample, fill the syringe with sample water and use the plunger to displace any blank water remaining in the filter.
3. Using the *sample dissolved-metals* bottle (SDM-); attach the filtering apparatus as in step 8 (above) using a new piece of Parafilm.
4. Fill the syringe with the sample from the STM- bottle and use plunger as needed. Repeat until the bottle is filled to its neck.
5. Disassemble the filtering apparatus. Recap the bottle, reseal the plastic bags, and set them aside.

Total Metals

6. Refill the *sample total bottle* (STM-) from the water body.
7. Recap the bottle and put it in its original double bags, reseal them, and set aside.

Total Mercury

8. Remove the *sample mercury bottle* (SHG-) from its double bags and collect a sample from the water body.
9. Recap the bottle and put it in its original double bags. Reseal the bags and set them aside.

Shipping

1. Put double-bagged glass bottles into bubble sleeves, then into plastic shipping containers.
2. Put the shipping containers into bubble bags and seal them.
3. Put all other sample bottles into the black box, including those in shipping containers.
4. **Do not** preserve samples in the field. Samples will be preserved by laboratory staff in a controlled environment to reduce contamination.
5. Put the black box and all unused and reusable equipment into the cooler (**do not** use ice).
6. Place all refuse (used filters, wrappings, gloves, plastic bags) in the plastic bag that was used for the ground cloth and dispose of it properly. **Do not** ship trash back to the laboratory.
7. Ship samples and all unused and reusable equipment to the TCEQ Houston Laboratory using next-day delivery to ensure timely preservation.

Each sample bottle has a unique number assigned by the laboratory. Record these numbers with other field information. Also, record these numbers on the TCEQ *Request for Analysis* sheets. Do not write on the bottles. If additional labeling of a sample is required, write on the plastic bag containing the bottle.

Requirements for Collecting QC Samples for Metals in Water

To detect contamination during sampling, blanks are submitted for analysis. Run a blank for each type of metal sample collected. Field blanks (FB) are required for total-metals

samples; equipment blanks (EB) for dissolved-metals samples. See Table 5.2 and Chapter 10 for detailed information on field QC samples.

Collecting Field Equipment Blanks

Before using any metals sampling equipment the laboratory or equipment cleaning contractor is required to generate equipment blanks to demonstrate that the equipment is free from contamination.

Equipment blanks must be run on all equipment being used in the field. Equipment blanks are run by the sampler at a frequency defined in Chapter 10, which has detailed information on field QC samples.

Note: For those using the TCEQ metals-in-water kits, the standard frequency for equipment blanks does not apply. Equipment blanks are collected and submitted with each sample. See Table 10.1.

Blank Water

Take an adequate supply of metals-free deionized water into the field for each field blank collected. Metals-free deionized water is supplied by the laboratory performing metals analysis. Keep the deionized-water containers clean and dust-free on the outside by wrapping them in plastic bags.

Organics-in-Water Samples

Collect organic samples at a depth of 0.3 m by submerging the sample container by hand. A discrete sampler (Van Dorn) may be used, if necessary. Since organic compounds tend to concentrate on the surface of the sampling device or container, do not rinse the sampling device and sample container with native water before filling it.

Sample Containers and Collection

Volatile Organics

Fill three 40 mL volatile-organics analysis (VOA) vials with no headspace or air bubbles. Slowly fill each container to prevent tiny air bubbles from purging the sample during collection. Avoid trapping air bubbles in the sample. Fill one vial at a time, allowing enough room to add 2-4 drops HCl to pH < 2. The meniscus formed by the sample will help prevent bubbles when capping the vial. After capping the vial, invert the sample to check for large bubbles. If bubbles are present uncap the vial and add more sample. Tape the three vials together, label them “VOA,” and submit them as a set. Cool them to < 6°C but do not freeze them.

Note: Submit a trip blank for VOA samples (three 40 mL VOA vials) with each ice chest full of such samples shipped to the lab. Prepare trip blanks in advance, just before the sampling trip, and transport them to the field. Ask the laboratory for DI water and specify that it is for a VOA trip blank. Trip blanks demonstrate that the containers and sample handling did not introduce contamination. Submit sample results for trip blanks to the TCEQ for storage in SWQMIS using the monitoring-type code “TB.” See Table 5.2 and Chapter 10 for detailed information on field QC samples.

