MEMORADUM

DIVISION OF WATER PROGRAM COORDINATION

Office of Water Quality Programs
Water Quality Monitoring & Assessment

SUBJECT: Guidance Memorandum No. 01-2003
Standard Operating Procedure for Clean Metals Sampling

TO: Regional Directors

FROM: Larry G. Lawson, P.E., Director
Division of Water Program Coordination

DATE: March 5, 2001

COPIES: Regional Permit Managers, Regional Compliance & Enforcement Managers, Regional Water Permit Managers, Al Pollock, Jean Gregory, Martin Ferguson, Dale Phillips, Ron Gregory, Don Smith, Gary Du, Charlie Morgan, and Roger Stewart

Attached is the final Standard Operating Procedure for the Collection of Freshwaters, Saltwaters, and Wastewaters for the Determination of Trace Elements.

This document has been updated to reflect recent changes we have made to our Water Quality Monitoring Module in CEDS, recent changes in sampling protocols, suggestions by staff to improve clarity and content, and the addition of the several other elements and the element mercury at ultra low concentrations.

Please contact Roger Stewart at 804/698-4449 with any questions about the application of this guidance.

Attachment

DISCLAIMER

This document provides procedural guidance to the permit staff. This document is guidance only. It does not establish or affect legal rights or obligations. It does not establish a binding norm and is not fully determinative of the issues addressed. Agency decisions in any particular case will be made by applying the State Water Control Law and the implementation regulations on the basis of the site specific facts.

STANDARD OPERATING PROCEDURE for the

Collection of Freshwaters, Saltwaters, and Wastewaters for the Determination of Trace Elements

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1. Scope

This Standard Operating Procedure is intended to be used by the Department's Ambient Water Quality Monitoring Staff and Permit Inspection Staff for the collection of freshwaters, saltwaters, and wastewaters with subsequent analysis by the Division of Consolidated Laboratory Services (DCLS) for dissolved and or total trace elements.

1.1 *Applicability*

T‚ ïreshwaters appropriate for collection include all surface waters and groundwaters with a specific conductivity of approximately 1000 umhos/cm or less. Appropriate wastewaters include treated effluents with specific conductivities less than 1000 umhos/cm). Saltwaters, brackish waters, highly turbid wastewaters, i.e. landfill leachates, are also appropriate for this procedure and are collected identically as the freshwaters but require special laboratory preparation and analysis.

The protocols contained in this Standard Operating Procedure are applicable to the compounds listed in Table 1 Target Analytes, page 13.

Additionally this SOP is intended for concentration ranges of toxic trace elements (toxic metals) below approximately 200 ug/L. The 200 ug/L threshold should be applied cautiously as this is onl' a generalization of the effect of cc .amination. For example, because of well documented contamination problems with Copper and Zinc, if a final effluent has historically had copper or zinc reported in the 200 ug/L range use of this protocol may reveal that the actual concentrations are significantly lower. However if the historical numbers for cadmium, arsenic, or mercury have been greater than 200 ug/L, use of this protocol may not affect these concentrations.

For concentrations above approximately 200 ug/L, existing 40 CFR 136 procedures are adequate and contain the necessary Quality Controls (including the requirement to collect blanks) to make reliable measurements in the high ug/L range. The United States EPA Region III has prepared extensive guidance for existing and new data that falls into this higher range.[1,2]

Table 1 lists the Method Detection Limits established for each parameter using the protocols specified in this guidance. Method Detection Limits (MDL) were measured using the procedure specified in 40 CFR 136, Appendix B.

2. Summary

Ambient samples are collected in midstream by submerging a 4 liter plastic bottle, (BRIDGE BOTTLE), see Figure 1 Bridge Bottle on page 18. Using a piece of flexible tubing connected to the bridge bottle and inline with a groundwater capsule filter (TUBING KIT), the sample is transferred by peristaltic pump from the bridge bottle into a plastic SAMPLE CONTAINER, see Figure 2 Loop Sample Container on page 19 and Figure 3 Sample Container Schematics on page 20. A provision is made where the bridge bottle is substituted for a sampling wand for collecting while wading, from a boat, or anytime close contact with the sampling zone is preferred, see Figure 4 Ambient Sampling Apparatus on page 21.

Effluent samples are collected directly into a SAMPLE CONTAINER by submerging a teflon tube into the sampling zone. Transfer is accomplished by using a piece of flexible tubing inline with the teflon tubing and capsule filter by peristaltic pump, see Figure 4 Ambient Sampling Apparatus on page 21.

For both the river and effluent samples a provision is made for rinsing the filter and collecting a field equipment blank prior to sample collection.

The use of two field technicians is highly recommended to aid in an efficient and successful trip.

3. Significance and Use

This method is primarily intended for the use in identifying and comparing dissolved trace metal concentrations to Virginia's Water Quality Standards. Water quality standards for dissolved metals are significant because the concentrations are significantly low (trace) and 2) the criteria are expressed as the dissolved metal species and not as total recoverable.

Recent findings that widely accepted field sampling methods and laboratory techniques have been responsible for significant contamination of historical data have prompted the development of this SOP. This SOP is intended to be used in situations when data on Water Quality Standards are needed or when VPDES permit discharge data are needed.

This SOP should be used when trace metal concentrations are expected to be in the sub mg/L range, typically less than 500 ug/L. At these concentrations contamination of the sample during collection and analysis is minimized or eliminated by following the SOP and taking precautions to avoid potential sources of contamination.

Contamination can occur from three main sources:

1. Improperly cleaned sample bottles and sampling equipment,
2. Improper handling of the apparatus,
3. Atmospheric debris and dust.

Bottles and equipment tested prior to field use are cleaned and tested as a quality control step at DCLS (Division of Consolidated Laboratory Service). Training on the sample collection protocols minimizes contamination introduced by improper technique. Atmospheric dust is controlled by the sampler design incorporat a closed loop collection fitting on the bridge bottle and the sample bottle, thereby minimizing the exposure of the sample to dust and debris.

When site conditions indicate a high potential for contamination, the protocol allows for the collection of field equipment blanks of ultra pure water immediately prior to using the apparatus.

4. Equipment Preparation and WQM Scheduling of Sample Kits

4.1 *Regional Field Equipment Preparation*

The field equipment needed to collect trace metals should be stored in a plastic container to prevent dust contamination.

Prior to sampling, the peristaltic pump batteries should be charged using the cigarette adapte d charger accompanying the pump. No other battery chargers should be used as the battery system is matched to the charger. A charged battery will work continuously for about 7 hours depending on the load and ambient temperatures.

Run through your checklist to ensure that you have adequate supplies to collect the scheduled samples. Gloves are the main item you should always have in excess.

4.2 *Ordering Kits*

It is appropriate to maintain an adequate supply of clean metals sampling tubing and containers.

Note that Blanks are handled as separate samples and one blank should be ordered for each ambient and effluent sample.

Ambient sampling sites should be established as stations in WQM prior to sample collection and then processed using the WQM system.

Prior to sample collection, the sample containers must be ordered directly from the laboratory and the samples must be scheduled through EDT.

ORDER SAMPLE CONTAINERS from DCLS by e-mailing Norma Roadcap (nroadcap@dgs.state.va.us) and Charlie Morgan (chmorgan@deq.state.va.us) with the number and type (by group codes) of samples you wish to collect, when they will be collected, and your region. **PLEASE ALLOW 6 WEEKS FOR DELIVERY.**

Please refer to Table 2 Parameter Group Codes on page 14 for the parameter codes to request for containers based on the sample matrix type.

Freshwater samples include the following supplies:

1. one bridge bottle,
2. one tubing kit,
3. two loop sample containers,
4. and two 100ml Mercury bottles.

Saltwater samples include the following supplies:

1. one tubing kit,
2. two loop sample containers, and
3. two 100ml Mercury bottles.

Effluent samples include the following supplies:

1. one tubing kit,
2. two loop sample containers, and
3. two 100ml Mercury bottles.

It is appropriate to store additional sample containers and kits for those situations that require rapid sample collection. The holding time for these should be a maximum of six months so replace the stored items with new kits more frequently.

4.3 *Monthly Run Schedule*

The vast majority of these samples collected by the department are for dissolved metals. Only when you have a special study should you in addition to collecting dissolved metals should you collect total as well. You should avoid collecting only total metals as this provides very little information to the department and the cost of analysis and field resource time is very high.

Schedule samples with DCLS through the WQM system using the group codes in Table 2 Parameter Group Codes on page 14.

Please refer to Figure 6 WQM Monthly Run Schedule Parameters on page 23. Refer to the Run ID that corresponds to your type of sample whether it is an effluent (EFF), freshwater (FRESH), or saltwater (SALT). Notice that the field equipment blanks no longer have a separate group code. It is extremely important that you properly identify the equipment blanks in the Blank/Dup field. Notice that there is not an EB for the total recoverable group code TCMETS. This is because the EB for DCMETS covers both group codes. However if you were to collect only total recoverables then it would be appropriate to have two TCMETS's one for the sample, R, and the other for the equipment blank, EB.

Because of the time and effort needed to collect metals an estimated four to five sites a day can be sampled per day.

5. Equipment and Supplies

5.1 *Items Which Should Be Stored in Equipment Box*

The supplies are those which are needed when sampling for metals and which should protected from dust are listed in Table 3 Equipment on page 15.

5.2 *Ancillary Items*

Other items which may be needed include those listed in Table 4 Ancillary Supplies on page 16.

Batteries need to be charged overnight. Prior to each sampling run check to make sure that you have enough supplies and that your portable battery is charged and functioning. The leads and fuse system on the batteries are delicate and prone to breaks and shorts. Batteries should be discharged completely and then recharged at least once every six months.

6. Sampling Apparatus, Bottles and Containers

DCLS will supply all the necessary SAMPLE CONTAINERS, BRIDGE BOTTLES, and TUBING KITS based on the number and types of samples ordered through WQM.

6.1.1 When placing orders for samples try to group four to five sites. DCLS will send out coolers with kits and bottles batched for the number of samples scheduled. The same cooler can be used when returning the samples to DCLS for analysis so keep this cooler handy for bottle return.

6.1.2 The tubing kits including the filters, bridge bottles, and mercury bottles are disposable/recyclable and should be discarded after each use.

7. Procedure

7.1 *Ambient Sample Collection Protocol For Freshwater and Saltwater Using the Bridge Bottle*

7.1.1 Equipment Setup

7.1.1.1 Locate an area where sample processing will occur. This should be an area free of falling debris and swirling dust, flat, smooth, and protected from the wind. The tailgate of a vehicle or the back of a Suburban are good locations.

7.1.1.2 Locate the equipment box and coolers containing the sample containers and kits in the area where sample processing will occur.

7.1.1.3 Cover the work area with a large piece of plastic film. Set out the pump and connect the battery. Switch pump on for a quick burst to check that it is working. Dial the pump speed to 5.

7.1.1.4 Remove a tubing kit, two loop sample containers, two mercury bottles and a bridge bottle from the cooler and place on the plastic near the pump.

7.1.1.5 Remove a pack of sample gloves from the storage container and place on the plastic.

7.1.1.6 Remove the plastic sample caddy from the storage box and place it on the sample processing area near the pump. Secure the sample bottles in the caddy.

7.1.2 Bridge Bottle Filling

7.1.2.1 Locate the sample weights for connection to the BRIDGE BOTTLE.

7.1.2.2 Locate the polypropylene sampling rope spool, cut a sufficient length of rope to allow for deployment.

7.1.2.3 Don one or two pairs of vinyl gloves using clean precautions.

7.1.2.4 Tie one end of the sampling rope to the five pound weight leaving approximately a 1' long er ' for connection to the BRIDGE BOTTLE.

7.1.2.5 Untie or open by tearing the top of the outer plastic bag containing the BRIDGE BOTTLE.

7.1.2.6 Reach into the outer bag and untie or tear the inner bag near the handle connection. Check the configuration of the tubing to ensure that proper filling will occur. Inspect the smaller vent tubing and adjust if it appears crimped due to storage. While the bottle is still in the inner bag it is acceptable to remove the top fitting to check the inner sipper tube. Adjust all fittings appropriately.

7.1.2.7 When the fittings have been properly secured and adjusted remove the BRIDGE BOTTLE from the inner bag and lay on the plastic film. Tie the weighted end of the rope onto the handle of the bottle leaving about 6" of line between the bottle and the weight.

7.1.2.8 Proceed to the sampling location with the B)GE BOTTLE apparatus. If appropriate carry several extra pairs of gloves to the site to facilitate bridge bottle handling.

7.1.2.9 When deploying from bridges with moderate to low stream velocities collect the sample upstream of the bridge by lowering the assembly into the water. Ensure that the assembly does not contact any structures or other objects as it is lowered into the water.

7.1.2.10 Once in the water the weight will partially submerge the BRIDGE BOTTLE, which will begin to fill. Check to insure the air release tube is above the water level and not obstructed. When the bottle is first submerged a good indication it is filling properly is a small slug of water may be expelled from the air vent tube. The bottle will fill quickly, within a few minutes, if it has been properly adjusted.

7.1.2.11 Problems with filling from bridges can occur when stream velocities are high. Sampling on the downstream side of bridges is acceptable to avoid the risk of losing the assembly due to the current sweeping it under a bridge or other obstruction. When stream velocities are high 7.5 pounds of weight will aid in sample collection. The added weight will cause the container to sink lower when partially filled which may submerge the vent tube. The vent tube can be extended past the bottom of the bottle to prevent filling with water when the weight is heavy or the water is rough.

7.1.2.12 Other problems with filling can occur when the inlet tube is clogged, the vent tube contains a slug of water or other obstruction, the vent tube is below the surface of the water, the weight is not positioned close enough to the bottle, or the vent tube or inlet tube has become disconnected from the bottle.

7.1.2.13 When the BRIDGE BOTTLE is approximately 1/2 to 2/3 full retrieve the bottle and return to the sample processing area. It is acceptable to allow the bridge bottle to sink completely below the surface as long as the inlet tube does not contact the bottom. Ensure that the assembly does not contact any structures or other objects as it is retrieved.

7.1.2.14 When deploying while wading or from a small craft the BRIDGE BOTTLE can be submerged by hand without the weights.

7.1.2.15 When the water level at the sample site is very shallow it may be difficult to submerge the BRIDGE BOTTLE deep enough to begin siphoning. The alternative is to use the effluent sample configuration where the stream sample is pumped directly into the loop sample container. Sampling in this manner requires the pump assembly to be transported to the site. This is best accomplished by attaching the pump assembly to a backpack.

7.1.2.16 Once the BRIDGE BOTTLE has been brought back to the sample processing area set it next to the pump and remove the weight. With the inlet and vent tubing properly configured the BRIDGE BOTTLE can remain on the plastic outside of a bag without any danger of atmospheric contamination.

7.1.3 Ambient Dissolved Grab Blanks

7.1.3.1 Refer to Figure 4 Ambient Sampling Apparatus on page 21 for the schematic of the field sampling equipment used to process blanks and samples.

7.1.3.2 Determine which tech will be clean hands and which will be dirty hands.

7.1.3.3 Dirty hands and clean hands don one or two pairs of vinyl gloves. Dirty hands opens the sample bottles outer plastic bag, clean hands opens the inner plastic bag. At this point there should be two loop bottles and two mercury bottles available to clean hands.

7.1.3.4 Dirty hands opens the grab kit's outer plastic bag, clean hands opens the inner plastic bag and removes the tubing assembly.

7.1.3.5 Clean hands disconnects one side of the sample loop on the first sample container. Clean hands connects the end of the tubing kit opposite the filter to the opened sample container. Remember the sample container is full of clean water from the lab.