Pesticides and Herbicides

The sample container for pesticides and herbicides is a new, clean, unused glass jar with a Teflon liner inside the cap, prerinsed with pesticide-grade hexane, acetone, or methylene chloride. Collect one liter of water for each of the three sample types (organophosphorus pesticides, organochlorine pesticides and chlorinated herbicides). **Each parameter group requires three separate 1 L jars.** If all three parameter groups are collected, nine 1 L jars must be submitted to the laboratory. Minimize the air space in the top of the jar. Preserve the sample immediately after collection by placing it on ice in the dark. In addition to other sample information, label the jar “ORGANICS—chlorinated herbicides,” “—organophosphorus pesticides,” or “—organochlorine pesticides,” depending on the sample type.

Semivolatile Organics

Sample containers for semivolatile organics must be new, clean, unused glass bottles with a Teflon liner inside the cap, and prerinsed with pesticide-grade hexane, acetone, or methylene chloride. Fill two 1-quart jars to the top and place them on ice in the dark. In addition to other sample information, label the jar “Semivolatiles.”

Note: Collect one sample, in a set of 10 or fewer (not blanks), in triplicate. This gives the laboratory enough sample volume for laboratory QC.

Sample Treatment in the Presence of Chlorine

Chlorine has an effect on pesticides, herbicides, and semivolatile organics. If instream chlorine residual is suspected, measure the chlorine residual using a separate subsample. Test strips or a standard chlorine residual test may be used as a way to determine the presence of chlorine and the need to treat water samples with sodium thiosulfate. Free chlorine will oxidize organic compounds in the water sample, even after it is collected.

If chlorine residual is above a detectable level (the pink color is observed upon adding the reagents or presence indicated by test strips), immediately add 100 mg of sodium thiosulfate to pesticide, herbicide, semivolatile, and VOA samples. Invert the sample until the sodium thiosulfate is dissolved. Record the chlorine residual concentration, or presence or absence, in the field logbook and on the request for analysis tag or chain of custody. If the chlorine residual is below detectable levels, no additional sample treatment is necessary.

Safety note: Although sodium thiosulfate has a low toxicity, it can cause eye irritation. Wear safety glasses during preparation of the sodium thiosulfate solution and when adding solution to the sample.

Methyl-Tert-Butyl Ether (MTBE)

Collect three VOA vials at each site. The three vials equal one sample; they may be taped together as one sample.

Preserve all vials with hydrochloric acid (HCl). Fill the vial by slowly submerging and cap it underwater. Later, remove the cap and add two drops of 1:1 HCl. Carefully recap the vial, avoiding the introduction of bubbles larger than a pea.

An alternative method is to acidify the vial prior to sampling. Ensure that the pH is less than 2. If the water may be alkaline or have a significant buffering capacity, or if there is

concern that pre-acidified samples may have the acid wash out, take a few practice vials to test with litmus paper. It may take more than two drops, and it will then be clear how to preserve the other samples that are being submitted to the lab. If an alternative method has proven successful, continue with that method.

Note: If vigorous foaming is observed following acidification, discard that sample and collect another set. Do not acidify the second set. Clearly mark the sample “not acidified” and the lab will run the analysis immediately. The holding time is 14 days with acid, 24 hours without acid.

Perchlorate

Surface water samples for perchlorate should be collected in a new unused 1 L polyethylene or glass container. Perchlorate samples do not require cooling, but can be put on ice with other samples. The sample holding time is 28 days.

Propellants, Explosives, and Pyrotechnics (PEPs)

Surface water samples for PEPs should be collected in triplicate at each site in 1 L brown glass containers that have been prerinsed with methylene chloride. Keep the samples out of direct sunlight and put them immediately on ice to maintain the temperature at < 6°C. The sample holding time is seven days under refrigeration.

Miscellaneous Parameters

Hexavalent Chromium

Acidification alters the hexavalent form of chromium. A separate, unacidified sample must be submitted if hexavalent chromium is to be analyzed. Filter, using the same procedure described for dissolved metals, and submit at least 500 mL of water. Collect the sample in a DI water-rinsed plastic or glass container, place it on ice, and ship it to the lab in time for analysis to begin within 24 hours of collection, preferably with at least 24 hours' notice. The lab must be notified when a hexavalent chromium sample will arrive. Hexavalent chromium is not usually analyzed on unfiltered samples and is not a routine parameter. However, criteria for this specific parameter are included in Table 1 of the TSWQS.

Cyanide

If a sample for cyanide is requested, a separate 1 L sample must be submitted in a separate plastic or glass container (a cubitainer, rinsed with deionized water, will work). Cyanide samples must be preserved immediately by the addition of ascorbic acid and sodium hydroxide, and then put on ice.

Chlorine Removal

Ascorbic acid is added first to remove chlorine when present. Unless it is known that chlorine or other oxidizers are **not** present, a test for chlorine residual should be made. Obviously, collection points from open waters in streams which are **not** immediately downstream from outfalls present little chance of chlorine being present. The decision to test for chlorine and to omit ascorbic acid is based on the circumstances at the time of collection. **Note:** Excess ascorbic acid interferes with the analysis.

Sample Preparation

Oxidizing agents such as chlorine decompose most cyanides. To dechlorinate a sample, add 0.2 g of ascorbic acid before adding sodium hydroxide (NaOH). Excess ascorbic acid can interfere with sample analysis at the lab. Ascorbic acid crystals are nontoxic and can be carried to the collection site.

Sample Preservation

After the ascorbic acid is added (or not, due to a negative chlorine residual test), add the 2 mL of 10 N NaOH (about six pellets or 2 mL of solution). The final pH must be greater than 12. To confirm this, a sampler who has not yet gained experience in determining the necessary amount may use pH test paper. The sample must be preserved with NaOH. Label the container “Preserved with NaOH” or “Preserved with ascorbic acid and NaOH.”

Samples must be analyzed as rapidly as possible after collection. If storage is required, store the samples in a refrigerator or in an ice chest filled with ice to maintain the temperature at < 6°C. The sample holding time under refrigeration is 14 days. Tests for cyanide are not usually conducted on filtered samples.

Handling and Shipping Samples

Ideally, samples are shipped on the same day they are collected. Due to increased shipping restrictions, samples being sent via a freight carrier may require additional packing. Even if care is taken to seal the ice chest, leaks can and do occur. To avoid leaks, place samples and ice in a large plastic bag inside the ice chest for shipping. The bag can be sealed by simply twisting it closed while removing excess air and taping the tail down. Leaking ice chests can cause samples to be returned or to arrive at the lab beyond the holding time. Some shipping companies, depending on the location, may require this extra step before shipping ice chests.

Place laboratory analytical request forms corresponding to samples in the ice chest in a Ziploc bag and tape the bag to the inside of the lid. Secure the lid with tape. This is essential if samples and ice are not in a large plastic bag. This method of handling chain-of-custody forms should not override existing protocols of the TCEQ region or sampling organization.

Take special care when shipping glass. When shipping a combination of plastic and glass, plastic containers can be used to cushion glass containers. If the majority of containers are glass, take extra care to prevent breakage during shipping by using suitable shipping materials (bubble wrap or plastic netting made for slipping over jars).

Data Reporting

Appropriate procedures and parameter codes necessary for submitting data are discussed in the *SWQM DMRG* (see Appendix A).

Table 5.2. Quick reference guide—water-sample collection methods, preservation, storage, and handling.

<i>Note:</i> If in doubt about containers, holding times, or preservation measures, call the laboratory receiving the sample(s).				
Parameters	Recommended Containers	Sample Volume (mL)	Preservation	General Holding Times
Routine Water-Chemistry Samples (3 containers: 2 unpreserved, 1 preserved with H ₂ SO ₄)				
Container 1				
Alkalinity, Chloride, Fluoride, Sulfate, TDS, TSS, VSS See individual volumes and holding times for parameters taken from Container 1 listed below	Plastic or glass	1000	Cool to < 6°C but not frozen	see below
Alkalinity		100		14 days
Chloride (Cl)		100		28 days
Fluoride (F)		100		28 days
Sulfate (SO ₄)		100		28 days
Total Dissolved Solids (TDS)—laboratory analysis of TDS is optional		200		7 days
Total Suspended Solids (TSS)		400		7 days
Volatile Suspended Solids (VSS)		400		7 days
Container 2				
NH₃, NO₃ + NO₂, TKN, TOC, TPO₄ See individual volumes and holding times required for parameters taken from Container 2 listed below	Plastic or glass	1000	2 mL 1:1 H ₂ SO ₄ to pH < 2 and cool to < 6°C but not frozen	see below
Ammonia (NH ₃)		150		28 days
Nitrate + Nitrite (NO ₃ + NO ₂)		150		28 days
Total Kjeldahl Nitrogen (TKN)		100		28 days
Total Organic Carbon (TOC)		100		28 days
Total Phosphorus (TPO ₄)		150		28 days
Container 3				
Chlorophyll Chlorophyll <i>a</i>	Amber glass or plastic	1000	Cool to < 6°C but not frozen, dark	<ul style="list-style-type: none"> • Filter ≤ 48 hours • Samples must be filtered as soon as possible and filters stored frozen up to 24 days
Container 4 (Optional)				
Orthophosphate (OP) field filter within 15 minutes of collection with a 0.45 μ filter; volume varies based on lab	Plastic	25–50 mL	Field filter; cool to < 6°C but not frozen	48 hours

Notes appear at the end of metals in water.