7.1.3.6 Dirty hands connects the peristaltic tubing at approximately the mid-point of the length to the field pump, clean hands inverts the sample container, and dirty hands switches on the pump.

7.1.3.7 Process the entire contents, 1000mls, of the sample container through the tubing and filter apparatus at a flow rate of 500mls/min (pump setting of 5). At the beginning of the sample processing orient the filter cartridge with the flow arrow pointing up. This will insure proper wetting of the filter.

7.1.3.8 When the last continuous stream of water enters the filter dirty hands switches off the pump. The filter must not be allowed to go dry. This is a change from the previous SOP and is necessary because of problems with excessive back pressure causing tubing separation from the filter.

7.1.3.9 This step is a rinse of the filter, which cleans and conditions the media. The rinse can be pumped directly to waste, as this is ultra pure water.

7.1.3.10 Clean hands disconnects the pump tubing from the empty loop bottle and reconnects this same end to the second loop bottle containing blank water. Remember that this second bottle is full of clean water from the lab. Clean hands inverts the container, dirty hands switches on the pump. Process the blank water from the loop bottle until approximately 125mls have been expelled from the filter. Dirty hands switches off the pump.

7.1.3.11 This step removes the last trace of conditioning water left in the filter. Clean hands opens the first mercury container and discards the water. Clean hands holds the outlet of the capsule filter just above the open mouth of the mercury bottle. Fill the mercury bottle to overflowing and cap. Make sure there are no air bubbles in the bottle that are larger than a pea. Connect the capsule filter outlet to the empty loop container via the sample loop tubing. Process the remaining contents, approximately 900mls, of the sample container through the tubing and filter apparatus into the first sample container taking care not to pump the filter dry.

7.1.3.12 Clean hands disconnects the outlet tubing from the blank sample container and immediately reconnects the loop tubing on the top of the blank bottle.

7.1.3.13 The field blanks collected in this manner are comprehensive blanks because they are collected in the same equipment as the sample and are processed like the sample through all steps of the protocol. This is the most important check of contamination in the protocol.

7.1.4 Ambient Dissolved Grab

7.1.4.1 Clean hands immediately (immediately means the sooner the switch is made the less likely contamination can adhere to the end of an open tube, immediately means less than one minute) disconnects the vent tubing from the BRIDGE BOTTLE and then connects the inlet side of the pump tubing in place of the vent tubing.

7.1.4.2 Dirty hands switches on the pump. Process the sample water from the BRIDGE BOTTLE until approximately 125mls have been expelled from the filter. Dirty hands switches off the pump.

7.1.4.3 Clean hands opens the second mercury container and discards the water. Clean hands holds the outlet of the capsule filter just above the open mouth of the mercury bottle. Fill the mercury bottle to overflowing and cap. Make sure there are no air bubbles in the bottle that are larger than a pea.

7.1.4.4 Clean hands unscrews the cap of the second loop sample container and discards the small amount of water remaining in the container. Clean hands returns the top to the container and then connects the capsule filter outlet to the second empty loop container via the sample loop tubing. Process the sample into the loop container until the container is full. Dirty hands switches off the pump. It is acceptable to fill the sample container to overflowing, however avoid filtering more than 1000 mls through the filter.

7.1.4.5 Clean hands disconnects the outlet tubing from the sample container and immediately reconnects the loop tubing back in place to seal the sample bottle.

7.1.4.6 Clean hands holds the blank loop container in a manner to allow dirty hands to place the WQM label directly on the midsection of the bottle. The mercury container also has a the WQM label placed on the midsection in the same manner as above. The mercury blank container is then placed into the inner bag of the blank loop container seals the inner bag. Dirty hands seals the outer bag.

7.1.4.7 This process is repeated for the sample bottle and mercury sample.

7.1.4.8 The blanks and samples should be immediately placed on ice in a separate sample cooler containing only clean metal containers. This is to prevent the wire sample tags from contaminating the clean samples.

7.1.4.9 It is no longer necessary to record the ultra bottle numbers but it is important that the WQM labels are used to correctly identify the samples and blanks. The container numbers chosen in WQM do not need to correspond to the ultra bottle numbers.

7.1.4.10 Rinse the rope and weights with ambient water to remove any visible dirt, place inside a plastic bag, and store in the storage container. Rope may be reused several times if rinsed frequently.

7.1.5 Ambient Total Recoverable Grabs

7.1.5.1 If total recoverable samples are to be collected in conjunction with dissolved samples, during all phases of sample collection of the dissolved samples the BRIDGE BOTTLE must be shaken to ensure proper mixing of suspended solids. Additionally during the total recoverable sample collection the BRIDGE BOTTLE must continue to be shaken.

7.1.5.2 When collecting for total recoverable samples after first collecting for dissolved samples the tubing used to collect the dissolved fractions must be protected after the last dissolved samples are collected.

7.1.5.3 Clean hands removes the capsule filter from the tubing. Clean hands opens the third mercury container and the third total recoverable loop bottle and discards the water. The loop bottle cap should be replaced immediately after discarding the water. Dirty hands switches on the pump and clean hands fill the mercury bottle to overflowing and then caps as described above. The tubing is then connected to the total recoverable loop container and it is also filled until full. Clean hands immediately reconnects the loop tubing to seal the container.

7.1.5.4 Clean hands holds the total recoverable loop container in a manner to allow dirty hands to place the WQM label directly on the midsection of the bottle. The mercury container also has a the WQM label placed on the midsection in the same manner as above. Clean hands places the mercury total recoverable container into the inner bag of the total recoverable loop container seals the inner bag. Dirty hands seals the outer bag.

7.1.5.5 The blanks and samples should be immediately placed on ice in a sample cooler.

7.1.6 Other Parameters

7.1.6.1 The clean protocol is complete at this step and field parameters can now be taken from the remaining water in the BRIDGE BOTTLE. Recommended field parameters include: pH, Conductivity, Temperature, and Dissolved Oxygen. Additional laboratory samples for the **solid** series and **total organic carbon** should be collected and identified by the group codes: **SOLID** and **TOC.**

7.1.6.2 Rinse the rope and weights with ambient water to remove any visible dirt, place inside a plastic bag, and store in the storage container. Rope may be reused several times if rinsed frequently.

7.2 *Effluent Sample Collection Protocol*

7.2.1 Equipment Setup

7.2.1.1 Locate an area near the final effluent sampling location where sample processing will occur. This should be an area free of falling debris and swirling dust, flat, smooth, and protected from the wind. The tailgate of a vehicle or the back of a Suburban are good locations.

7.2.1.2 Locate the equipment box and coolers containing the sample containers and kits in the area where sample processing will occur.

7.2.1.3 Cover the work area with a large piece of plastic film. Set out the pump and connect the battery. Switch pump on for a quick burst to check that it is working. Dial the pump speed to 5.

7.2.1.4 Remove a tubing kit and two sample containers from the cooler and place on the plastic near the pump.

7.2.1.5 Remove a pack of sample gloves from the storage container and place on the plastic. Refer to, for the schematic of the field sampling equipment used to collect treatment plant grab samples.

7.2.1.6 Remove the plastic sample caddy from the storage box and place it on the sample processing area near the pump.

7.2.1.7 Locate the sample wand used for positioning the teflon sample tubing into the effluent sampling zone, see Figure 4 Ambient Sampling Apparatus on page 21.

7.2.2 Effluent Dissolved and/or Total Recoverable Grab Blanks and Samples

7.2.2.1 Refer to Figure 5 Effluent Sampling Apparatus on page 22 for the schematic of the field sampling equipment used to process blanks and samples.

7.2.2.2 The effluent grab blanks and samples are collected in exactly the same manner as the ambient grab blanks and samples. Please refer to sections 7.1.3, 7.1.4, and 7.1.5.

7.2.2.3 Beginning with section 7.1.4 instead of collecting from a bridge bottle it is preferred to use a PVC sample wand equipped with a special notch to hold the teflon tubing, see page 22.

7.2.2.4 Clean hands presents a section of the Teflon tubing just past the inlet to dirty hands who then attaches the tubing to the sample wand.

7.2.2.5 The entire assembly: sample caddy containing the empty sample container, sample tubing, pump/battery, and sample wand are transported to the effluent sampling location.

7.2.2.6 Dirty hands places the sample wand into the collection zone taking precaution not to touch the tip of the sampling tube on any items. Once the sample tube is located in the effluent take precaution not to let the tip contact anything but water.

7.2.2.7 At this point refer to 7.1.4.2 on how to process samples. The procedure is complete once you have reached step 7.1.5.5.

8. Sample Shipping[3]

8.1 *Supplies and Materials*

8.1.1 Shipping cooler which is insulated, with a polyethylene lid. A 28 quart cooler is sufficient size to hold sample bottles, wet ice packs, and protective material. It has a detachable lid, no drain hole, and is easy to clean. It is a convenient size and shape for handling, stacking, and storing as it not too heavy when fully packed.

8.1.2 Liner Bags which are 30 gallon plastic trash bags with a dimension of 30" X 36" X 1mil.

8.1.3 Plastic bubble wrap packing material with 1/2" bubbles in 12" X 16" sheets used for wrapping the 1 liter sample containers. The material is available in various configurations with the 1' wide roll suitable for the loop containers.

8.1.4 Rubber bands size 33 or large enough to secure the bubble wrap around 1 liter containers packed in two ziplocks.

8.1.5 Ice bags which are heavy duty 1 gallon ziplock bags.

8.1.6 Wet ice cubes.

8.1.7 1 Liter plastic scoop.

8.1.8 Strapping tape, 1" filament type.

8.1.9 Duct tape, 2" utility type.

8.1.10 Sealing tape, 3" clear acrylic adhesive holds well in cold temperatures, stays transparent for long periods, and is suitable for sealing ice bags and protective labels on bottles and coolers.

8.1.11 Packing list envelopes, clear plastic self adhesive type. Overnight services are a good source.

8.1.12 Address Labels, specific to the carrier.

8.2 ***Sample Packaging***

8.2.1 Immediately following sample collection place sample bottles in storage cooler with bagged wet ice and chill prior to packing shipping coolers.

8.2.2 Insert two trash bags into the cooler for double lining.

8.2.3 Just prior to packing the sample coolers, prepare ice packs with fresh ice cubes. Fill each ice bag with approximately 1.5 pounds of ice. A one liter scoop is a good amount. Seal each ziplock bag expelling as much air as possible and seal. If shipping conditions are expected to be severe, i.e. rough treatment, the ice bags can be further secured with clear sealing tape.

8.2.4 Place the chilled sample containers upright into the lined cooler and surround with ice packs. The sample containers and ice should be tightly packed. When the cooler is properly packed there will be no extra space left in the cooler.

8.2.5 The number of containers that can be packed into a cooler along with a sufficient amount of ice will obviously depend on the cooler dimensions and the ratio of ice to containers. Generally five 1 liter plastic bottles with bubble wrap and seven ice packs will fit into a 28 quart cooler. The weight of the cooler should not exceed 70 pounds.

8.2.6 Seal each liner bag by twisting the top of the bag and tying in a knot.

8.2.7 If appropriate attach a packing list envelope to the underside of the shipping cooler lid, insert the appropriate sample documentation (e.g. chain of custody form, field data sheets, or special lab instructions) and seal the envelope for protection.

8.2.8 Close the lid, seal horizontal joints with duct tape, and secure with strapping tape.

8.2.9 Attach address label to side of cooler and protect with clear sealing tape.

8.3 ***Sample Transportation***

8.3.1 Samples shipped by common carrier must comply with applicable Department of Transportation Hazardous Materials Regulations, 40 CFR Part 172. The person offering such material for transportation is responsible for ensuring such compliance. See 40 CFR Part 136 Table II for guidance on applicability of preserved environmental samples.

8.3.2 Ship samples on the day of collection and use a reliable courier service for priority or next day delivery.

8.3.3 A large amount of effort is required to sample four to five sites and a large amount of work preparing the sample equipment and containers has taken place. Four samples represents $1000.00 in equipment preparation and analytical costs so coordinate sample shipment closely with DCLS and continue follow-up communication until delivery is confirmed and condition of samples upon receipt is verified.

8.3.4 The above sample packaging and transportation are provided for those samples that are to be shipped long distances generally interstate and are intended for worst case shipping conditions.

8.3.5 For those samples shipped via our standard DCLS courier service no special precautions beyond normal shipping procedures are required.

9. Quality Control

9.1.1 The protocols in this SOP are designed to include all the necessary Quality Control steps needed to produce reliable accurate data.

9.1.2 Table 5 Quality Control Recommendations for Trace Metals Sample Collection on page 17 lists the critical control points of the sampling protocol. These control points are the minimum steps required for the collection of samples. When field contamination is detected additional blanks and other quality control samples are absolutely necessary to identify and correct the problem.

9.1.3 Field equipment blanks (identified as EB with a depth of 0.0 in WQM) should be collected with every sample including the a mercury blank. If total recoverable samples are also collected a dissolved equipment blank will be representative of the total recoverable sample. If only total recoverable samples are collected then a field equipment blank is required.

9.1.4 For effluent sites blank samples must be collected prior to each and all trace metal samples.

9.1.5 If ambient site conditions indicate potential problems then it would be wise to collect additional samples. Some site conditions which would warrant blanks prior to sample collection are:

1. road construction producing visible dust,
2. any operation causing visible dust emissions,
3. high total suspended solids conditions instream,
4. recent deicing of bridges,
5. high traffic volume on bridge and,
6. heavy rain events during sampling.

Periodically, at a frequency of greater than 10%, field duplicates should be collected. Field duplicates for ambient sample collection involve processing an additional blank and sample from the BRIDGE BOTTLE.

Field duplicates for effluent sample collection involve processing an additional blank and sample in series from the effluent and may produce variable results due to the component of temporal variability.

10. Referenced Documents

The methods and research articles used to develop the field sampling equipment are:

1. Benolt, Gaboury, Clean Technique Measurement of Pb, Ag, and Cd in Freshwater: A Redefinition of Metal Pollution, Environ. Sci. Technol., Vol. 28, No. 11, 1994.
2. Horowitz, A.J. et. al., The Effect of Membrane Filtration Artifacts on dissolved Trace Element Concentrations, Wat. Res. Vol. 26, No. 6, pp. 753-763, 1992.
3. Horowitz, Arthur J., et.al., On the Problems Associated with Using Filtration to Define

Trace Element Concentrations in Natural Water Samples, U.S. Geological Survey.

4. Martin, Gary R., et.al.,), A Comparison of Surface-grab and Cross Sectionally Integrated Stream-water-quality Sampling Methods, Water Environment Research, Volume 64, 866 (1992.
5. Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, EPA 821-R-95-034, April 1995.
6. Geological Survey Protocol for the Collection and Processing of Surface-Water Samples for the Subsequent Determination of Inorganic Constituents in Filtered Water. United States Geological Survey , Open-File Report 94-539.

These methods provide an excellent source of information on the proper handling of sampling equipment and the collection of samples for the analysis of trace metals. The techniques used to collect contamination free environmental samples are involved and require a significant understanding of the principles of trace analysis. It is beyond the scope of this SOP to provide all the details that would be necessary to allow an inexperienced field team to collect trace metal samples. These protocols should be used by persons experienced in the collection of environmental samples for trace analysis and who are familiar with the sources and magnitude of ambient contamination.