(continued)

Table 5.2. Quick reference guide—water sample collection methods, preservation, storage, and handling (continued).

Procedures for Collecting Routine Water-Chemistry Samples				
<ul style="list-style-type: none"> • Label containers before collection with tag number, station location, date, and sample type. • Write an X on the container lid to identify the acidified sample. • If containers are new and unused or cleaned in a laboratory rinsing with ambient water is not required. However, containers may be rinsed with ambient water. Rinse three times and discard water away for sample location. Choose and method and be consistent. • Fill each container with ambient water by submerging container approximately 0.3 m below the surface. Collect stream samples in the centroid of flow. • Acidify the X container immediately after collection; place all containers on ice immediately. “Immediately” is defined as within 15 minutes of collection. 				
Shipping Procedures				
<ul style="list-style-type: none"> • Due to increased shipping restrictions, samples being sent via a freight carrier may require additional packing. This varies by location. • If required, place samples and ice in a large plastic bag inside the ice chest for shipping. Seal the bag by simply twisting it closed while removing excess air and taping the tail down. Leaking ice chests will cause samples to be returned or to arrive at the lab beyond the holding time. • Place laboratory analytical request forms corresponding to samples in the ice chest in a Ziploc bag and taped to the inside of the lid. Secure the ice-chest lid with tape. • Ship samples on ice and cooled to < 6°C. Samples arriving past the holding time will not be analyzed for certain parameters. Samples are ideally shipped within 24 hours, and never later than 48 hours. • Take care when shipping glass. When shipping a combination of plastic and glass, plastic containers can be used to cushion glass containers. If the majority of containers are glass, extra care must be taken to prevent breakage during shipping. Suitable shipping materials include bubble wrap or plastic netting made for slipping over jars. 				
Optional Water Quality Parameters				
Parameters	Recommended Containers	Sample Volume (mL)	Preservation	General Holding Times
Oil and Grease (hexane extraction method)	Glass jar with Teflon-lined lid, rinsed with hexane or methylene chloride	1,000	2.5 mL 1:1 HCl to pH between 1.5 to 2.5; cool to < 6°C but not frozen, dark; do not use H ₂ SO ₄ .	28 days
Phenols	Glass jar with Teflon-lined lid	1,000	2 mL 1:1 H ₂ SO ₄ to pH < 2; cool to < 6°C but not frozen, dark	28 days
Cyanide	Plastic	1,000	Add 0.2 g ascorbic acid to dechlorinate sample, if necessary; add about 2 mL 1:1 NaOH to pH > 12; cool to < 6°C but not frozen, dark	14 days
Biochemical Oxygen Demand	Plastic	1,000	Cool to < 6°C but not frozen, dark	48 hours
Chemical Oxygen Demand	Plastic	110	2 mL 1:1 H ₂ SO ₄ to pH < 2; cool to < 6°C but not frozen, dark	28 days

(continued)

Table 5.2. Quick reference guide—water sample collection methods, preservation, storage, and handling (continued).

METALS IN WATER				
Parameters	Recommended Containers	Sample Volume (mL)	Preservation	General Holding Times
Routine Dissolved Metals arsenic cadmium calcium chromium copper iron lead magnesium manganese nickel silver zinc	HNO ₃ -cleaned plastic bottle	250	Filter at sample site; preserved by lab with ultra-pure HNO ₃ to pH < 2	6 months
Routine Total Metals Selenium	HNO ₃ -cleaned plastic bottle	250	Preserved by lab with ultra-pure HNO ₃ to pH < 2	6 months
Routine Total Mercury Mercury	HNO ₃ -cleaned glass or Teflon bottle	250	Preserved by lab with ultra-pure HNO ₃ to pH < 2	28 days
Total Hardness Laboratory analysis can be run on sample from the total-metals container; a separate sample is not required if submitting a total metals sample	Plastic	250	Cool to < 6°C but not frozen Add 1–2 mL of HNO ₃ to pH < 2; preserve in the field	6 months
Hexavalent Chromium (Not routine)	Plastic or glass	600	Cool to < 6°C but not frozen, dark, no acid; filter	24 hours; must notify lab in advance

(continued)

Table 5.2. Quick reference guide—water sample collection methods, preservation, storage, and handling (continued).