Table 1 Target Analytes

Parameter	CAS number	Method Detection Limits, µg/L FRESHWATER	ICPMS USN SALTWATER	ICPMS USN TR FRESHWATER	ICPMS USN TR SALTWATER	ICPMS	ICP AES USN	ATOMIC FLUOR
Aluminium	7429-90-5	0.02	0.43	0.04	0.43	0.60		
Antimony	7440-36-0	0.01	0.17	0.03	0.17	0.01		
Arsenic	7440-38-2	0.01	0.15	0.03	0.15	0.10	5.37	
Barium	7440-39-3					0.03		
Beryllium	7440-41-7	0.03				0.07		
Cadmium	7440-43-9	0.01	0.24	0.04	0.24	0.01	2.37	
Calcium	7440-70-2					54	0.08	
Chromium	7440-47-3	0.01		0.04		0.05	2.27	
Copper	7440-50-8	0.02	0.23	0.06	0.23	0.02	4.98	
Iron	7439-89-6					3.10	2.30	
Lead	7439-92-1	0.02	0.27	0.03	0.27	0.01		
Magnesium	7439-95-4					1.10	0.00	
Manganese	7439-96-5	0.01	0.26	0.03	0.26	0.08	0.58	
Mercury	7439-97-6		0.00050		0.00050			0.0005
Nickel	7440-02-0	0.02	0.25	0.02	0.25	0.01	1.71	
Selenium	7782-49-2	0.04	0.16	0.06	0.16	0.10		
Silver	7440-22-4	0.01		0.03		0.03		
Thallium	7440-28-0					0.04		
Zinc	7440-66-6	0.15	0.97	0.03	0.97	0.15	1.95	

ICPMS USN inductively coupled plasma mass spectrometry sample introducted by ultrasonic nebulization
ICPMS USN TR inductively coupled plasma mass spectrometry sample introducted by ultrasonic nebulization total recoverable
ICPMS inductively coupled plasma mass spectrometry
ICP AES USN inductively coupled plasma atomic emission spectrometry sample introduction by ultrasonic nebulization
ATOMIC FLUOR atomic fluorescence spectrometry

Table 2 Parameter Group Codes

FRESHWATER	
DCMET	Dissolved clean metals in freshwater
TCMET	Total clean metals in freshwater

SALTWATER	
DCMETS	Dissolved clean metals in saltwater
TCMETS	Total clean metals in saltwater

EFFLUENT	
CMEFF	Dissolved clean metals in effluents
TCMEFF	Total clean metals in effluents

N.B. All of the above group codes include mercury and the associated extra container. For mercury only please see the group codes belo.

MERCURY ONLY	
DCHG	Dissolved mercury in freshwater
TCHG	Total mercury in freshwater

Table 3 Equipment

	Item	Supplier	Catalog Number
1	peristaltic pump unit	Cole-Parmer	H-07533-40
2	quick release pump head	Cole-Parmer	H-07518-60
3	cigarette lighter adapter cable	Cole-Parmer	H-07573-02
4	portable battery pack	Cole-Parmer	H-03276-50
5	powder free vinyl gloves	Fisher Scientific	11-387-3
6	clear colorless polyethylene drop cloth	hardware store	4 to 6 mil
7	preprinted laserjet waterproof labels	Avery	5163
8	indelible markers	Sharpies	office supply
9	bridge bottle	DCLS	N/A
10	bridge bottle tubing kit	DCLS	N/A
11	teflon tubing kit	DCLS	N/A
12	samples bottles	DCLS	N/A
13	one gallon ziplock bags	grocery store	N/A
14	two gallon ziplock bags	grocery store	N/A
15	bridge bottle weights	sporting goods store	N/A
16	white polypropylene line	hardware store	N/A

Table 4 Ancillary Supplies

	Item	Supplier	Catalog Number
1	plastic bubble wrap	consolidated plastics	87600LG
2	rubber bands	office supply store	large
3	ice	grocery store	N/A
4	duct tape	hardware store	N/A
5	knife or cutters	hardware store	N/A
6	fuses for pump and battery	hardware store	N/A

Table 5 Quality Control Recommendations for Trace Metals Sample Collection

SAMPLING REQUIREMENTS	CRITERIA	FREQUENCY
Type of method	Performanced based by demonstration of no detectable contamination of target analytes or interferences in samples or blanks. Method 1669 and the sampling apparatus and techniques used by the DEQ are recommended for sample collection.	Demonstration contamination free samples and blanks everytine a variation is made to the method
Media Type	Freshwater and treated final effluent wastewater for dissolved and total recoverable metals.	NA
Training	Sample collection by only thoroughly trained personnel. Personnel must demonstrate proficiency in collecting contaminant free blanks and samples.	Train a minimum of one time prior any sample collection. Stop and provide additional training if field QC demonstrates problems until the criteria is achieved.
Filtration	0.45 um Capsule filter with nominal surface area of 600 cm^2. Maximum sample volume 1000 mls through single use filter.	Onsite at time of collection or within one hour for composite samples after the sample sequence is complete.
Sample containers	no detectable target analytes above MDL.	minimum of 1% of containers checked by the laboratory per batch after intial demonstration of acceptable blank QC.
Sampling equipment	no detectable target analytes above MDL.	minimum of 1% of equipment checked by the laboratory per batch after intial demonstration of acceptable blank QC.
Comprehensive grab field blank	blanks must be < 10% sample concentration or if sample is < MDL field blank contamination os OK.	Process one with every sample collected. When duplicate samples are collected only one blank is necessary.
Comprehensive composite field blank	Blanks must be < 10% sample concnetration or is sample is < MDL field blank contamination is OK.	Process one per site for every ten samples. When 10% frequency rule is applied blanks are to be collected with the first sample. Process field blank every time equipment is field cleaned to be reused between sites or sample events.
Field duplicate	Statistically equivalent to the RPD of the matrix spike and matrix spike duplicates for quantifiable concentrations	Process one per site for every ten samples.
Preservation	Samples must be iced in the field. Composite samples must be iced during collection. pH < 2 within 72 hours of collection and samples must remain in original containers for a minimum of 18 hours prior to digestion or analysis.	All samples must be acid preserved in the field or laboratory with ultra pure HNO_3 to pH < 2. Samples should be iced in field immediately after collecting.
Documentation	Sampling activities must be documented on paper or by computerized sample tracking.	Documentation must be done per sample per site.

Figure 1 Bridge Bottle

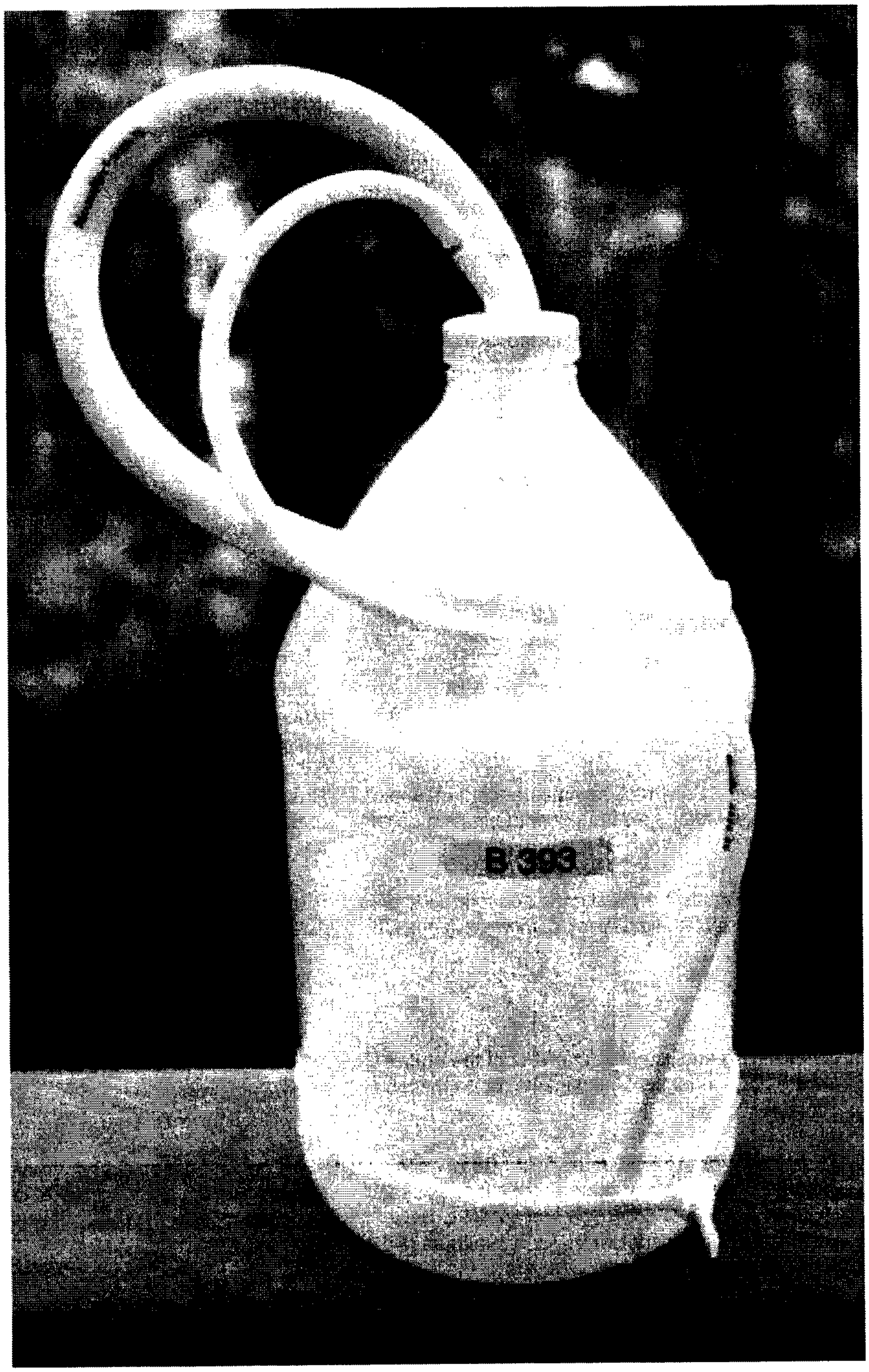
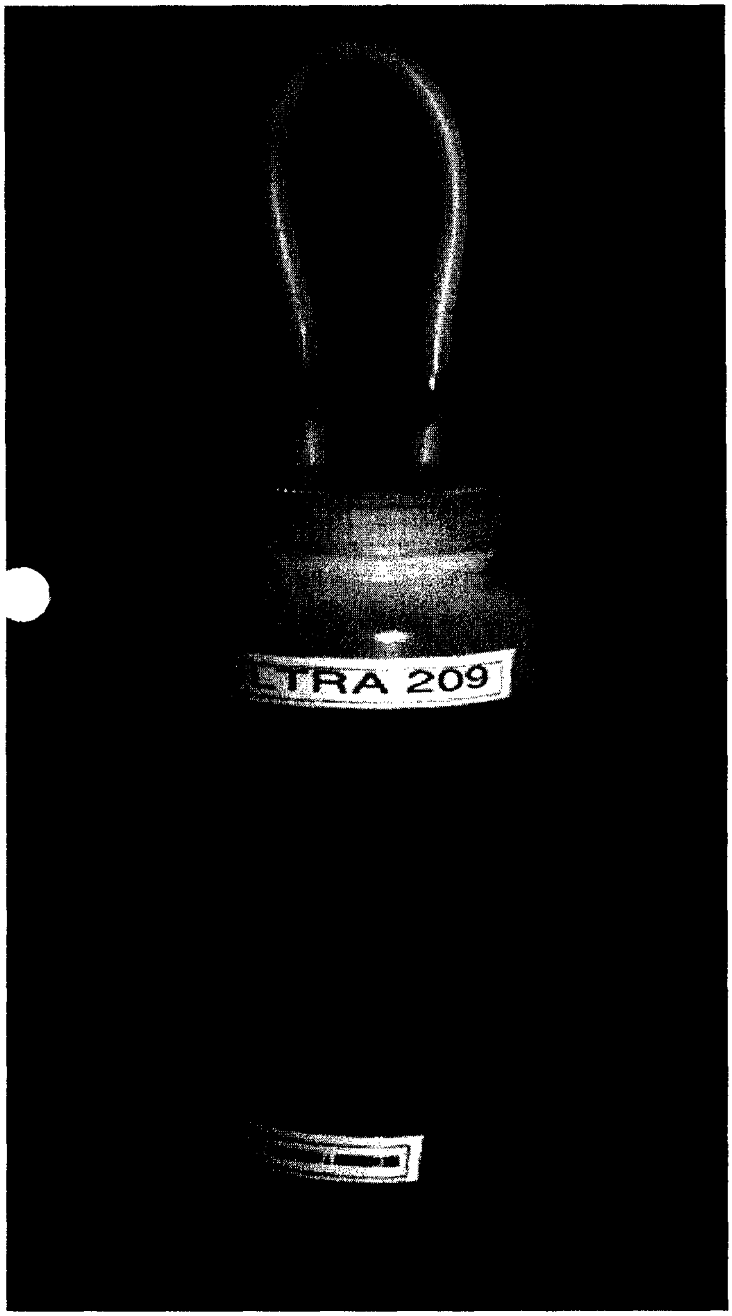