ORGANICS and PESTICIDES IN WATER				
Parameters	Recommended Containers	Sample Volume (mL)	Preservation	General Holding Times
Volatile Organics (VOA)	Three 40 mL VOA Vials	120	Add 2–4 drops HCL to pH < 2; cool to < 6°C, dark but do not freeze	14 days
MTBE (methyl-tert-butyl ether)	Three 40 mL VOA vials	120	Cool to < 6°C but not frozen, dark; or add 2–4 drops HCl to pH < 2 and cool to < 6°C, dark	14 days preserved, 24 hours unpreserved
ORGANICS Pesticides • Organophosphorus pesticides • Organochlorine pesticides Herbicides • Chlorinated herbicides Semivolatile Organics	Three 1 liter amber glass jars with Teflon-lined lid per parameter group; must be prerinsed with hexane, acetone, or methylene chloride <i>Note:</i> Each parameter group requires 3 L of sample; if all three parameter groups are requested submit nine 1 L jars	3,000 (3 L) for each parameter group	Cool to < 6°C but not frozen, dark If chlorine is present, add 0.1 g sodium thiosulfate to dechlorinate	7 days until extraction
Propellants, Explosives, and Pyrotechnics (PEPs)	Three 1 liter amber glass jars with Teflon-lined lid per sample type; must be prerinsed with methylene chloride	3,000	Cool to < 6°C but not frozen, dark	7 days
Perchlorate	1 qt glass or plastic container	1,000	None	28 days
Procedure for Collecting Organics in Water				
<ul style="list-style-type: none"> • Label each container with tag number, station location, date, and <i>ORGANICS—organophosphorus pesticides, —organochlorine pesticides, —chlorinated herbicides, or SEMIVOLATILES</i> (depending on sample type). • Fill quart jar(s) to the top. Collect from a depth of 0.3 m. To avoid atmospheric contamination, sample jars may be filled and capped under water. Put in the dark and on ice. • For a sample set of 10 or fewer, submit samples in triplicate (send in three jars instead of one per sample type) for laboratory QC. 				

Table 5.3. Summary of quality-control samples for water.

<p><i>Field Split (FS)—Conventionals in Water</i></p> <ul style="list-style-type: none"> • Field splits represent variability introduced during preservation and handling and at the lab. Submit field splits with every 10th sample. If fewer than 10 samples are collected in a month, submit one set of splits for that month. This requirement applies to conventional water samples only. • Collect two sets of conventional water samples from the same ambient water sample, using the same method. Use identical procedures in handling, storing, shipping, and analyzing samples. This applies to all cases of routine surface water collection procedures, including instream grab samples, bucket grab samples from bridges, pumps, and other water-sampling devices. • Each set of samples is to have a separate tag number. Submit both sets of water samples to the same lab for analysis.
<p><i>VOA Trip Blank (TB)—Volatile Organics</i></p> <ul style="list-style-type: none"> • Run trip blanks for volatile organic samples only. • Submit one set of DI water samples for each ice chest containing volatile organic samples. • VOA trip blanks are samples prepared in the laboratory with pure laboratory water, preserved as required. Transport to the sample site, handle like other VOA samples, and ship to the laboratory for analysis. Do not open trip blanks in the field. • VOA trip blanks are used to check contamination of the sample through leaching of the septum. • Submit trip blanks to the same lab for analysis.
<p><i>Field Blank (FB)—Total Metals Collected without Equipment</i></p> <ul style="list-style-type: none"> • Field blanks are required for total metals collected directly from a water body. This QC sample must be collected in the field. • Collect blanks at the last station of a sampling trip or sampling day. • Obtain reagent-grade water from a laboratory. • In the field, fill sample containers with reagent-grade water. Field blanks are handled, stored, shipped, and analyzed the same as ambient water samples. • A field equipment blank is submitted with every 10th sample, per day or per sample run. If fewer than 10 samples are collected in a day, submit blank per day or per sample run. • Note: For those using the TCEQ metals-in-water kits, the standard frequency for equipment blanks does not apply. Equipment blanks are collected and submitted with each sample. • Field blanks are not routinely required for routine chemistry, pesticides, or semivolatile organics, but may be inserted into the sample regime, if needed for a specific reason.
<p><i>Equipment Blank (EB)—Dissolved Metals and Total Metals Collected with Equipment</i></p> <ul style="list-style-type: none"> • Collect field equipment blanks at the last station of a sampling trip or sampling day. • Submit a field equipment blank with every 10th sample, per day or per sample run. If fewer than 10 samples are collected in a day, submit one blank per day or per sample run. • Note: For those using the TCEQ metals-in-water kits, the standard frequency for equipment blanks does not apply. Equipment blanks are collected and submitted with each sample. • Obtain reagent-grade water from the lab.
<p>Note: This summary table includes only basic QC sample requirements for routine sample collection. See Chapter 10 for details on optional QC samples.</p>