Figure 2 Loop Sample Container and Mercury Container



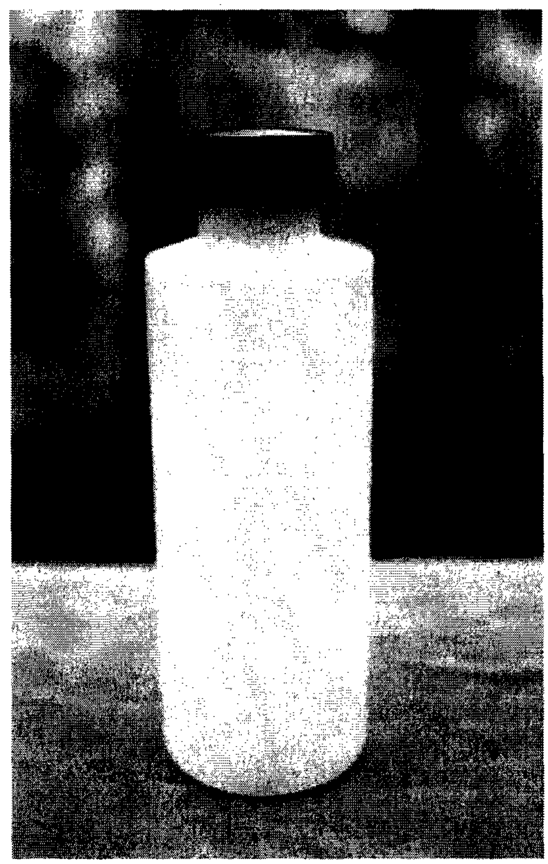


Figure 3 Sample Container Schematics

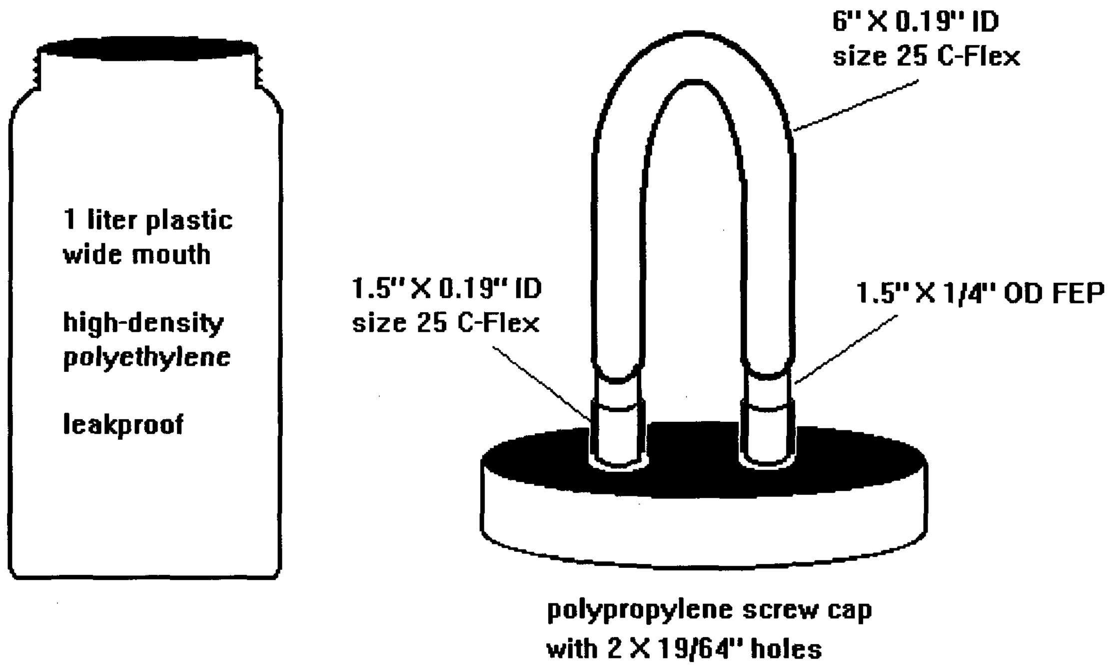
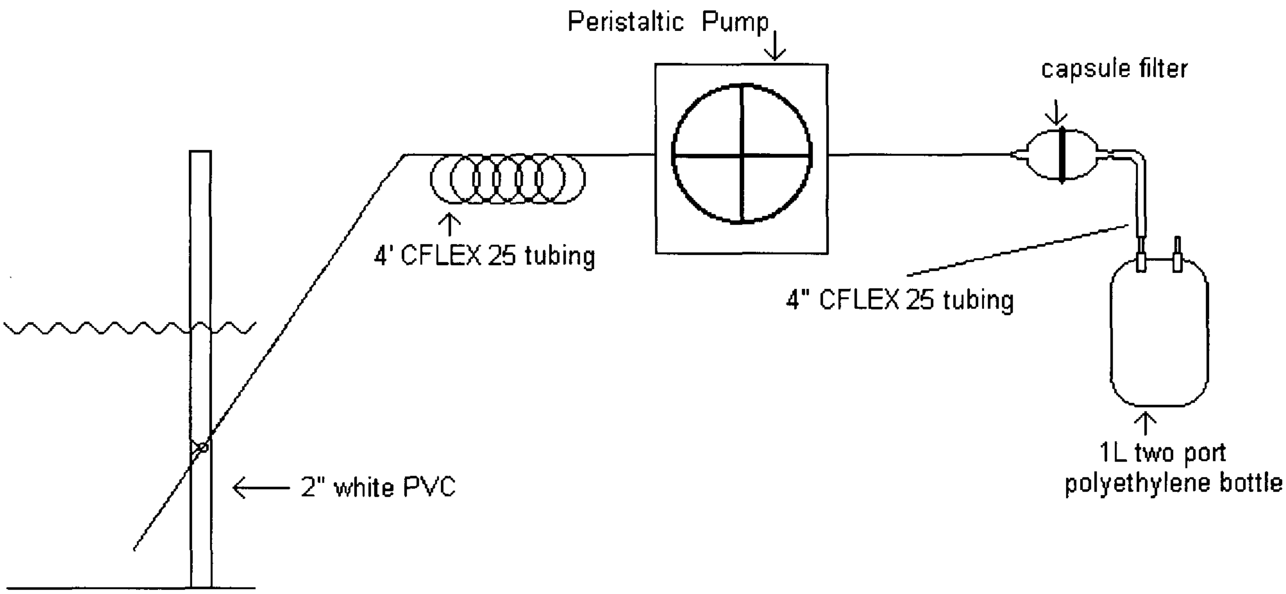


Figure 4 Ambient Sampling Apparatus



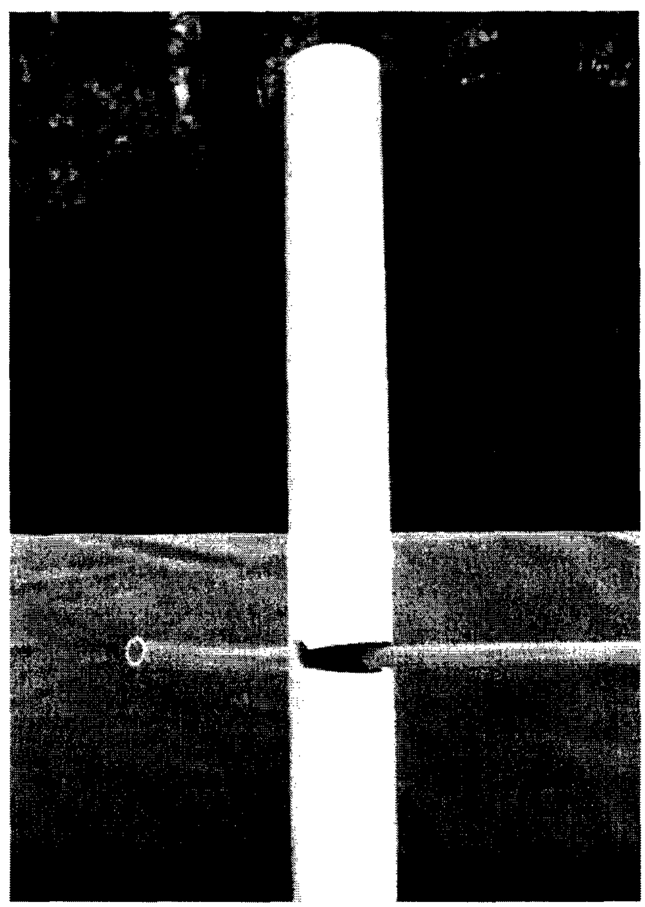


Figure 5 Effluent Sampling Apparatus

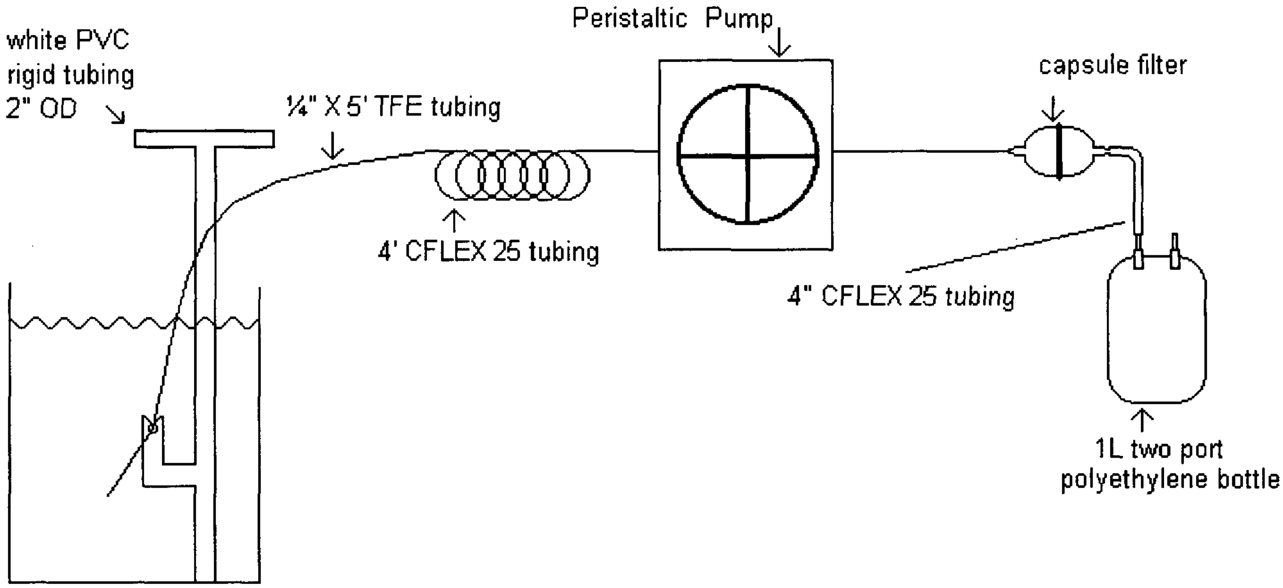
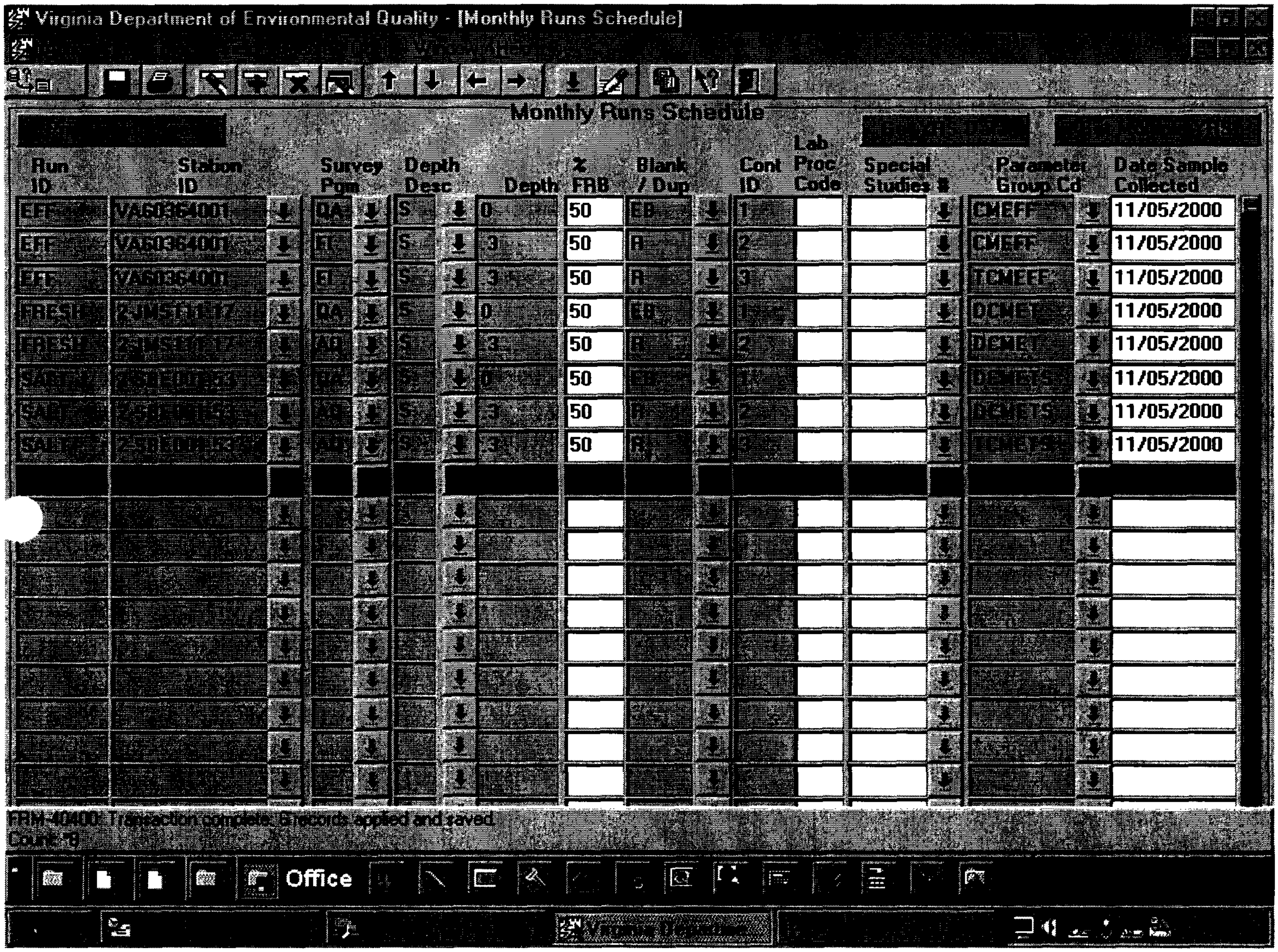


Figure 6 WQM Monthly Run Schedule Parameters



11. Quick Reference Guide

11.1 *Ambient Sample Collection Quick Reference*

11.1.1 Tie the 5 pound weight to the bridge bottle.

11.1.2 Collect the sample using the bridge bottle.

11.1.3 Untie the 5 pound weight.

11.1.4 Connect the tube to the first loop container.

11.1.5 Rinse the filter with the contents of the container.

11.1.6 Remove the tube from the empty bottle and place on the second loop container.

11.1.7 Pump 125mls of water to waste through the filter to purge previous sample.

11.1.8 Fill the mercury blank and seal.

11.1.9 Connect the filter to the empty first loop container.

11.1.10 Pump out of the second loop container into the first without letting the filter go dry.

11.1.11 Seal the blank loop container.

11.1.12 Remove the tube from the now empty second loop container and reconnect the tube to the bridge bottle vent tube.

11.1.13 Pump 125mls of water to waste through the filter to purge previous sample.

11.1.14 Collect the mercury sample.

11.1.15 Unscrew the lid of the second loop container and discard the water and replace the lid.

11.1.16 Connect the filter to the second loop container and fill.

11.1.17 Seal the sample containers.

11.1.18 Remove the filter and collect the total recoverables.

11.1.19 Collect field parameters.

11.1.20 Pack in ice and transport.

11.2 *Effluent Sample Collection Quick Reference*

11.2.1 Connect the tube to the first loop container.

11.2.2 Rinse the filter with the contents of the container.

11.2.3 Remove the tube from the empty bottle and place on the second loop container.

11.2.4 Pump 125mls of water to waste through the filter to purge previous sample.

11.2.5 Fill the mercury blank and seal.

11.2.6 Connect the filter to the empty first loop container.

11.2.7 Pump out of the second loop container into the first without letting the filter go dry.

11.2.8 Seal the blank loop container.

11.2.9 Remove the tube from the now empty second loop container and connect the tube to the sample wand.

11.2.10 Pump 125mls of water to waste through the filter to purge previous sample.

11.2.11 Collect the mercury sample.

11.2.12 Unscrew the lid of the second loop container and discard the water and replace the lid.

11.2.13 Connect the filter to the second loop container and fill.

11.2.14 Seal the sample containers.

11.2.15 Remove the filter and collect the total recoverables.

11.2.16 Collect field parameters.

11.2.17 Pack in ice and transport.

11.3 *Ambient Sample Collection Without the Bridge Bottle Quick Reference*

11.3.1 Connect the tube to the first loop container.

11.3.2 Rinse the filter with the contents of the container.

11.3.3 Remove the tube from the empty bottle and place on the second loop container.

11.3.4 Pump 125mls of water to waste through the filter to purge previous sample.

11.3.5 Fill the mercury blank and seal.

11.3.6 Connect the filter to the empty first loop container.

11.3.7 Pump out of the second loop container into the first without letting the filter go dry.

11.3.8 Seal the blank loop container.

1 9 Remove the tube from the now empty second loop container and connect the tube to the sample wand.

11.3.10 Pump 125mls of water to waste through the filter to purge previous sample.

11.3.11 Collect the mercury sample.

11.3.12 Unscrew the lid of the second loop container and discard the water and replace the lid.

11.3.13 Connect the filter to the second loop container and fill.

11.3.14 Seal the sample containers.

11.3.15 Remove the filter and collect the total recoverables.

11.3.16 Collect field parameters.

11.3.17 Pack in ice and transport.

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[1] NPDES Self-Monitoring Data and Data Audit Inspections (DAIs), United States Environmental Protection Agency Region III, C -al Regional Laboratory, Fall 1994.

[2] Metals' Data Position Paper, United States Environmental Protection Agency Region III, Rev 5.0, May 1, 1995.

[3] Tom Fieldsend of Sample Control Center, Operated by DynCorp Environmental for USEPAs Engineering and Anaylsis Division provided the protocol for sample shipping.